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(Conducted March – May 1995)*

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by

**Mary E. Barr, Ann R. Schake,
David A. Romero, and Gordon D. Jarvinen**

ABSTRACT

The scope of this project is to determine the feasibility of washing plutonium-containing combustible residues using ultrasonic disruption as a method for dislodging particulates. Removal of plutonium particulates and, to a lesser extent, solubilized plutonium from the organic substrate should substantially reduce potential fire, explosion or radioactive release hazards due to radiolytic hydrogen generation or high flammability. Tests were conducted on polypropylene filters which were used as pre-filters in the rich-residue ion-exchange process at the Los Alamos Plutonium Facility. These filters are similar to the Ful-Flo® cartridges used at Rocky Flats that make up a substantial fraction of the combustible residues with the highest hazard rating. Batch experiments were run on crushed filter material in order to determine the amount of Pu removed by stirring, stirring and sonication, and stirring and sonication with the introduction of Pu-chelating water-soluble polymers or surfactants. Significantly more Pu is removed using sonication and sonication with chelators than is removed with mechanical stirring alone.

OBJECTIVES

Rocky Flats is mandated to stabilize a large assortment of Pu-containing waste which presents a potential fire or explosion hazard due to radiolytic hydrogen generation or reactive combinations of organic materials and oxidizers. These combustible wastes consist mainly of cellulosic items (e.g., rags, paper, booties), ion-exchange resins, and polymeric materials (mostly polyvinylchloride, polyethylene, and polypropylene) commonly used in plutonium glovebox operations. The overall goal of the proposed treatment process is to selectively wash certain types of plutonium-containing residues at the Rocky Flats Plant to make the bulk of the material low level waste and to produce a relatively small volume of concentrated TRU material. While achieving decontamination levels which allow for direct disposal of the bulk materials as low-level waste is certainly desirable, it is not an essential part of the stabilization mandate. For example, it may be possible to wash and remove reactive nitric acid or nitrate salts from combustibles and mitigate a hazard without removing substantial amounts of plutonium. Our goal is to determine the conditions and operating procedures

under which residue washing/sonication with surfactants or water-soluble chelating polymers can be used to transform contaminated materials into acceptable waste forms.

Washing can be a fast, simple procedure which is run under ambient temperatures and pressures with no strong acids or bases. The surfactants and water-soluble chelating polymers are non-RCRA-listed chemicals with minimal chemical exposure hazards. The general treatment scenario first involves size reduction of the waste to about 1-5 mm. The size-reduced material is then washed with water-soluble chelating polymer solutions or surfactant solutions to promote plutonium dissolution and separation of plutonium particulates from the bulk material. In the simplest version of the process, the chelating polymers act also as the surfactants. It may be advantageous to use sonication techniques to improve the washing process. The wash mixture is separated from the bulk solids by decantation or filtration. The wash mixture is microfiltered to remove undissolved plutonium oxide and other particulates. The filtrate could then be ultrafiltered to remove the polymer containing the chelated Pu and Am which produces a very low level water for recycle or further processing depending on the amount of dissolved salts or organic compounds leached from the residue. The chelating polymer loaded with actinides can be recycled using a periodic regeneration step or calcined to yield a stable solid. The relatively small volume of TRU-containing solids resulting from the microfiltration and ultrafiltration operations can now be readily packaged in a form acceptable for long-term storage or for disposal at WIPP. The most desirable result is for the bulk of the original residue to reach low-level waste standards so that it can be packaged for disposal in a low-level repository. However, as noted above, it may be possible to mitigate safety concerns without washing to low-level standards.

RESULTS

Experimental Outline

A small-scale washing apparatus was developed as shown below. Ultrasonic disruption (also called sonication) was targeted as a method for facilitating the dislodging of particulates which could then be trapped on a separate filter. Sonication employs the phenomenon of 'cavitation.' Cavitation is the rapid and repeated formation, and resulting implosion, of microbubbles in the liquid, resulting in the propagation of microscopic shock waves. The collapsing bubbles produce localized pressures and temperatures of ca. 300 atm. and 3,000K. The sonication apparatus used (a probe system) operates at 20 kHz, which is a much more disruptive frequency than is encountered with laboratory ultrasonic cleaning units (40 kHz). Our decision to use the ultrasonic probe resulted from three primary considerations: we were interested in determining what enhancements to Pu-removal would result from adding sonication alone to the washing procedure, we were concerned that much of the Pu-chelating polymeric material would be wasted trying to dissolve the larger particles which could be simply filtered out, and we hoped that ultrasonic disruption would facilitate dissolution of small particles by the chelators.

