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1.0 ABSTRACT

Small scale experimentation was conducted with incinerator ash in the nitric/hydrofluoric acid cascade dissolver and the anion exchange systems at Rocky Flats and Los Alamos National Laboratories for the purpose of determining the following: To determine the relationship between calcium fluoride dissolution feed levels and plutonium dissolution yields. To determine the relationship between calcium fluoride feed levels to dissolution, and the performance of anion exchange when processing dissolution filtrate. To determine the effect of carbonaceous materials on the dissolution and anion exchange when recovering plutonium from incinerator ash.

2.0. INTRODUCTION

Rocky Flats generates many plutonium contaminated residues from which plutonium can be economically recovered. These residues include but, are not limited to, dirty plutonium dioxide, sand, slag and crucible (S,S&C), dirty plutonium tetrafluoride, incinerator ash, and the heels from all of these residues. Plutonium is recovered from the residues by means of aqueous processing. The head-end portion of the recovery flowsheet includes materials sizing, then dissolution in nitric/hydrofluoric acid in the cascade dissolver system. After plutonium valence and acid molarity adjustments are made, the filtrate from dissolution is then processed through nitrate anion exchange to recover and purify the plutonium.

As a part of the Plutonium Technology Committee (PTC), which was organized to coordinate research activities between Rocky Flats and Los Alamos National Laboratories, the Incinerator Ash Processing Working Group (IAPWG) was organized to support the Plutonium Recovery Option Verification Exercise (PROVE). PROVE, is to be a single train of aqueous processes, including dissolution, ion exchange, precipitation, and direct oxide reduction of plutonium, using incinerator ash as feed. IAPWG investigated problems that result from processing incinerator ash, and attempted to determine the optimal fluoride dissolution concentration. The experimentation was conducted in a small scale dissolution and dissolution filtrate ion exchange system. In the IAPWG charter, there were three objectives; 1) to determine the optimal fluoride feed concentrations needed for the dissolution of plutonium from incinerator ash, 2) to determine the effect fluoride on anion exchange plutonium loading efficiencies (when not adding

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aluminum nitrate to incinerator ash filtrate as a fluoride complexing agent), and 3) to determine the effect of unburned carbonaceous material on anion exchange plutonium loading efficiencies.

2.1 INCINERATOR ASH REACTIONS IN THE NITRIC/HYDROFLUORIC ACID SYSTEM

Of the above mentioned residues, incinerator ash has the leanest plutonium content and, is the most difficult to dissolve because of high concentrations of silicon dioxide (silica). In the nitric/hydrofluoric acid system, silica reacts with HF to form SiF_4 (g), SiF_4 (g) then reacts with water to form fluosilicic acid and silica. The silica accumulates in the off-gas piping, eventually clogging the system. When fluoride complexing agents are added to remove corrosive fluoride from the filtrate solutions, the complexing agent reacts with fluosilicic acid to remove the fluoride ion and a silica precipitate is formed.[1] Relatively large amounts of silica precipitate from the solution clogging filters, settling to the bottom of storage tanks, and fouling ion exchange resin beds. The fluoride complexing agent was eliminated from all experimentation described in this report.

Another major constituent of Incinerator ash is carbon or carbonaceous compounds which result from incomplete burning. The majority of the feed to the incinerator includes polyethylene bottles, plastic glovebox bags, paper towel wipes, rags, surgeons gloves, and plastic tape. The operating temperature of the incinerator is approximately 850°C but, the incinerator is highly inefficient and the temperature may vary, resulting in incomplete combustion. When introduced into the nitric/hydrofluoric acid system, unburned hydrocarbons (carbonaceous materials) react violently resulting in foaming.

Past experience, in production equipment, has proven that the plutonium sorption capacity of the anion exchange resin is greatly reduced when processing filtrate generated from incinerator ash. Engineers working with the anion exchange system, speculated that the reduced resin capacity was caused by silica and carbonaceous materials.

2.2 PRODUCTION PROCESS DESCRIPTION AND OPERATION

2.2.1 DISSOLUTION

The production dissolution flowsheet is illustrated in Figure 2.2.1.1.

Pulverized incinerator ash is combined with a fluoride ion source, usually calcium fluoride, and loaded into the hopper of a screw feeder, which feeds into the top of a trough. The solid is combined with nitric acid and water, and the slurry mixture slides down the trough into the top of the first of three cascade dissolvers.

