INEEL/CON-02-00725
PREPRINT

Supercritical Fluid Extraction of Plutonium and Americium from Soil

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August 4, 2002 – August 8, 2002

Spectrum 2002

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Abstract-

Supercritical fluid extraction (SFE) of plutonium and americium from soil was successfully demonstrated using supercritical fluid carbon dioxide solvent augmented with organophosphorus and beta-diketone complexants. Spiked Idaho soils were chemically and radiologically characterized, then extracted with supercritical fluid carbon dioxide at 2,900 psi and 65 ^{o}C containing varying concentrations of tributyl phosphate (TBP) and thenoyltrifluoroacetone (TTA). A single 45 minute SFE with 2.7 mol% TBP and 3.2 mol% TTA provided as much as 88% ± 6.0 extraction of americium and 69% ± 5.0 extraction of plutonium. Use of 5.3 mol% TBP with 6.8 mol% of the more acidic beta-diketone hexafluoroacetylacetone (HFA) provided 95% ± 3.0 extraction of americium and 83% ± 5.0 extraction of plutonium in a single 45 minute SFE at 3,750 psi and 95 ^{o}C. Sequential chemical extraction techniques were used to chemically characterize soil partitioning of plutonium and americium in pre-SFE soil samples. Sequential chemical extraction techniques demonstrated that spiked plutonium resides primarily (76.6%) in the sesquioxide fraction with minor amounts being absorbed by the oxidizable fraction (10.6%) and residual fractions (12.8%). Post-SFE soils subjected to sequential chemical extraction characterization demonstrated that 97% of the oxidizable, 78% of the sesquioxide and 80% of the residual plutonium could be removed using SFE. These preliminary results show that SFE may be an effective solvent extraction technique for removal of actinide contaminants from soil.

I. INTRODUCTION

The United States Department of Energy (DOE) manages approximately 1.9 billion cubic meters of radionuclide contaminated environmental media, 4.1 million cubic meters of stored, contaminated waste and 32 million cubic meters of mine tailings at 150 different sites located in 30 different states [1, 2]. This environmental legacy is a result of the massive industrial complex responsible for defense related and non-defense related research, development and testing of nuclear weapons, nuclear propulsion systems and commercial nuclear power systems. Cleaning up the environmental legacy is expected to cost several hundred billion dollars over the next 5 to 7 decades. To reduce costs and speed remediation efforts the DOE has invested in waste treatment and environmental remediation research.

Remediation of solid and liquid environmental media contaminated with actinides and fission products is a challenging task. The challenge calls for removing contaminants from solid and liquid media to concentrations which are below release criteria; preferably without generation of considerable secondary waste streams and without denaturing the media such that it can be returned to the environment. Other factors which must be considered include cost, safety and public acceptance. Physical and chemical separation techniques for removal of actinides and fission products from contaminated soil and water have met with varying success [3 - 6]. The most promising *in-situ* soil treatment techniques focus on sequestration of radionuclides and methods for keeping surface water and groundwater away from the source term. *In-situ* treatment of radionuclide contaminated groundwater and aquifer zones has been approached through use of selective barriers or selective adsorbents which pass water but sequester metals. *Ex-situ* treatment of radionuclide contaminated water primarily involves pump-and-treat, where treatment can be any number of chemical or physical methods which remove radionuclides from water (e.g., chemical precipitation, ion exchange, adsorption, filtration, etc.). *Ex-situ* soil treatment techniques have been

investigated but there are no effective methods developed which can remove recalcitrant and strongly adsorbed radionuclides from the soil without significant loss of soil mass or denaturation of the soil. The best technique demonstrated to date has been soil collection followed by above ground isolation and storage. Physical separation technologies, such as robotic soil sorters or magnetic separation techniques, have been demonstrated to be effective only in certain cases. Whereas those techniques provide some volume minimization relief they fail at removing metal species which are strongly sorbed to soil. Chemical treatment and soil washing techniques have been investigated and continue to undergo further research and development targeted at enhancing extraction efficiency.

