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A Small-Scale Study on the Dissolution and Anion-Exchange Recovery of Plutonium from Rocky Flats Plant Incinerator Ash

Los Alamos

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A SMALL-SCALE STUDY ON THE DISSOLUTION AND ANION-EXCHANGE RECOVERY OF PLUTONIUM FROM ROCKY FLATS PLANT INCINERATOR ASH

by

Thomas W. Blum, Robert G. Behrens,
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ABSTRACT

Incinerator ash has been processed successfully at plutonium production sites for many years, but not without some difficulty. Problems arise from complicated ash chemistries that adversely affect process operations and efficiencies. We performed small-scale experiments to examine four specific areas identified by Rocky Flats Plant personnel as sufficiently important to warrant further investigation to determine (1) the optimal feed fluoride concentration (the relationship between fluoride concentration and overall plutonium/ash dissolution in the nitric/hydrofluoric acid system), (2) the effect of free fluoride on anion exchange performance if aluminum nitrate is not added to ash filtrates as a complexing agent, (3) possible equipment corrosion problems resulting from potentially large quantities of uncomplexed fluoride, and (4) the effects of unburned carbonaceous material on anion exchange behavior. Our findings are reported.

INTRODUCTION

Combustible wastes are generated from plutonium processing activities across the defense programs complex. Because these residues typically do not meet discard limits, they are incinerated to reduce their volume and convert them to a form more suitable for reclamation of their plutonium content.

Ash from the incineration of these materials has proven to be one of the more difficult matrices from which to solubilize plutonium, often requiring three or more passes before a discardable residue is obtained. Poor dissolution characteristics coupled with low plutonium content have made ash one of the less desirable scraps to process. However, as plutonium streams become leaner, ash processing becomes increasingly important in the plutonium recovery cycle.

Although incinerator ash has been successfully processed at production sites for a number of years, there have been obstacles other than the difficulty of dissolution. Complications arise as a result of contaminants found in ash that adversely affect process operations and efficiencies. Two contaminants that have long plagued ash processing are silicon and carbon.

Silica, which is abundant in ash, reacts with fluoride to produce $SiF_4(g)$ that reacts with water to form fluorosilicic acid and silicon solids that plug offgas systems.[1,2] Additionally, aluminum nitrate, which is added to dissolver filtrates to complex free fluoride, complexes with silicon species present to form a troublesome gelatinous precipitate that readily plugs filters. If this gel is not completely removed, solids collect in storage tanks and diminished flow or plugging of ion-exchange systems occurs.

Carbon, reported as high as 36 wt % in Rocky Flats Plant ash,[3] can most often be attributed to incomplete combustion of glove-box gloves and plastics during incineration. At Los Alamos, experience with processing off-site incinerator ash has shown that high-carbon ash presents a myriad of problems, including (a) excessive foaming during ash addition to the dissolver when using nitric/hydrofluoric acid mixtures, (b) poor filtration, (c) a viscous residue buildup on equipment, and (d) fouling of anion-exchange columns.[4] Reburning incinerator ash at 600°C for a period of 4 hours has been shown to be a simple and effective method for carbon removal.[5] Accordingly, Los Alamos has employed rotary calcination for this purpose and has successfully mitigated downstream problems associated with carbon.

At Rocky Flats Plant (RFP), a major effort is under way to upgrade existing plutonium processing facilities. Of particular interest is the ash processing area (PROVE) now under construction. Because PROVE has been selected as a test facility to verify the RFP approach to upgrading other process areas, representatives from sites across the production complex were called upon to perform a technology assessment on it. Their work culminated in the PROVE Technology Assessment Report (PTAR) that brought to light concerns warranting further investigation[6] and resulted in the addition of an Incinerator Ash Processing Working Group (IAPWG) to existing technology exchange programs between Los Alamos and RFP.

This report is Part I of a three-part series documenting the results of a small-scale incinerator ash study conducted at Los Alamos by IAWPG members to address specific concerns outlined in the PTAR. Parts II and III will follow upon completion of production-scale verification testing and ash characterization studies in progress at Los Alamos and small-scale studies at RFP that parallel the work reported here.

EXPERIMENTAL

Four specific areas associated with ash processing were identified by RFP as sufficiently important to warrant further investigation: (1) the relationship between the calcium fluoride addition rate and overall plutonium/ash dissolution when dissolving ash in the nitric/hydrofluoric acid system, (2) the effect of free fluoride on anion-exchange performance if aluminum nitrate is not added to ash filtrate as a complexing agent, (3) possible equipment corrosion problems resulting from potentially large quantities of uncomplexed fluoride, and (4) the effects of ash carbonaceous material on anion-exchange behavior.