Production Ash Dissolution

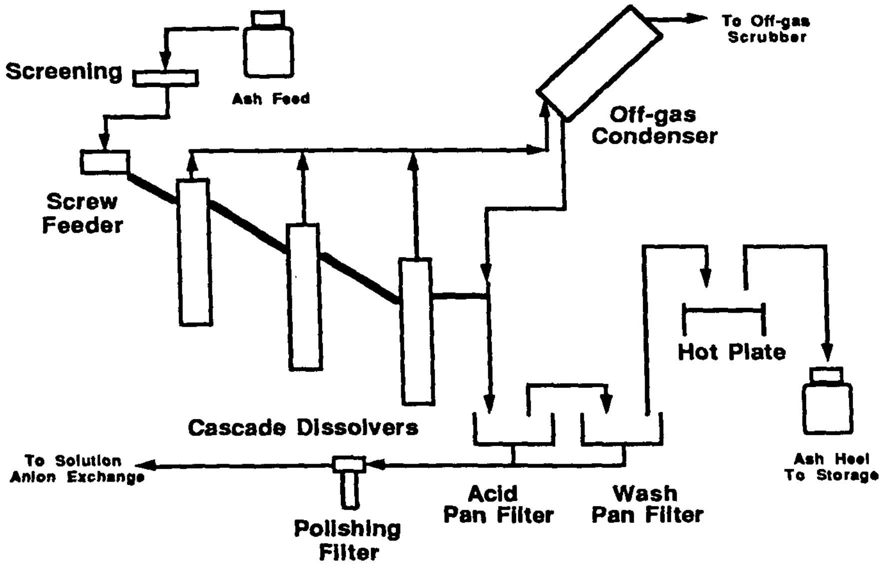


Figure 2.2.1.1

Each dissolver is agitated using an air-lift system in which air is injected into the bottom of a draft tube placed concentrically in the dissolver unit. The purpose of the injected air is to decrease the density of the slurry in the bottom of the draft tube so that the slurry will rise in the tube. Slots are machined in the bottom and at the slurry overflow levels of the draft tube so that the slurry is drawn up the draft tube from the bottom and discharged to the annulus portion of the dissolver, where it is then circulated back to the bottom of the dissolver.[2]

The dissolvers are kept under slightly negative pressure so that agitation air and slurry vapors can be pulled from the dissolvers into an off-gas header system. The operating temperature of the dissolvers is 100 ± 5 °C. Dissolution off-gas vapors are passed through a condenser to vapors, and entrained liquids, and then discharged into the building off-gas scrubbing system. Many problems having to do with the precipitation of silica are encountered in the off-gas system. The air-lift dissolver is illustrated in figure 2.1.2.

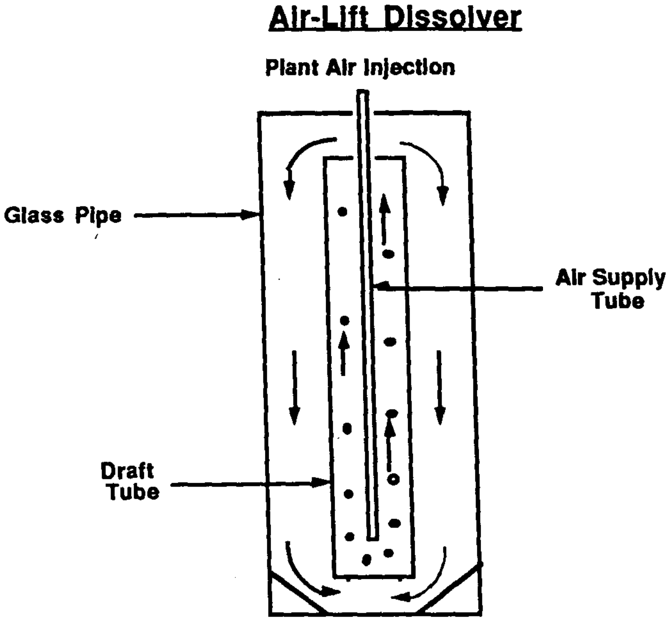


Figure 2.1.2

The slurry from the third dissolver is discharged to a nutsche (pan) filter in which the filter cloth had a nominal pore size of 25 microns. The solution is then passed through a cartridge filter which has a nominal pore size of 1 micron, and then transferred to ion exchange feed tanks. The solids which accumulated on the filters are transferred to a second pan filter and water washed, then dried and packaged for recycle or for waste disposal.

Aluminum nitrate hydrated with nine water molecules (ANN), aided by a flocculent, is added to the anion exchange feed tank to complex any fluoride, for the purpose of reducing corrosion. Silica solids were found to precipitate from the solutions when ANN was added, so the solutions are recycled through a cartridge filter to remove the solids, in the ion exchange feed tanks. Despite the filtration, silica solids are still found to deposit in process piping and foul anion exchange resins.

2.2.2 ANION EXCHANGE

The production nitric acid anion exchange system flowsheet is illustrated in Figure 2.2.2.1.

An exclusive quality of the tetravalent plutonium (plutonium (IV)) ion is utilized to perform the separation and purification of plutonium at Rocky Flats. Tetravalent plutonium is unique in that the plutonium (IV)/nitrate complexes change as the nitric acid concentration changes. In dilute nitric acid, the plutonium (IV) complexes are almost completely cationic and will not be absorbed on the anion exchange resin. At nitric acid concentrations from 4.0 M and higher, plutonium (IV) exists as the plutonium hexanitrate and the plutonium pentanitrate ion ($Pu(NO_3)_6^{2-}$ and $Pu(NO_3)_5^-$), which are strongly sorbed into the anion exchange resin.[3]