The Pu-chelating water-soluble polymer used in these tests consists of a derivatized PEI (polyethyleneimine) backbone. In the sample used, ca. 50% of the nitrogens of the PEI have methylphosphonic acid groups attached.¹ These groups bind Pu(III), Pu(IV), and Pu(VI) strongly at near neutral pH's. The extent to which the chelating polymer solutions can promote dissolution of plutonium oxide is a complex function of the past history of the oxide particles (high-fired oxide material is the most difficult to dissolve), the intimacy of the solid-solution mixing, the length of time in contact with the wash solution, the temperature, and the chemistry of the complexing and redox agents present in the wash solution. Studies conducted at Los Alamos on the dissolution of plutonium polymers and plutonium in soils with synthetic and natural chelators have demonstrated substantial dissolution (>30%) at near neutral pH over several days. It was hoped that the addition of sonication to this step would substantially enhance the rate of dissolution of the Pu particles by increasing the available surface area of the particles. The introduction of Pu-chelating water-soluble polymers into the washing procedure facilitates the recovery of solubilized Pu from these waste streams via ultrafiltration separation of the Pu-bearing polymers from the aqueous effluent.

Schematic of the PEIP polymer used

The surfactant compound hexametaphosphate (HMP) was used in these tests to try and increase particulate removal from the plastic matrix. This surfactant had been found to be the most effective of about a dozen surfactants tested at TA-55 in soil washing studies to remove plutonium and uranium by magnetic separation techniques.

Experimental Parameters

The filter cartridges used at the Los Alamos Plutonium Facility at TA-55 closely resemble the Ful-Flo® cartridges used at Rocky Flats. A used 12" polypropylene filter from the rich-residue ion exchange line at TA-55 was frozen in liquid nitrogen and crushed inside the glovebox. The large chunks of material were cut into smaller pieces (ca. 1 cm) using scissors and then divided into sample masses of ca. 20g. The filter material clearly had substantial amounts of gray particulate material entrained in the fibers. Samples were assayed for Pu using a sensitive counter for x-rays in the 11-22 keV range called MADAM (for multiple assay dual analysis measurement). The lower limit of detection was estimated to be about 10 micrograms of plutonium for the plastic matrix we were examining. This is easily sensitive enough to determine if the low-level activity value, <100 nCi/g, has been reached. Each sample was introduced to the 4-inch diameter glass reaction vessel and enough tap water was added to bring the solution level in the vessel to ~1/2 height (ca. 1.5 L). Some particulate material comes loose when the filter is introduced into the vessel, so the solution was recycled through the filtration cartridge at a rate of ca. 1 L/min until all visible particles were gone. The rate of stirring was adjusted such that the material was as evenly distributed within the vessel as possible. Stirring and macrofiltration of the material occurred throughout the entire experiment. Sonication was conducted in a 60% pulse mode, so 1 hour lapsed time equates to 36 minutes of active sonication. Addition of PEIP at the 0.1 wt% level in these experiments represents about a 100-fold molar excess of phosphonic acid groups to Pu. However, the amount of other metals present in the particulate matter caught on the filter material was not determined for these experiments. Other metals such as iron(III) can certainly compete with Pu for binding sites on the chelating polymer.