Although it was our desire to extend the scope of this study beyond the four areas identified, this was determined to be impossible if changes to the flowsheet were to be implemented in time for the scheduled PROVE startup. Therefore, we were limited to using as-designed PROVE operating parameters that may or may not be optimum for achieving maximum process efficiency or product quality.

The projected study was divided into two separate phases. In Phase I, both Los Alamos and RFP were to conduct a series of six small-scale scouting tests using varying levels of calcium fluoride to determine the optimum fluoride concentration for promoting plutonium/ash dissolution. The corrosion potential and effective capacity of the anion-exchange column were to be evaluated for each solution. To examine the effects of ash carbonaceous material on anion-exchange behavior, RFP would use virgin ash (untreated), whereas Los Alamos would use ash that had been calcined. In Phase II, conducted only at Los Alamos, production scale verification tests were to be performed using an optimum fluoride concentration determined from performance criteria evaluated in Phase I.

Equipment

Two-inch cascading air-lift dissolvers were designed and fabricated at Los Alamos for the dissolution of incinerator ash and a 3-in. anion-exchange column was assembled for the separation and recovery of plutonium from the ash filtrate. An identical set of equipment was transferred to RFP for use in parallel experiments.

The cascade dissolver (Fig. 1) was assembled using three 2-in. diameter by 12-in. long glass-pipe dissolvers with heads fabricated from chlorinated polyvinylchloride (CPVC) stock. The dissolvers, in series, were air-sparged and fed by gravity from one to the other. A sampling valve was placed on the underside of the overflow pipe between dissolvers. Each dissolver was heated externally with a hot plate to an operating temperature of 100 ± 5°C. Dissolver leachate was circulated by draft-tube (1-in. × 17-3/4-in.) air action that facilitated particle suspension for maximum liquid/solid contact. Air, regulated through a supply manifold equipped with metering valves, was delivered independently to each dissolver at a rate of 600 cm^3/min. Off-gas vapors were collected in a 3-in. diameter by 12-in. long flanged glass-pipe scrubber, partially filled with water and fitted with a cooling coil supplied by a closed-loop negative-pressure chilled water system. Ash, calcium fluoride, and nitric acid were introduced through a feed inlet funnel mounted on the first dissolver. Ash and calcium fluoride were manually added, whereas nitric acid addition was controlled using a peristaltic pump between the acid feed tank and the first dissolver. Leachate exiting the third dissolver overflowed to a filterboat fitted with a 5-μm filtering cloth and was collected and stored in clean 6-in. glass receiver tanks.

The anion-exchange column (Fig. 2) was constructed using a 3-in. by 12-in. glass pipe and CPVC flanges fitted with a high-density polyethylene frit. Flow control was maintained using a peristaltic pump. Effluent, wash, and eluate streams were collected in clean 6-in. glass receiving tanks. All column runs were monitored using a computer-based on-line gamma monitor similar to that employed on our production columns.[7,8]