Production Anion Exchange

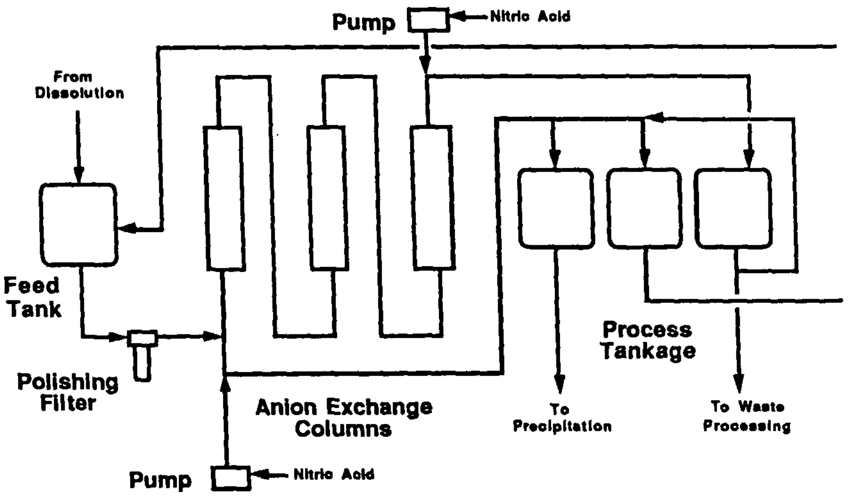


Figure 2.2.2.1

The plutonium must be in the tetravalent state for the anionic plutonium nitrate complexes to form. Prior to the feed (loading) step, any hexavalent plutonium is reduced to the trivalent state using ferrous sulfamate ($Fe(SO_3NH_2)_2$) and then oxidized to the tetravalent state using sodium nitrite ($NaNO_2$). Then by adjusting the feed solution to 7 to 8 M nitric acid and passing the solution over the resin, the plutonium (IV) nitrate complexes will be absorbed. Then by washing the resin to remove impurities, and finally by eluting the complex from the resin with 0.35 M nitric acid, the plutonium (IV) ion can be separated from almost all other impurities.

Each of the four anion exchange steps, and the respective acid concentration and step description is listed in Table 2.2.2.1. [4]

Table 2.2.2.1- Anion Exchange Steps

Step	Acid Concentration (M)	Step Description
Conditioner	7.5	Conditioning of the column to 7.5 M for loading.
Feed	7.5	Absorption of plutonium (IV) on the resin bed.
Wash	7.5	Removes a high percentage of the impurities which do not load, or are slightly absorbed.
Elution	0.35	Plutonium is remove from the anion exchange resin.

3.0 EXPERIMENTAL APPROACH

Experimentation was conducted in a small scale cascade dissolver system, 1/23 the volume of the 6 inch diameter columns to be used in PROVE. Untreated, or uncalcined (none of the incinerator ash had undergone any type of treatment prior to experimentation) ash was the only feed used during the experimentation described in this report. Six runs were made with five different calcium fluoride dissolution feed concentrations; 0.4, 0.1, 0.25, 0.35, 0.5, and 0.4 M. Filtrate generated from the dissolution of the ash was then processed through a small scale anion exchange column, 1/20 the volume of the 5 inch columns to be used in PROVE. No fluoride complexing agents (ANN) were added to remove corrosive fluoride before anion exchange. Six identical tests, with identical equipment and operating parameters, were conducted at Los Alamos National Laboratories (LANL) with incinerator ash that had been calcined at 600 °C for approximately 4 hours. The experimentation conducted at LANL was performed by T. W. Blum and the information is used through this report.[5] The purpose of the recalcination was to remove as much carbonaceous material, before dissolution, as possible. With data from the uncalcined and calcined experiments, a comparison can be made to determine the effect of unburned carbonaceous material on dissolution efficiencies and on anion exchange plutonium loading efficiencies. Also, the test comparison can be used to determine the optimal fluoride feed concentrations needed for the dissolution of plutonium from incinerator ash, and to determine the effect of fluoride on anion exchange plutonium loading efficiencies.

3.1 EQUIPMENT

The Dissolution system consisted of 3-2 inch diameter by 12 inch tall glass pipe dissolver columns. The top Flanges were machined from CPVC, and were linked with 1/2 inch PVC piping which carried the slurry from one dissolver to the next, and to the pan filter (1 micron pore size) in a cascade manner. The dissolver bottom flanges were constructed of 304L stainless steel and each sat directly on an electrically heated hot plate. Each dissolver was agitated by an air-lift system as in the production full scale units. Air was injected into each dissolver at approximately 600 cc per minute. The approximate volume of each dissolver was 0.62 liters. The nitric acid feed was supplied by a laboratory scale peristaltic pump.

The dissolution system is illustrated in figure 3.1.1.