Experiment 1 provided an overview of the effects of sonication, surfactant and the PEIP polymer on plutonium removal. Aliquots of the solution (5 mL) were taken after each of the following sequential steps upon a single sample: 1) stirring only, 2) stirring/sonication (1 hr), 3) stirring, sonication with the addition of 0.1% (by weight) of HMP (1 hr), and 4) stirring/sonication with HMP with the addition of 0.1% (by weight) of PEIP polymer (1 hr). The 5 mL aliquots were filtered through a 0.45 micron syringe filter to remove particulates and then assayed for total alpha activity using a liquid scintillation counter. The activity that passed through the 0.45 micron filter is catalogued as "solubilized" Pu, but it should be recognized that a substantial portion of this Pu activity could be incorporated in colloidal-sized particles. The washed polymer was rinsed with water, dried, and assayed for residual Pu. Any particulate Pu removed during the experimental run was captured on the macrofilter and not assayed.

TABLE 1.

Initial Pu(mg)/g(sample) = 2.59 Residual Pu(mg)/g(sample) = 0.55
Pu removed = 79%

Step #	solubilized Pu(mg)/g(sample)
1 stirring	0.010
2 stirring/sonication	0.013
3 stir/sonicate/HMP	0.051
4 stir/sonicate/HMP/PEIP	0.069

In Experiment 2, we examined the effects of mechanical stirring alone, stirring and sonication and stirring and sonication with the addition of HMP or PEIP separately. Five runs were performed based on the procedure outlined in Experiment 1: Run #1) stirring of the crushed filter material in tap water for two hours, Run #2) stirring (10 min.) followed by stirring/sonication in tap water (2 hr), Runs #3 and #4) stirring (10 min), followed by stirring/sonication with HMP (2 hr), and Run #5) stirring (10 min), followed by stirring/sonication with 0.1% (by weight) of the PEIP polymer (2 hr). Aliquots (5 mL) were taken after stirring and at the end of the run. The 5 mL aliquots were filtered through a 0.45 micron syringe filter to remove particulates and then assayed for total alpha activity using a liquid scintillation counter. The washed solid was rinsed with water, dried, and assayed for residual Pu. Any particulate Pu removed during the experimental run was captured on the macrofilter and not assayed. The results of the five runs are given in Table 2 below.

TABLE 2.			
Run #	Initial Pu(mg)/g (sample) on the sample	Final Pu(mg)/g (sample) on the sample	% Pu removed
1	1.48	0.88	41
2	1.50	0.20	87
3	2.11	0.40	81
4	2.38	0.21	91
5	2.37	0.48	80

Analysis of results

The Pu activity on the filter material was reduced 41% to 91% during these washing operations. The Pu remaining is still almost three orders of magnitude above the low-level limit which is near 1 microgram per gram of solid. However, it is worth noting that these relatively mild treatment conditions removed at least as much Pu as did 6 hours of treatment with refluxing concentrated HCl containing 0.5 F HF (average dissolution efficiency 76%) in experiments with similar Pu-contaminated filter materials reported previously.²

Experiment 1: The assays for solubilized Pu in experiment 1 provide useful information. Stirring alone knocks off some loose particles, while sonication removes more tightly bound particles, resulting in material which *looks* appreciably cleaner. These particles are captured by the macrofilter and do not appear in any Pu assay. Sonication in tap water appears to minimally increase the amount of *solubilized* Pu. The addition of HMP to sonicated solutions, however, produces a significant increase in the amount of solubilized Pu. The addition of PEIP appears to further increase the amount of solubilized Pu, but the presence of HMP in the solution precludes quantitative analysis of the effect of PEIP alone.

Experiment 2: The series of runs in experiment 2 allows for analysis of the effects of each washing step separately. As observed above, stirring alone is capable of removing loose particles of Pu solids and of dissolving water-soluble Pu compounds or dispersing colloidal particles deposited on the original filter. Sonication appears to knock off more tightly bound particles of Pu solids, resulting in a cleaner residue (run #2 vs. run #1). One other advantage of sonication is that the sonicated material is more thoroughly wetted. Polypropylene is both hydrophobic and less dense than water.

Especially with air entrained in the material, it has a tendency to float on top of the aqueous solution, even with vigorous stirring. Sonication removes the entrained air and makes the surface of the polypropylene more wettable. This results in a more intimate contact with the solution which facilitates particulate separation and/or dissolution.