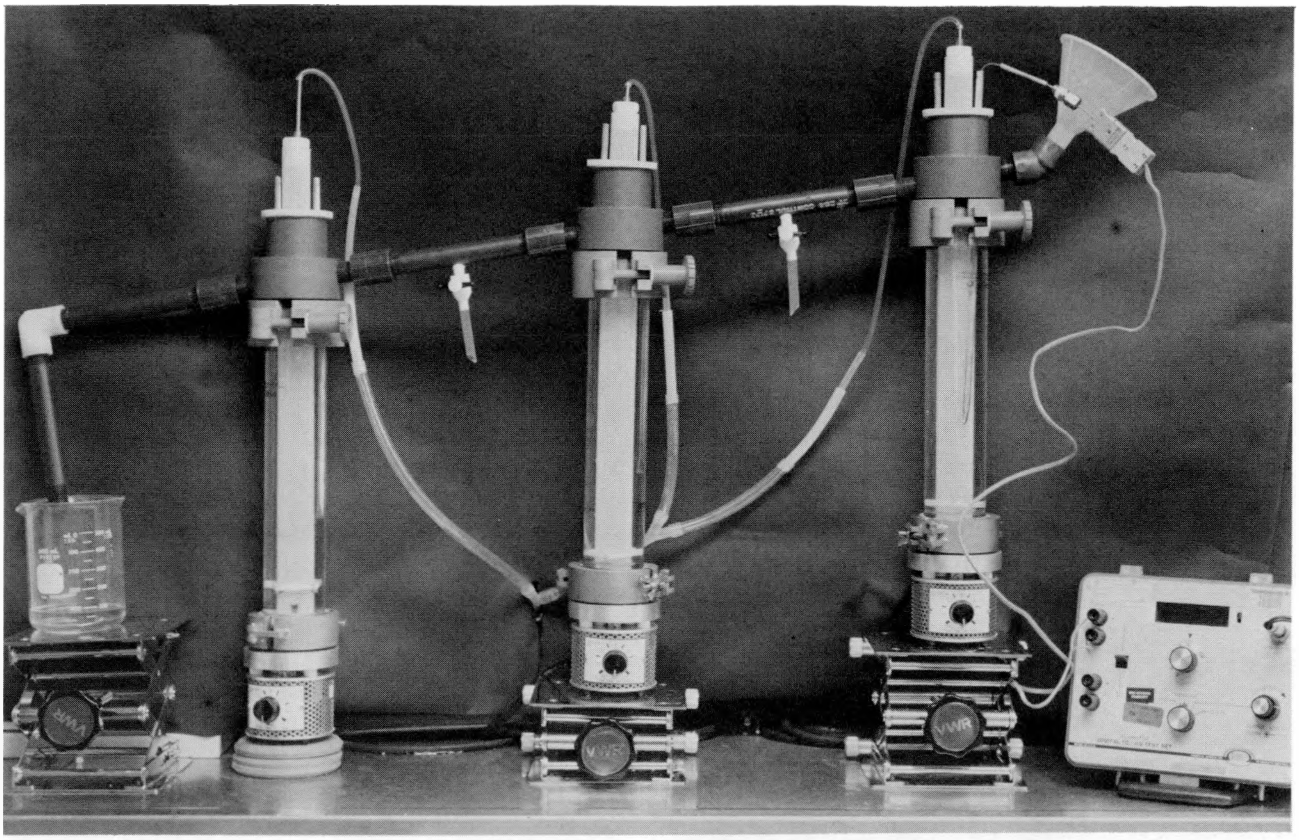

Fig. 1. Cascade dissolver system used for small-scale incinerator ash dissolution studies.

Ash Feed Preparation

The virgin ash used in this study was packaged in eight cans that had been shipped to and stored at Los Alamos in the early 1980s. When the cans were opened, three distinct color variations were observed. Because this might indicate a differing composition, and because we wanted to establish repeatability of results using differing ash feeds, we elected to combine similarly colored materials and divide the ash into three lots.

Two of the three feed lots resulting from this division were used in this study. These were individually calcined for a minimum of 4 hours at 600°C, pulverized, screened through a 40-mesh sieve, blended well with a V-blender, rescreened, and packaged for subsequent use. A reasonably high degree of confidence in the homogeniety of each lot following this procedure was supported by work performed at Los Alamos by S. D. Fink et al.[9]

Anion-Exchange Feed Preparation

Before the anion-exchange purification step, ash filtrates were spectrophotometrically examined to determine if plutonium was in the preferred Pu(IV) oxidation state. Results indicated that no valence adjustment was required. As a final step in preparing feed solutions for anion exchange, acid and plutonium concentrations were adjusted to approximately 7.5 M and 1.5 g/L, respectively.

Feed and Flow Rates

With the exception of calcium fluoride, which was controlled to achieve a specific feed fluoride concentration, feed and solution flow rates were proportionately adjusted to as-designed PROVE process operating parameters. In PROVE, nitric acid and incinerator ash will be delivered to the dissolvers at 18 L and 1.2 kg per hour. Anion-exchange feed, wash, and elutriant solutions will be delivered at 150, 100, and 85 L per hour, respectively. (It is important to note that Los Alamos maintains a position different from that of RFP on how to "proportionately" adjust anion-exchange operating parameters. This will be discussed further under Anion Exchange in the Results and Discussion section.)

Anion-Exchange Resin

The anion exchanger used was Lewatit MP-500-FK, 40–70 mesh, macroporous resin. The resin was converted from the chloride to the nitrate form using Los Alamos/MST-12 Standard Operating Procedure 461-REC-R02.[10]