Metal complexation followed by supercritical fluid extraction (SFE) is a relatively new solvent extraction technique which couples the energy efficiency of a supercritical fluid process with the extractive power of more than 5 decades of research in extractive radiochemistry [7]. The technique is performed by dissolving a metal complexing agent in supercritical fluid carbon dioxide. The augmented solvent is then passed through the solid or liquid matrix containing the radionuclide. A chemical reaction occurs between the radionuclide and the metal complexing agent. An organometallic complex is formed which itself is soluble in the supercritical fluid. As the solvent flows through the matrix the organometallic complex is swept out. A downstream reduction in pressure effectively precipitates and isolates the metal complex. The solvent is recyclable and the complexing agent can also be regenerated if desired.

Metal-complexation/SFE using carbon dioxide has been successfully demonstrated for removal of lanthanides, actinides and various other fission products from solids and liquids [8 - 18]. Direct dissolution of recalcitrant uranium oxides using nitric acid and metal-complexing agents in supercritical fluid carbon dioxide has also been reported [19 - 25]. In this paper we explored supercritical fluid extraction of sorbed plutonium and americium from soil using common organophosphorus and beta-diketone complexants.

II. EXPERIMENTAL METHODS

Clean soils were chosen from geographical locations at and near the Radioactive Waste Management Complex (RWMC) at the Idaho National Engineering and Environmental Laboratory (INEEL). The RWMC at the INEEL served as a DOE burial ground from the early 1950s through to the 1970s and contains numerous pits, trenches and soil vaults wherein soil contaminated with actinides and fission products is known to exist. Soil samples were air dried, sieved to 50 mesh, then partitioned into 100 g batches. A slurry was made by adding demineralized water to the 100 g soil batches and the slurry was then spiked with varying amounts of a stock solution which contained approximately 26 μCi/mL ^{239}Pu and approximately 0.2 μCi/mL ^{241}Am in 8 M nitric acid. Spikes were added in small (<0.1 ml) aliquots with 1 minute stirring intervals between additions. Plutonium and americium nitrates were spiked onto the clean RWMC soils at activities ranging from 100 nCi/g (3.7 X 10^3 Bq/g) to as high as 1000 nCi/g (3.7 X 10^4 Bq/g). The samples were then air dried and radiologically characterized using both gamma-ray spectroscopy and alpha spectrometry techniques.

Sequential chemical extraction analysis was performed on 10 g batches of spiked soils. Sequential chemical extraction techniques were the same as those employed by Litaor *et al* [26], Tessier *et al* [27], and Schultz *et al* [28, 29]. All three techniques were employed for comparative purposes on pre-SFE samples, but only the technique of Litaor *et al* was used to characterize plutonium and americium in the post-SFE samples. That technique was viewed as the most conservative.

Plutonium and americium were extracted from spiked INEEL soil samples using supercritical fluid carbon dioxide augmented with commonly known beta-diketones and neutral oxygen donor ligands. Ten gram batches of the spiked soils were loaded into a supercritical fluid extraction vessel which was comprised of a ½ inch o.d. piece of 316 stainless steel high pressure tubing approximately

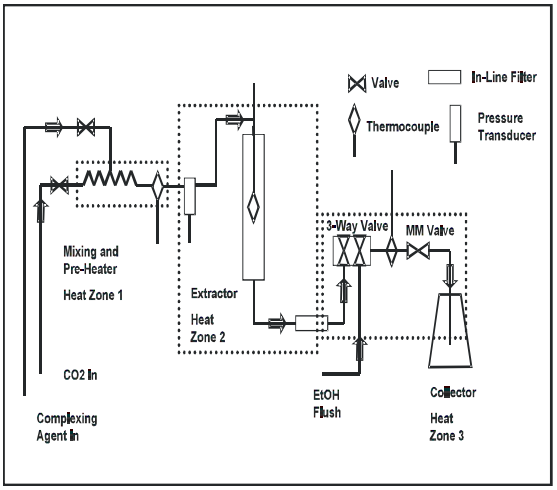

Figure 1. Flow Schematic for SFE System

17 inches long. Supercritical carbon dioxide was passed over the soil samples at a pressure of 2,900 psi, a temperature of 65 ^{o}C, and a flow rate of 3.5 milliliters per minute for approximately 45 minutes while temperature and pressure equilibrated. Once