Small Scale Dissolution System

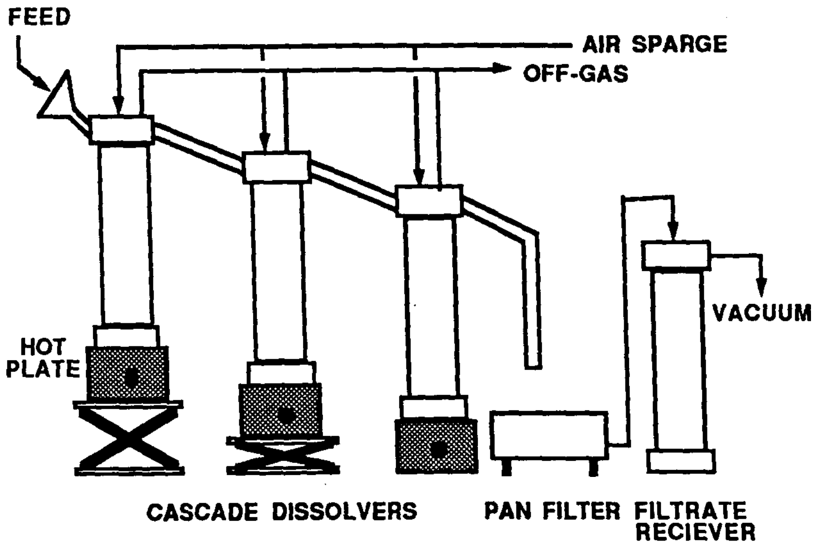


Figure 3.1.1

The anion exchange column was constructed from 3 inch diameter glass pipe, was 12 inches in height, and had a column volume of approximately 1.2 liters. The end flanges were made from CPVC plastic and a high density polyethylene frit was used to contain the anion exchange resin in the column. The anion exchange resin used was Lewatit MP-500-FK, 40-70 mesh, macroporous resin. The feed was supplied by a laboratory scale peristaltic pump. The anion exchange system is illustrated in figure 3.1.2.

Anion Exchange System

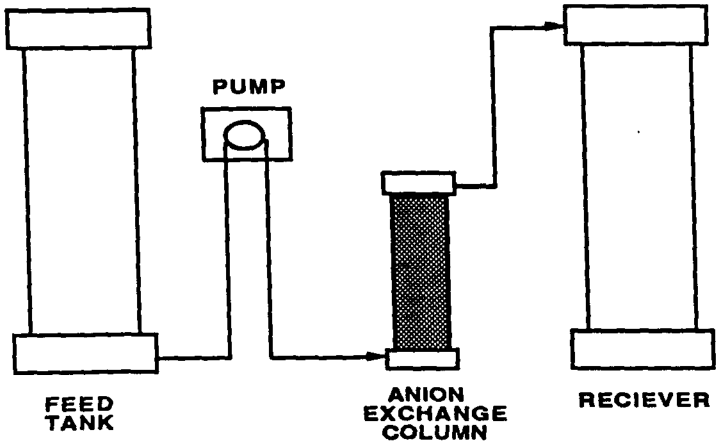


Figure 3.1.2

3.2 SAMPLE ANALYTICAL METHODOLOGY

During experimentation, solid and liquid samples were sent to the analytical laboratories for assays on elements such as Plutonium, Americium, Fluoride, Chloride, Carbon, Hydrogen, and general metal ions. Six different techniques were used to develop assay data requested from the analytical laboratories. Listed in Table 3.2.1 is the desired measurement, analytical technique used to make the measurement, and an approximate standard deviation in the analytical method.[6]

Table 3.2.1 - Analytical Technique Information

Material	Desired Measurement	Technique	Standard Deviation
Solid	Plutonium, Americium	X-ray Fluoresence	10 - 15 %
	Fluoride, Chloride	Specific Ion Electrode	10 - 20 %
	Carbon/Hydrogen	Mass Spectrometry	< 1 %
	General	Emissions Spectroscopy	50 - 100 %
Liquid	Plutonium > 10 g/l, Americium	X-ray Fluoresence	<5 %
	Plutonium < 10 g/l, Americium	Radio Assay	10 - 20 %
	Acid Concentration	NaOH Titration	5 - 10 %
	Fluoride	Specific Ion Electrode	10 - 20 %
	Chloride	Modified Vohlrad	10 -15 %
	General	Emissions Spectroscopy	50 - 100 %

3.3 DISSOLUTION

Six dissolution runs were made each with a different calcium fluoride dissolution feed concentration. All other operating parameters were fixed. Calcium fluoride feed concentrations are listed in Table 3.3.1.

Table 3.3.1 - Calcium Fluoride Feed Rates

Run No.	Fluoride conc. (M)	Feed Rate (g/hr)
1	0.40	12.0
2	0.01	3.0
3	0.25	7.6
4	0.35	10.7
5	0.50	15.2
6	0.40	12.0

Feed Preparation

The ash feed was screened through a 45 mesh screen, which removed matter such as brush bristles, ceramics and glass, then the ash was weighed for feed and mass balance calculations. The proper amount of calcium fluoride was added to the entire batch of ash and mixed thoroughly. A number of one hour batches of the ash/calcium fluoride feed mixture were prepared and transferred to the dissolution glovebox.

Cascade Dissolvers

Small scale solid and liquid feed rates were calculated by multiplying the full scale fed rate by the scaling factor of 1/23. Full scale PROVE and small scale ash dissolution operating parameters are listed in Table 3.3.2.