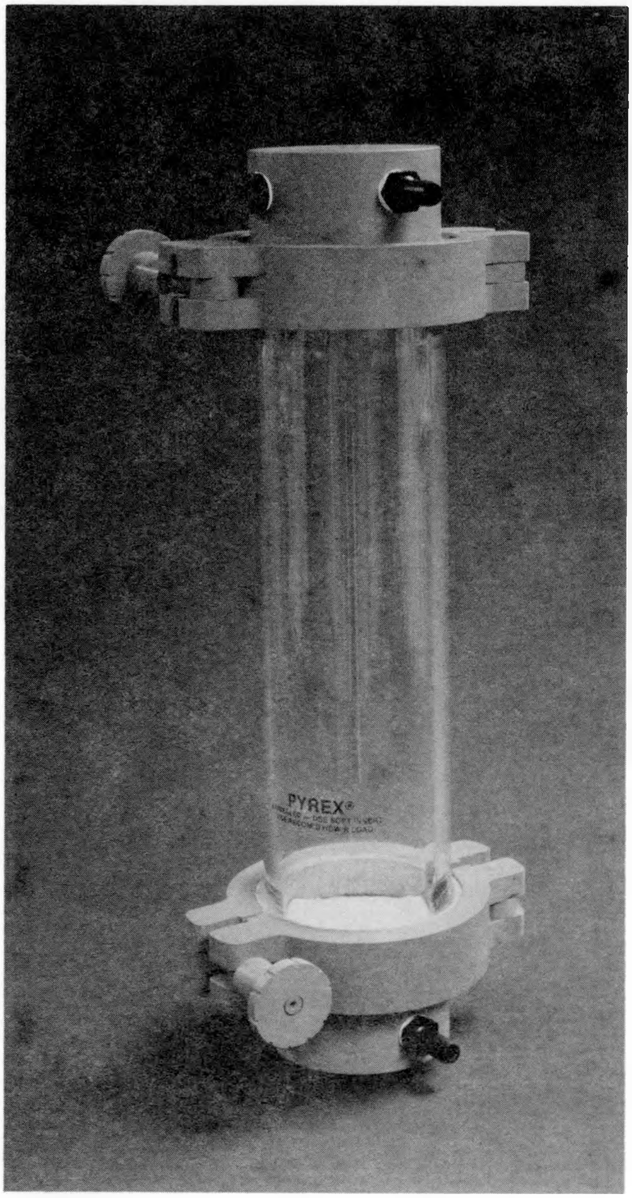

Fig. 2. Anion-exchange column used for small-scale incinerator ash studies.

Assays

During or following each processing step, samples were analyzed for plutonium or elemental impurities. All solid materials, except for the ash feed, which was blended well, were mixed just before sampling. Accordingly, the sample taken may not have been representative and is subject to error greater than that inherent in the method of analysis. Where an analytical technique required that a solid sample first be solubilized, a sealed-reflux dissolution was performed.[11]

With the exception of the elements noted below, all elemental values reported were determined by using DC-arc emission spectroscopy. This technique has a factor of 2 accuracy and a precision of 50% relative standard deviation (RSD). Plutonium values were determined by radiochemical methods having a stated accuracy of 2–5% RSD. Fluoride and chloride concentrations were determined using ion-selective electrodes having an estimated precision of 5% RSD for either element. For comparison, fluoride concentrations were also determined using on-site analytical capabilities. Samples were analyzed using ion-selective electrodes and a standard addition method of analysis. The uncertainty of measurement for this technique is 10% at the 95% confidence level.

Carbon and hydrogen were determined by mass spectrometry. The accuracy for this method is typically 0.25%. Nitrogen was determined by the Kjeldahl-Nessler method.

Plutonium concentration adjustments on anion-exchange feeds were based on gamma assays for plutonium using an in-line solution assay instrument. Operating experience has demonstrated an accuracy of approximately 5% for this instrument. The adjusted feed was then resampled for plutonium concentration determination by radiochemistry.

Experimental Procedure

Dissolution. A series of six separate small-scale dissolutions were performed using feed fluoride concentrations of 0.4, 0.1, 0.25, 0.35, 0.5, and 0.4 M respectively. Ash from blend lot 1 was exhausted after run 4, and ash from blend lot 2 was used for the remaining two dissolutions. Before each experiment, ash and calcium fluoride were weighed and packaged in aliquots sized to achieve the desired hourly addition rate. Because the scaled-down equipment did not permit using an auger feeder, we manually added one quarter of an aliquot every 15 min. Bulk concentrated nitric acid was diluted to 9 M with deionized water and fed continuously to the dissolvers during the run. At termination, a 2-L aliquot was collected for corrosion testing. The remaining filtrate was transferred to and processed through anion-exchange before proceeding with the next dissolution. The dissolvers were disassembled for cleanout, gloveboxes were cleaned, and a material balance was established.

Corrosion Studies. Because the aluminum nitrate addition step was eliminated, there was concern over the resistance of 304L stainless steel to general and localized fluoride-induced corrosion. A cyclic potentiodynamic polarization scan was performed on each filtrate solution generated at the varying feed fluoride addition levels. From these scans and measured polarization resistances, localized corrosion and instantaneous general corrosion rates were determined.