Figure 2. Photo of Extraction Apparatus

the system had equilibrated tributyl phosphate (TBP) and thenoyltrifluoroacetone (TTA) were added to the supercritical fluid solvent stream at a constant flow rate and the augmented solvent was then passed over the soil sample for another 45 minutes. Numerous extractions were performed on different soil samples where the TBP concentration was ranged from 0.27 to 2.7 mol% and the TTA concentration was ranged from 0.32 to 3.2 mol%. Different extraction parameters were changed (temperature, pressure, addition of solvent

Figure 3. Extract from SFE Process

modifiers, extraction time) to determine their effects on extraction efficiency. SFE was also performed on spiked soil samples using TBP and the more acidic beta-diketone hexafluoroacetyl-acetone (HFA). For those extractions the TBP concentration was ranged from 2.7 to 5.3 mol% and the HFA concentration was ranged from 3.5 to 6.8 mol%. Various extraction parameters (temperature, pressure, addition of solvent modifiers) were also changed to determine their effects on extraction efficiency. A flow schematic of the SFE system is shown in Figure 1. A photograph of the extraction system in a radiological control hood is shown in Figure 2, and a photograph of the actinide-ligand extract is shown in Figure 3.

Post-SFE soils and the liquid extract were radiologically characterized using both gamma-ray spectroscopy and alpha spectrometry techniques. Sequential chemical extractions were performed on post-SFE soils to obtain information related to the percent plutonium removed from the various soil fractions.

III. RESULTS

Sequential chemical extractions using three different procedures for comparison were conducted. The results for plutonium are found in Figure 4. The data indicate there is variability in the results between different procedures. The procedure of Litaor *et al* was viewed as the most conservative because it tended to extract plutonium

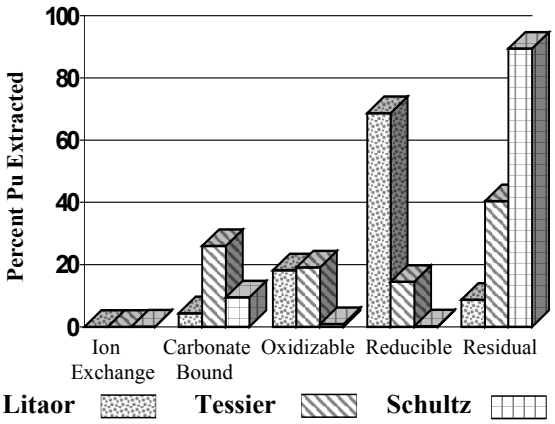

Figure 4. Comparison of Three Different Sequential Chemical Extraction Techniques for Plutonium Extraction from Pre-SFE INEEL Soils.

from all phases leaving approximately 12.8% assigned to the residual. It should be noted that sequential chemical extractions are not a direct indicator of plutonium or americium speciation. Different procedures and different reagents can produce dissimilar results. The data are however useful for qualitative assessment of the susceptibility of bound metal to redistribution as the result of addition of a given chemical agent.

Neither plutonium nitrate or oxides nor americium nitrate or oxides are soluble in carbon dioxide alone. Plutonium extraction efficiency

Table I. SFE Results Using the TTA/TBP System

Initial Conditions	% Extracted Pu	Am
Initial Extraction Conditions: 2,900 psi, 65 °C 45 min., 3.5 ml/min, [TBP] = 0.27 mol%, [TTA] = 0.33 mol%	17 ± 3.8	32 ± 4.9
Initial Conditions Plus Add Modifiers		
2 mol% Water	17 ± 5.0	21 ± 6.0
5 mol% Ethanol	45 ± 8.0	59 ± 4.0
Initial Conditions Plus Increase Extraction Time		
From 45 minutes to 4 Hours (240 min.)	17 ± 5.0	26 ± 6.0
Initial Conditions Plus Increase Extraction Pressure		
From 2,900 psi to 3,750 psi	29 ± 2.5	51 ± 1.5
Initial Conditions Plus Increase Complexing Agent Concentration		
[TBP] = 2.7 mol%, [TTA] = 3.2 mol%	69 ± 5.0	88 ± 6.0