Table 3.3.2 - Dissolution Operating Parameters

Stream	PRMP Feed Rates	Small Scale Feed Rate
Incinerator Ash	1.2 kg/hr	52 g/hr
Calcium Fluoride	282 g/hr	See Table 3.2.x
12 M Nitric Acid	13.7 l/hr	596 ml/hr
0.35 M Nitric Acid	4.3 l/hr	187 ml/hr

The ash/calcium fluoride feed mixture was loaded into a funnel at approximately 1/4 hour time intervals. Nine normal Nitric acid (the combination of 12 and 0.35 M feeds) was pumped into the feed funnel at a flowrate of 783 ml per hour. The acid solution washed the solids down the funnel and into the first of three air-lift circulated, cascade dissolvers. The temperature of the each dissolver was maintained at 100 ± 5 ° C. The combined volume of the three dissolver columns was 1.85 liters, giving a slurry residence time of approximately 2.36 hours.

Filtration

Solutions were vacuumed through the pan filter (1 micron pore size) to a filtrate receiver. Solids that accumulated in the pan filter were transferred to a hot plate where they were dried. The solids were then weighed and removed from the glovebox to be assayed.

Off-gas System

Agitation Air and solution vapors were collected by a header system under slightly negative pressure. The off-gas was then passed through a 4 liter vacuum flask water scrubber to remove silicon tetrafluoride gas and any entrained liquids.

Sample Analysis

All solids (ash feeds and heels) were analyzed for plutonium content by both non-destructive and chemical methods. Samples of each solid were taken for general impurities analysis by emissions spectroscopy. Some solids were analyzed for carbon, nitrogen and hydrogen content. All liquids (filtrates, scrubber solutions, and other wastes) were analyzed for plutonium, chloride, fluoride, and nitric acid concentration. Samples of each liquid were taken for general impurities analysis by emissions spectroscopy.

3.4 ANION EXCHANGE

The operating parameters for the anion exchange of dissolution filtrate, like dissolution, were based on those for the PROVE process.

Feed Preparation

Plutonium must be in the tetravalent state in order for the plutonium to efficiently load on the anion exchange resin. If any plutonium exists in the hexavalent state it is reduced to the trivalent state using ferrous sulfamate and then oxidized to the tetravalent state using sodium nitrite, before the feed step. During experimentation, we were unable to determine the quantity of plutonium in each of the valence states, therefore the amount of valence adjustment reagent needed was calculated using formulas based on anion exchange feed volumes (as suggested by PROVE personnel) rather than actual ion concentrations. The amounts of reagents added were calculated using Equations 3.4.1 and 3.4.2.[7]

Equation 3.4.1 $Fe(SO_3NH_2)_2$ (40 wt %) = 2 ml per liter of filtrate solution

Equation 3.4.2 $NaNO_2 = 2 \times (Fe(SO_3NH_2)_2$ (40 wt %)) concentration

Filtrate Processing

Filtrate solution flow direction through the anion exchange column, acid concentration, and total through-put volumes used for each step are listed in Table 3.4.1. Since the anion exchange feed concentration for PROVE was estimated to be between 1.0 and 2.0 g/l, the anion exchange feed plutonium concentration, for the purposes of this experiment, was adjusted to approximately 1.5 g/l. The anion exchange resin used was Lewatit MP-500-FK, 40-70 mesh, macroporous resin. [4]

Table 3.4.1 - Anion Exchange Operating Parameters

Step	Feed Rate (mL/min)	Total Volume[a]	HNO_3 Conc (M)	Flow Direction
Conditioner	34.0	1.2	7.5	Top to Bottom
Feed	610.0	- - -	7.5	Bottom To Top
Wash	34.0	1.2	7.5	Bottom To Top
Elution	34.0	2.2	0.35	Top to Bottom

a - Number of anion exchange column volumes.

The small scale feed rate was calculated by using a direct ratio of the cross sectional areas of each column. A cross-sectional factor (Equation 3.4.2) for the small scale unit was set equal to a cross-sectional factor for the full scale unit, with the only unknown being the small scale feed rate. The feed rate for the 3 inch diameter column was calculated to be approximately 650 ml/min. The feed flowrate factor is listed below. All other anion exchange step flow rates were set much lower (2 liters per hour) than the feed step rate so that each step would be as effective as possible.

Equation 3.4.3

$$\text{Cross Sectional Factor} = \frac{\text{Plutonium Concentration (g/l) X Feed Rate (l/hr)}}{\text{Column Cross Sectional Area}}$$

Breakthrough

In order to determine the plutonium loading capacity of the anion exchange resin, a plutonium breakthrough point was arbitrarily determined to be 5 percent of the feed concentration, or approximately 0.075 g/l plutonium. Plutonium breakthrough data can be used in determining if a general correlation exists between the point at which the feed cycle breakthrough is reached and the calcium fluoride feed rate to dissolution. This data can also be used to determine if the carbonaceous residues in uncalcined incinerator ash (RFP) filtrate lowers the plutonium loading efficiency of anion exchange resin as compared to filtrate generated from recalcined incinerator ash (LANL).