Anion-Exchange. A comparative determination of column capacity for each solution was the method of choice for evaluating the effects of uncomplexed fluoride on anion-exchange behavior. As noted by Marsh and Gallegos,[12]

> The effective capacity of an anion exchange column may be determined in various ways. Some investigators have chosen to report the quantity of plutonium retained on the ion exchange column when the plutonium exiting the column (breakthrough) reaches predetermined levels. . .
>
> We chose instead to determine the saturation capacity of the anion exchange column by loading each column with a volume of feed solution that contained an excess of plutonium.

Although we agree with their approach, the limited quantity of ash feed available restricted us to using the "breakthrough" technique. Accordingly, we chose to base all column capacity determinations on a 5% level of plutonium breakthrough.

To minimize variability introduced when processing anion-exchange feeds with differing plutonium values, we adjusted feed plutonium concentrations to approximately 1.5 g/L. Grab samples were taken from the effluent stream at 2.5- to 5.0-L intervals and analyzed for plutonium. From the feed plutonium concentration, plutonium in the effluent, sample number, and corresponding effluent volume collected, we were able to determine the column capacity at 5% breakthrough.

In all tests, the column was loaded and washed (7.5 M nitric acid) in the upflow direction, and eluted using a downward flow of 0.35 M nitric acid.

RESULTS AND DISCUSSION

Ash Feed

Table I shows the composition of ash before and after rotary calcination and of the ash heel following each of the six dissolutions. A loss in net weight was seen and is attributed to impurities that react with oxygen during burning (rotary calcination) and are removed in the off gas. Conversely, one would expect the nonvolatile impurities to become more concentrated, but many of these also show a decrease in relative concentration following rotary calcination. This indicates the limitations of emission spectroscopy and accordingly, the results presented should be interpreted as qualitative only. It is interesting to note, however, that with the exception of plutonium, chlorine, and possibly sodium, no preferential dissolution is evident.

Dissolution Studies

To determine the level of fluoride best suited for plutonium dissolution, criteria other than the amount of plutonium solubilized were considered; for example, the ratio of plutonium to bulk ash dissolved, which if in proper proportions, could result in a discardable heel. Also, one would hope to minimize the formation of SiF_4 and plugging of the off-gas system by limiting the amount of fluoride added to the minimum amount needed for optimum plutonium dissolution.

Inevitably some spillage occurs when processing nuclear materials in a glove box. Because of the difficulty in determining the amount of plutonium or bulk ash lost to a spill, we elected not to consider these losses when calculating the plutonium and bulk ash dissolution efficiencies. Accordingly, the computed efficiencies may be slightly higher than the values reported.

We computed plutonium (P_d) and ash (A_d) dissolution efficiency as follows:

$$P_d = \frac{P_f + P_l}{A_p} \times 100$$

and

$$A_d = 1 - \frac{(F - F_p) + (H - H_p)}{A - A_p} \times 100$$

where

A = net weight of ash feed, grams;
A_p = weight of plutonium in ash feed, grams;
F = weight of filter residue, grams;
F_p = weight of plutonium in the filter residue, grams;
H = weight of ash heel, grams;
H_p = weight of plutonium in the ash heel, grams;
P_f = weight of plutonium in the ash filtrate, grams; and
P_l = weight of plutonium in the leachate, grams.

As shown in Fig. 3, the amount of plutonium and bulk ash dissolved increased with increasing fluoride concentrations up to 0.35 M and leveled off thereafter. The one exception is the marked difference in bulk dissolution from lot 1 to lot 2 at 0.4 M fluoride. As a result of this difference, the heel left after processing ash from lot 2 was discardable.

Plugging of the off-gas system was encountered when the feed fluoride concentration exceeded 0.4 M. Because

Table I. Composition of Rocky Flats Plant incinerator ash before and after rotary calcination, and ash heel following dissolution at fluoride concentrations of 0.1 to 0.5 M.