The "solubilized" Pu data for the runs of experiment 2 were not very useful because there appears to be an increasing "background" of solubilized Pu that probably results from the materials deposited on the 5 micron filter cartridge during each run. The same filter cartridge was used in each run to minimize waste. There was a trend of increasing soluble plutonium for each successive run just after stirring with tap water. In fact, this "soluble" material was observed to actually decrease after addition of HMP or PEIP in some runs. This suggests that the hexametaphosphate or the PEIP polymer can precipitate or coagulate Pu-containing material that had previously passed through the 0.45 micron filter. This deposition of Pu-containing material from solution could actually add Pu back to the polymer and degrade the performance of the washing operation. Clearly, the solid gathered on the 5 micron filter needs to be removed between runs and other surfactants/detergents need to be considered for this process in future development work.

RECOMMENDATIONS

Material size reduction: The crude form of cryogenic crushing used to prepare the samples does not yield the fine, homogenous material that mechanized cryogenic crushing produces. Preliminary cold lab experiments with polypropylene cartridges loaded with carbon or iron hydroxide definitively showed that the more finely divided material was cleaned comprehensively by sonication, whereas the larger chunks of material were not. Thus, the samples used in the experiments were not optimal for sonic cleaning. Mechanized cryogenic crushing is advised, and we anticipate access to such a machine in the Pu facility in the very near future.

Sonication procedures: The sonication probe used in these experiments has a very limited area of effectiveness which is directly beneath the tip. Thus, homogeneous material distribution is essential in order for all the slurried material to experience sufficient sonication action. This distribution is facilitated by rapid stirring and small particle size, but may be further facilitated by use of a sonication bath unit instead of a probe. The benefits of adding ultrasonic disruption to the washing process are unambiguous: 1) sonication dislodges more particles than stirring alone, 2) sonication increases the effectiveness of surfactant and polymeric chelators to solubilize Pu.

Time, Temperature, Surfactants, and Redox Agents: These are all potentially important variables in the washing operation that we have not had time to evaluate. These factors have major effects on other actinide decontamination operations that have been reported in the literature.

Macrofiltration: Due to waste minimization concerns, it was decided to trap all >5 micron particles for each run cumulatively on a single polypropylene cartridge filter. We are investigating the possibility of using in-line disk filters, so that the particulates from each run can be analyzed for Pu. However, most disk filters are unable to handle the solution flow rates (about 1 L/min) and the overall mass of particulates.

Polymer filtration: The ultrafiltration unit was not used in these experiments because we simply wanted to determine the amount of Pu removed from the washed polymer. While the near neutral pH of the experimental solutions was already less than the point of zero charge for PuO₂ (ca. pH of 9), some judicious manipulation of solution pH may further facilitate dissolution. Additional testing of methods to enhance the rate at which these polymers attack and dissolve Pu-containing particulates is strongly advised. Simple chelators like HMP may facilitate dissolution,

but the polymeric nature of PEIC enables Pu capture through ultrafiltration of the solution. In the absence of full-scale Pu recovery procedures, ultrafiltration of polymeric chelate/Pu complexes is a simple, effective method of removing solubilized Pu from the aqueous media.

CONCLUSIONS

These initial experiments indicate that washing with sonication and surfactants is a viable method of reducing the Pu contamination in combustible residues. The water-soluble Pu chelators facilitate both Pu dissolution and recovery from the wash solution. The washed polymer still had plutonium activity two to three orders of magnitude above low-level amounts, but we feel there is still much room for optimization of the process. Material size reduction appears to be an essential aspect of effective sonic cleaning and we anticipate great improvements in the size reduction operation with the use of cryogenic grinding unit as is now available in the LANL TA-55 Plutonium Facility.

¹ "Evaluation of synthetic water-soluble metal-binding polymers with ultrafiltration for selective concentration of americium and plutonium," B.F. Smith, R.R. Gibson, G.D. Jarvinen, M.M. Jones, M.T. Lu, T.W. Robison, N.C. Schroeder and N. Stalnaker, *J. Radioanal. Nucl. Chem.*, 1998, 234, 219-223.

² "Pilot Scale Cartridge Filter Leaching and Plutonium Precipitation," M. A. H. Reimus, J. R. Stevens, and T. E. Boyd, LA-12948-MS, April 1995.