Sample Analysis

Samples were taken during each step of the anion exchange process. Because all that was needed from the conditioner step was to verify that no plutonium was coming from the column, conditioner samples were taken every 10 minutes. During the loading (feed) step, samples were taken every 4 minutes, so that the plutonium breakthrough point could be determined. In order to verify that plutonium was not being washed from the resin, samples were taken every 5 minutes during the wash step. During the elution step, samples were taken every 4 minutes in order to develope a plutonium elution curve. Samples were also submitted to verify nitric acid concentrations during all steps.

4.0. RESULTS AND DISCUSSION

Two particular types of information were obtained in order to determine the effect of carbonaceous material on dissolution and anion exchange operating efficiencies; 1) plutonium and bulk dissolution efficiencies and, 2) Anion exchange loading efficiencies. This information, in addition to general composition information, is presented in this section.

4.1 DISSOLUTION EXPERIMENTATION

The efficiencies of plutonium and bulk dissolution were calculated using equations 4.1.1 and 4.1.2 respectively.

Equation 4.1.1 $P_d = (P_f/A_p) \times 100$

Equation 4.1.2 $B_d = [1 - (H - H_p)/(A - A_p)] \times 100$

where

A = net weight of ash feed, grams
A_p = weight of plutonium in ash feed, grams
B_d = Bulk incinerator ash dissolution efficiency, %
H = weight of ash heel, grams
H_p = weight of plutonium in ash heel, grams
P_d = plutonium dissolution efficiency, %
P_f = weight of plutonium in the dissolution filtrate, grams

The plutonium and bulk dissolution efficiencies for tests using calcined incinerator ash as feed were consistently higher than the efficiencies for tests using uncalcined incinerator ash as feed. When comparing the runs with identical calcium fluoride feed rates (comparing uncalcined run 1 with calcined run 1, etc.), the average difference between plutonium dissolution efficiencies was 13.7 percent, whereas the average difference between bulk dissolution efficiencies was 16.7 percent. One possible explanation for the efficiency differences may be that carbonaceous material in the uncalcined ash filtrate competes for the fluoride ion which is essential for the rapid dissolution of plutonium. Another explanation could be that the concentration of plutonium in the calcined incinerator ash feed was from 2 to 4 percent higher than that in the uncalcined feed.

Plutonium incinerator ash feed and heel assays are listed in Table 4.1.1. Plutonium and bulk dissolution efficiencies for calcined (LANL) incinerator ash and uncalcined (RFP) incinerator ash feed are listed in Table 4.1.2.

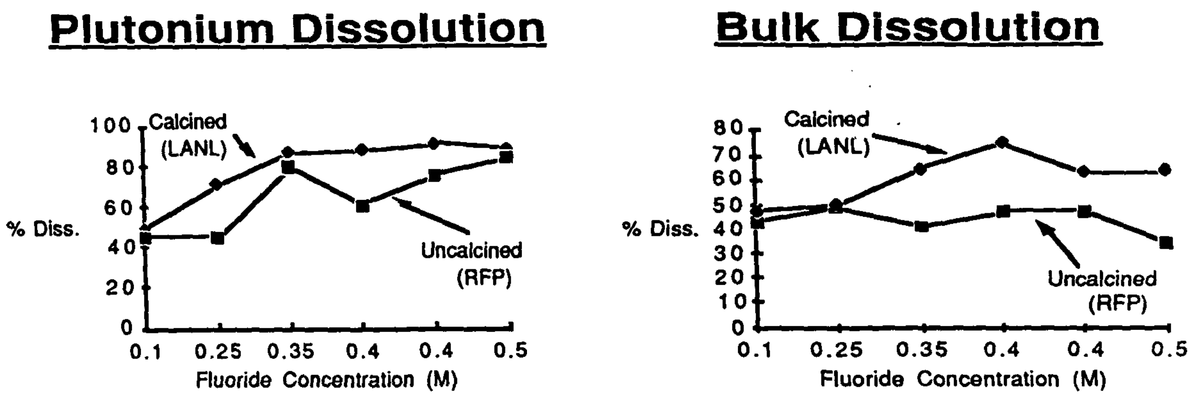
Table 4.1.1 - Uncalcined Ash Feed and Heel Assays

Run No.	Feed Assay (g/g)	Heel Assay (g/g)
1	0.060	0.024
2	0.060	0.058
3	0.087	0.075
4	0.062	0.026
5	0.059	0.009
6	0.077	0.010

Table 4.1.2 - Plutonium and Bulk Dissolution Efficiencies

		Calcined (LANL)		Uncalcined (RFP)	
Run No.	Fluoride (M)	Bulk %	Plutonium %	Bulk %	Plutonium%
1	0.4	74.7	87.9	47.1	60.6
2	0.1	46.6	49.4	43.3	45.2
3	0.25	49.5	70.9	49.4	44.0
4	0.35	65.2	86.9	40.9	80.4
5	0.5	64.2	87.9	34.5	85.2
6	0.4	63.0	90.6	47.4	75.8

In general, as the fluoride feed concentration increased, the plutonium dissolution efficiency increased. The highest dissolution efficiencies were achieved at fluoride concentrations of 0.35 M and higher for both the uncalcined incinerator ash and the calcined incinerator ash tests. No obvious correlation existed between the calcium fluoride feed concentrations and bulk dissolution efficiencies. Figure 4.1.1 illustrates the plutonium and Bulk dissolution efficiencies as a function of fluoride concentration for both the uncalcined incinerator ash and the calcined incinerator ash feeds.