	Ash Lot 1		Filter Residues				Ash Lot 1		Filter Residues	
	Uncalcined	Calcined	Run 1	Run 2	Run 3	Run 4	Uncalcined	Calcined	Run 5	Run 6
Net Weight	5031.5g	4824.7g					2898.8g	2762.6g		
Plutonium	0.138g/g	0.145g/g	0.0419g/g	0.09g/g	0.0621g/g	0.489g/g	0.0862g/g	0.0907g/g	0.0141g/g	0.0166g/g
Carbon	8%	0.26%	0.40%	0.35%		0.60%	7%	0.32%	0.71%	0.74%
Hydrogen	0.6%	0.16%	0.27%	1.80%		0.28%	0.50%	0.09%	1.40%	1.60%
Nitrogen	370						280			
Chlorine	2.5%	2.9%	0.13%	0.07%	0.09%	0.06%	3.3%		0.07%	0.08%
Fluorine			2.20%	1.60%	1.60%	1.80%			1.60%	1.70%
Calcium	15%	6%	2%	3%		2%	8%	8%	2%	1.50%
Iron	15%	5%	5%	5%	5%	5%	5%	5%	8%	4%
Magnesium	10%	1%	1%	1%	1%	1%	3%	1%	4000	3000
Phosphorus	<3000	<3000	<3000	<3000	<3000	<3000	<3000	5000	<3000	<1000
Titanium	5%	3%	4%	3%	2%	4%	5%	4%	5%	4%
Zirconium	5000	2000	3000	200	200	5000	<100	500	2000	1500
Aluminum	5%	5%	3%	2%	1.5%	3%	5%	5%	3%	4%
Cadmium	1000	500	100	100	100	100	500	400	200	400
Gallium	2000	2000	2000	300	300	500	500	2000	200	<100
Manganese	3%	7000	5000	6000	5000	5000	1%	5000	3000	2000
Lead	2%	1%	3000	3000	3000	3000	4%	2%	4000	5000
Boron	1000	1000	1000	500	800	1000	2000	1000	700	500
Silcon	20%	7%	10%	15%	8%	10%	15%	10%	10%	10%
Barium	2%	8000	3000	4000	4000	1.5%	1.5%	1%	4000	5000
Sodium	3%	1.5%	2000	2000	1000	1000	2%	1.5%	2500	5000
Beryllium	1500	2000	400	300	200	200	3000	4000	200	500
Chromium	3%	2%	2%	3%	2%	2%	2%	2%	1.5%	1%
Potassium	3%	5%	8000	7000	4000	5000	20%	10%	7000	1%
Copper	1.5%	7000	3000	5000	4000	4000	2%	1%	3000	3000
Nickel	3%	1.5%	2%	2%	2%	2%	2%	2%	1%	5000
Zinc	4%	1%	1%	5000	5000	5000	3%	2%	5000	5000
Silver	500	<100	<100	500	500	50	<30	<100	200	300
Vanadium	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100
Cerium	<500	<500	<500	<500	<500	<500	<500	<500	<500	<500
Germanium	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100
Molybdenum	5000	4000	2000	1000	1000	3000	<300	2000	1000	800
Tungsten	<3000	<3000	<3000	<3000	<3000	<3000	<3000	<3000	<3000	<3000
Cobalt	<100	<100	<100	<300	<300	<300	<100	<100	<100	<300
Hafnium	<300	<500	<500	<300	<300	<300	<300	<500	<300	<300
Tin	<300	<300	<300	<300	<300	<300	4000	<300	1500	<300
Niobium	<300	<300	<300	<300	<300	<300	<300	<300	<300	<300
Strontium	2000	1000	1000	200	200	400	3000	1000	300	500
Bismuth	<100	<100	<100	<100	<100	<100	<100	<100	<100	<100
Lithium	500	300	100	100	<100	<100	<300	200	<100	<100
Yttrium	500	1000	100	30	30	100	<100	100	<100	300

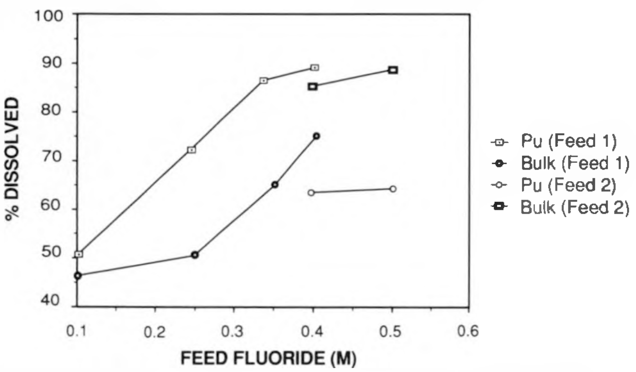

Fig. 3. Single-pass plutonium and bulk ash dissolution efficiencies at fluoride concentrations of 0.1–0.5M.

we were first inclined to attribute this to a change in feed (blend lot 2 was used for the 0.5 M test), we elected to repeat dissolution at 0.4 M using feed from lot 2. When plugging was not observed in the repeated run, we assumed that fluoride added in excess of 0.4 M increased SiF_4(g) formation.