Table II. SFE Results Using the HFA/TBP System

Initial Conditions	% Extracted Pu	Am
Initial Extraction Conditions: 2,900 psi, 65 °C 45 min., 3.5 ml/min, [TBP] = 2.7 mol%, [HFA] = 3.5 mol%	76 ± 2.0	93 ± 1.0
Initial Conditions Plus Add Modifier		
5 mol% Ethanol	74 ± 10.6	90 ± 2.7
Initial Conditions Plus Increase Temperature, Pressure, Complexing Agent Concentration		
3,750 psi, 95 °C, [TBP] = 5.3 mol%, [HFA] = 6.8 mol%	83 ± 5.0	95 ± 3.0

from spiked INEEL soils was less than 20% when 2.7 mol% tributyl phosphate was used as the sole complexing agent. Neither plutonium nor americium were extracted when various beta-diketones were used as the sole complexing agents.

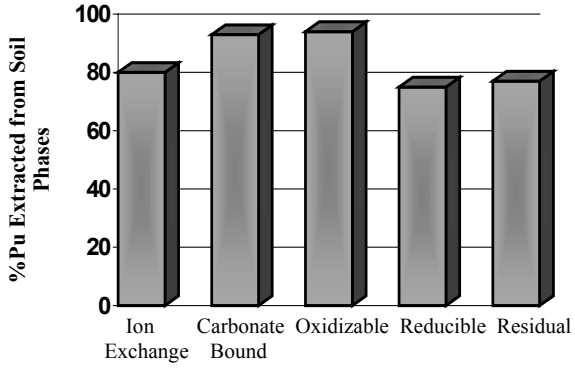

Figure 5. Percent Plutonium Extracted from Different Operational Soil Phases

However, when a dual ligand system comprised of 2.7 mol% tributyl phosphate and 3.2 mol% thenoyltrifluoroacetone was used, as much as 69%± 5.0 of the plutonium and 88% ± 6.0 of the americium could be extracted from spiked INEEL soils. Whereas addition of ethanol or water as co-solvents had minor beneficial effects, those effects were not as great as saturating the critical fluid phase with the extracting agents. Increasing the extraction run time, increasing pressure and performing multiple extractions on the same sample had only minor beneficial effects and were thus deemed unworthy of further pursuit. The SFE results for the TBP/TTA system are given in Table I.

When 3.5 mol% of the acidic beta-diketone hexafluoroacetylacetone was used in combination with 2.7 mol% tributyl phosphate, 80% of the plutonium and 93% of the americium could be extracted in a single 45 minute extraction at 65 degrees Celcius. When the ligand concentrations

were increased to 6.8 mol% hexafluoroacetyl-acetone and 5.3 mol% tributyl phosphate, and the extraction temperature was increased to 95 degrees Celcius, a maximum of 83% plutonium and 95% americium were extracted. The SFE results for the HFA/TBP system are given in Table II.

Experimental results from sequential chemical extractions performed on post-SFE soils (Figure 5) using the HFA/TBP system show that most of the remaining plutonium that was not removed by SFE is associated with the reducible mineral fraction of the soil. The amount of plutonium recovered from the ion exchangeable, acetate-soluble (carbonate bound) and hypochlorite-oxidizable fractions were two to three orders of magnitude less in the post-SFE soils. This may be contrasted with pre-SFE soil, where most plutonium was found in the hypochlorite-oxidizable and iron mineral fractions. Note also that some of the plutonium residing in the residual fraction of the pre-SFE soils was removed by the SFE treatment using the HFA/TBP system.

IV. CONCLUSION

SFE results and sequential chemical extraction characterization of pre- and post-SFE soils suggest that the best gains in supercritical fluid extraction efficiency can be made by designing a supercritical fluid extraction process which targets the reducible mineral fraction of the soil. These preliminary results also indicate that metal-complexation followed by supercritical fluid extraction holds potential as being a highly effective, safe and energy efficient process for removal of strongly adsorbed and recalcitrant radionuclide species from solid environmental media.

ACKNOWLEDGMENT

This work was funded in part by BNFL Group. Work was performed under contract number DE-AC07-99ID13727.

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