Plutonium Dissolution

Bulk Dissolution

Figure 4.1.1

None of the ash heels produced from the uncalcined ash dissolution runs had a low enough plutonium assay to be considered below discard limits by Rocky Flats economic discard standards. The uncalcined ash heel assays are listed in Table 4.1.1.

Tables 4.1.3 and 4.1.4 list the composition of uncalcined incinerator ash feeds and heels for runs 1 and 2. The elements most likely to be over 1 percent of the total mass of the ash feed and heel were calcium, chromium, iron, and titanium, with aluminum, and silicon making up a large majority of the compositions. Analytical results for runs 3 through 6, other than plutonium and americium assays, had not been received prior to publication.

Tables 4.1.5 and 4.1.6 list the compositions of uncalcined incinerator ash filtrate for runs 1 through 5. The elements with the highest concentrations were aluminum, calcium, chromium, iron, potassium, molybdenum, and nickel. The average filtrate plutonium concentration was 2.75 grams per liter of solution, and the average nitric acid concentration was 10.3 M.
Analytical results for run 6 had not been received prior to publication.

Table 4.1.3 - Uncalcined Ash and Ash Heel Emissions Spectroscopy Results

Element (ppm)	Feed Run 1	Heel Run 1	Feed Run 2	Heel Run 2
Ag	500	1000	750	2500
Al	10000	10000	>10000	>10000
As	<50	<50	<50	<50
B	500	100	500	750
Bi	<5	<5	<5	<5
Ca	10000	5000	>10000	>10000
Cd	500	500	<10	1000
Co	<50	<50	<50	250
Cr	5000	5000	2500	>10000
Cu	1000	500	2500	2500
Fe	10000	5000	>10000	>10000
Ge	<5	<5	<5	<5
Hg	10	10	<5	<5
In	<10	<10	<10	75
K	5000	1000	>10000	7500
Mg	1000	1000	2500	5000
Mn	500	500	750	1000
Mo	<50	<50	500	1000
Nb	500	100	<500	<500
Ni	1000	1000	5000	7500
P	100	<50	2500	2500
Pb	1000	500	2500	5000
Sb	<10	<10	500	2500
Si	>10000	>10000	>10000	>10000
Sn	100	<10	500	2500
Sr	<500	<500	<500	750
Te	<10	<10	<10	<10
Ti	10000	10000	>10000	>10000
Tl	<50	<50	<50	<50
V	100	100	<10	<10
Zn	<100	<100	1000	1000
Zr	<50	<50	<50	750

Table 4.1.4 - Uncalcined Ash and Ash Heel Compositions

Element (wt%)	Feed Run 1	Heel Run 1	Feed Run 2	Heel Run 2
Pu	6.00	2.40	6.00	5.50
Am			1.0X10-4	4.9X10-5
F -	3.50	0.98	2.00	1.00
Cl-	1.20	0.04		
C	15.00	22.00		6.00
H	1.80	0.90		0.00

Table 4.5 - Uncalcined ash Filtrate Emissions Spectroscopy Results

Element (ppm)	Run 1	Run 2	Run 3	Run 4	Run 5
Ag	5	<1	<1	<1	<1
Al	1600	1100	1500	1600	1900
As	<50	<50	<50	<50	<50
B	28	0	14	33	36
Bi	<5	<5	<5	<5	<5
Ca	>2000	1800	>2000	>2000	>2000
Cd	75	<10	20	23	21
Co	<50	<50	<50	30	18
Cr	540	150	150	210	15
Cu	450	120	180	460	470
Fe	150	1400	2000	>200	2000
Ge	<5	<5	<5	<5	150
Hg	<5	<5	<5	<5	<5
In	<10	<10	11	<10	<5
K	>1000	>2000	>2000	>2000	<10
Mg	230	180	180	190	>2000
Mn	120	24	50	150	180
Mo	200	100	1800	1400	120
Nb	<500	<500	<500	<500	<500
Ni	940	310	500	710	550
P	240	59	56	<50	<50
Pb	420	160	400	500	500
Sb	100	<10	220	40	34
Si	150	11	21	24	29
Sn	140	63	40	140	100
Sr	<500	<500	<500	<500	<500
Te	70	<10	<10	<10	<10
Ti	380	100	150	190	290
Tl	<50	<50	<50	<50	<50
V	<10	<10	<10	<10	<10
Zn	220	41	72	56	57
Zr	<50	<50	900	50	47

Table 4.1.66 - Uncalcined Ash Filtrate Compositions

Element	Run 1	Run 2	Run 3	Run 4	Run 5
Pu (g/l)	2.02	2.40	2.65	2.81	3.88
Am (g/l)	1.41X10-3	1.93X10-2	2.71X10-3	3.33X10-3	3.44X10-3
H+ (M)	10.10	9.96	11.53	10.30	9.77
F- (g/l)	1.32	1.94	1.71	2.17	2.78
Cl- (g/l)	<0.5	1.28	0.71	0.99	1.83