Corrosion Studies

A portion of the 2-L aliquots collected from five of the six dissolution filtrates were tested with solution-annealed or sensitized 304 L stainless steel coupons. Table II shows the general corrosion rates found for the five ash filtrates tested. An increase in the rate of corrosion was observed at elevated temperature; however, results were within the acceptable limits established at RFP. Solutions retested following aluminum nitrate addition showed no significant difference in the rate of corrosion. No localized attack was found at either room or elevated (90–95°C) temperatures.

Anion Exchange

Earlier we stated that "flow rates were proportionately adjusted." However, scale reduction based on column diameter proportionately adjusts the feed flowrate (mg Pu min^{-1} cm^{-2} of resin), whereas scale reduction by bed depth proportionately adjusts the volume flow rate or bed residence time [ml min^{-1} cm^{-2} of resin or column volumes (cv)/hour]. It is believed by Los Alamos investigators that volume flow rate is a concern of importance when processing and proportionally adjusting plutonium-lean solutions.

Table II. General corrosion rates for 304L stainless steel exposed to filtrate solutions from the dissolution of incinerator ash in 9 M nitric acid with 0.1 to 0.5 M fluoride.

	GENERAL CORROSION RATES mils/year	
Coupon Type	Room Temperature	Elevated Temperature
Solution Annealed	0.07 to 0.54	18.2 to 46.5
Sensitized	0.63 to 33.1	151 to 169

In our study, scale reduction was performed based on column diameter only. Therefore, conservatively estimating that the resin occupies 50% of the total column volume, the feed residence time was approximately 1 min. Because plutonium absorption is kinetically limited, a substantial reduction in bed residence time could impact resin performance—even Lewatit, which is known for its outstanding sorption kinetics. As shown in Table III, our volume flow rate was about 10 times greater than that planned in PROVE. (The PROVE anion-exchange system is composed of two 6-in. diameter by 60-in. long columns.)

Table III. Anion-exchange operating parameters used in small-scale studies and PROVE.

	Small-Scale Studies	PROVE
Flow (L/hour)	37.5	150
Feed (Pu in g/L)	~1.5	~1.5
Feed Flow rate (mg Pu min^{-1} cm^{-2})	22.6	22.6
Column Volume (L)	1.39	150
Volume Flow rate (cv/h)	27.0	2.75

Table IV shows the plutonium, aluminum, and fluoride concentrations of anion-exchange feed before adjustment and the column capacity at the varying feed fluoride levels used at dissolution. As can be seen, the column capacity at 5% plutonium breakthrough was not determined for runs 1 and 2. Although the column appeared to be loaded and breakthrough was presumed to have occurred, the lag time between effluent sample submittal and the reporting did not lead to early recognition of this error.

Table IV. Anion-exchange column capacity at 5% plutonium breakthrough using ash filtrate feeds containing varying ratios of F/Al/Pu in 7.5 M HNO_3.

Anion Exchange Feed (non-adjusted)							Capacity	
Run	Pu(g/l)	Al(g/l)	F(g/l)	F:Al	Al:Pu	F:Pu	Column	Operating
1	5.3	1.0	2.2	3.1	1.7	5.2	>61	>44
2	5.2	1.5	1.9	1.8	2.6	4.7	>62	>44
3	7.5	1.2	2.5	3.0	1.4	4.2	74.3	53.5
4	11.0	2.7	2.3	1.2	2.2	2.7	91.8	66.1
5	4.8	*	2.9	*	*	7.6	84.6	60.9
6	3.9	*	4.7	*	*	15.4	74.5	53.6

Anion-exchange feed from dissolution using 0.35 M fluoride had the lowest F:Al:Pu ratio and the highest column plutonium loading at 5% breakthrough. In contrast, we found the next highest column plutonium loadings were attained using feed having the greatest Pu:F ratios. However, the data are incomplete because of an oversight in requesting aluminum for feeds 5 and 6. This was not recognized until after the sample was discarded.

It is important to note that the fluoride values shown in Table IV do not necessarily indicate the level or presence of free fluoride. In fact, we suspect that the abundance of silicon, aluminum, and tantalum present in ash is sufficient to complex any fluoride present over the entire range added at dissolution.

Ryan et al.[13] determined the equilibrium and operational capacity of Lewatit MP-500-FK resin from 7M HNO_3 as a function of solution-phase plutonium concentration. Using a 1.08 g Pu/L feed at a flowrate of 16 mg Pu min^{-1} cm^{-2} (17.8 cv/hour), they estimated the equilibrium capacity to be 86.5 g Pu/L resin. With the same feed, they recommend a maximum operating capacity of about 67 g Pu/L resin for a primary column of a two-column series.

In our small-scale system where the feed flow rate was approximately 23 mg Pu min^{-1} cm^{-2} (27 cv/hr), a wetted resin capacity of 54 to 66 g Pu/L was realized at 5% plutonium breakthrough.

Marsh[14] found that the distribution coefficient ($\mathbf{K}_d$) of plutonium was measurably suppressed at all levels of fluoride tested, no matter how much aluminum was added, for dynamic contact periods from 10 to 60 min. From the data presented in Fig. 4 having F:Al:Pu ratios that nearly approximate ours, it would appear that the K_d of plutonium may not be significantly affected at contact periods of less than 1–2 min.

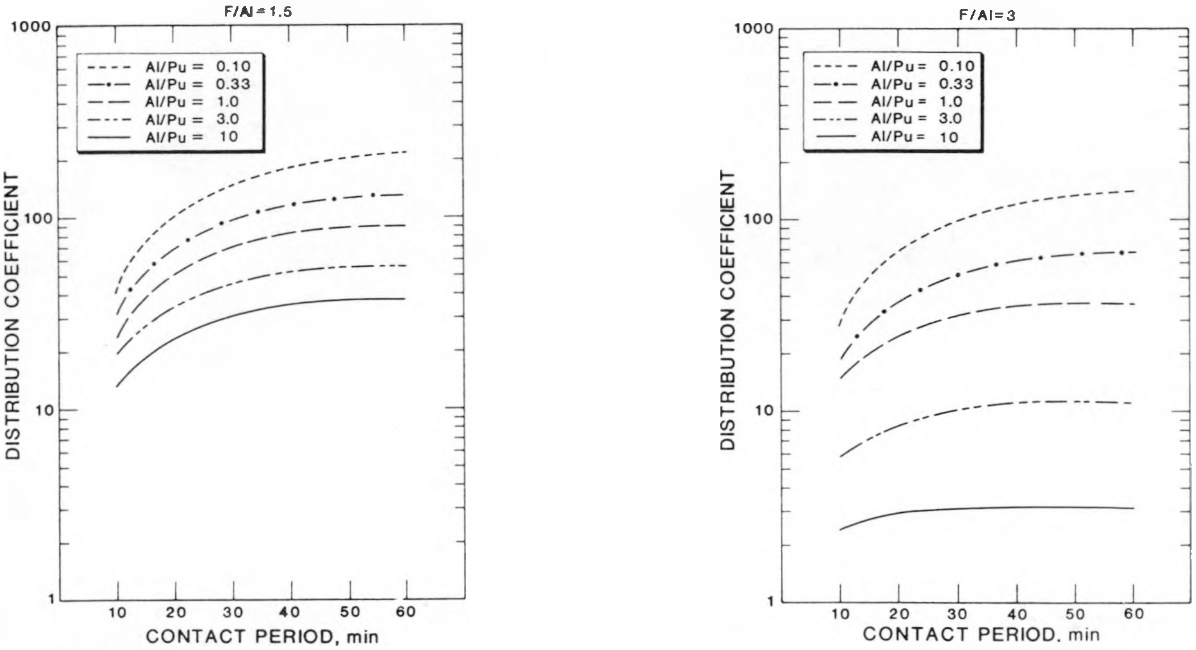

Fig. 4. Sorption of Pu(IV) on Lewatit MP-500-FK anion exchange resin from 7 M nitric acid that contains varying ratios of aluminum to plutonium for F/Al = 1.5 and 3.0, as a function of dynamic contact time. Data from Marsh (1987).

CONCLUSIONS

It would be purely speculative at this point to draw any conclusions until our counterparts at RFP have completed small-scale parallel studies and we have conducted production-scale verification testing. However, a few preliminary observations may be in order.

1. The quantity of plutonium solubilized from incinerator ash tested is comparable at added fluoride levels of 0.35, 0.40, and 0.5 M.
2. It would appear possible to obtain a discardable ash heel following single-pass dissolution by adding an amount of fluoride just sufficient to promote maximum plutonium dissolution while leaving the major fraction of the bulk ash behind. For some types of incinerator ash, 0.4 M fluoride addition may be well suited.
3. For ash tested, as feed fluoride is increased above 0.4 M, off-gas plugging becomes a concern.
4. All dissolver filtrates tested were within RFP acceptable limits of corrosion. It would appear that the aluminum nitrate addition may be eliminated without severely affecting the lifetime of equipment.
5. Throughout our studies we observed no discoloration of anion exchange resin. However, RFP has reported a darkened resin bed and a diminished column capacity after one run. Experience at Los Alamos coupled with the preliminary findings at RFP indicate that the presence of carbon in ash adversely effects anion-exchange performance.

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