4.2 ANION EXCHANGE EXPERIMENTATION

In order to determine the plutonium loading capacity of the 1.2 liters of anion exchange resin, a plutonium breakthrough point was arbitrarily determined to be 5 percent of the feed concentration, or approximately 0.075 g/l plutonium. The point at which the breakthrough plutonium concentration was reached, is listed in Table 4.2.1. The breakthrough point is described as the total amount of plutonium fed to the column when 5 percent of the feed concentration was reached. The loading capacity of the Lewatit MP-500-FK, 40-70 mesh, macroporous resin at a flow rate of 16 mg Pu min^{-1} cm^{-2}, as determined by Ryan, Bray and Wheelwright, is 67 grams of plutonium per liter of resin.[8] The flow rate for our system was approximately 21 mg Pu min^{-1} cm^{-2}.

Table 4.2.1 - Anion Exchange Feed Concentrations and Breakthrough

		Calcined (LANL)		Uncalcined (RFP)	
Run No.	Fluoride (M)	Pu (g/l)	Breakthrough (g)	Pu (g/l)	Breakthrough (g)
1	0.4	1.67	61.0	1.5	27.5
2	0.1	1.38	62.0	1.5	27.5
3	0.25	1.35	74.3	1.5	17.6
4	0.35	1.53	91.8	1.31	34.8
5	0.5	1.41	84.6	1.5	33.8
6	0.4	1.42	74.5	1.5	29.3

The plutonium loading capacity of the anion exchange resin for both uncalcined and calcined incinerator ash experimentation is listed in Table 4.2.2. The plutonium loading capacity of the resin when processing filtrate generated from uncalcined incinerator ash was from one half to one quarter of the resin capacity when processing filtrate generated from calcined incinerator ash. The resin plutonium loading capacity for the filtrate generated from the calcined incinerator ash, was comparable to that determined by Ryan, Bray and Wheelwright. Loading capacities could not be calculated for calcined ash runs 1 and 2 because all of the feed filtrate was processed through the column before the breakthrough point was reached. Plutonium Breakthrough data are illustrated in Figure 4.2.1.

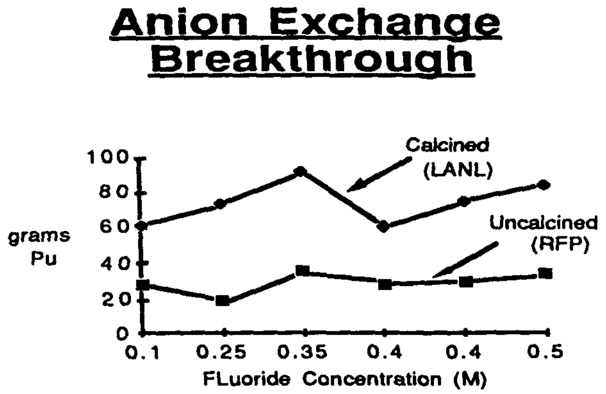


Figure 4.2.1

Table 4.2.2 - Plutonium Loading Capacities (PLC)

Run	Calcined Ash Resin Capacity (g/l)	Uncalcined ash Resin Capacity (g/l)	(Uncal. PLC) X 100 / (Cal. PLC)
1	- - -	22.9	>45
2	- - -	22.9	>44
3	61.9	14.7	24
4	76.5	29.0	38
5	70.5	28.2	40
6	62.1	24.4	39

As stated in the experimental section of this document, the operating parameters (with the exception of the calcium fluoride feed rates) and all equipment were identical for all tests. The reason that such large differences exists between the calcined and uncalcined anion exchange plutonium loading capacity, seems to be the presence of carbonaceous material in the filtrate generated from the uncalcined incinerator ash. Further research needs to be conducted to determine the mechanism by which the anion exchange resin loading capacity is reduced. At this point in time, any attempt to explain the capacity reduction would be speculation. No obvious correlation exists between the calcium fluoride feed concentrations and the plutonium loading capacities.

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5.0 EXPERIMENTAL SUMMARY AND RECOMMENDATIONS

5.1 EXPERIMENTAL SUMMARY

Listed below is a summary of information presented in section 4.0, Results and Discussion.

5.1.1 DISSOLUTION

1. Plutonium and bulk dissolution as a function of calcium fluoride feed concentrations:
   In general, as the fluoride feed concentration increased, the plutonium dissolution efficiency increased. The highest plutonium dissolution efficiencies were achieved at fluoride concentrations of 0.35 M and higher for both the uncalcined incinerator ash and the calcined incinerator ash tests.

   No obvious correlation existed between the calcium fluoride feed concentrations and bulk dissolution efficiencies. None of the ash heels produced from the uncalcined ash dissolution runs had a low enough plutonium assay to be considered below discard limits by Rocky Flats economic discard standards.

2. Plutonium and bulk dissolution as a function of calcination:
   When comparing the runs with identical calcium fluoride feed rates (comparing uncalcined run 1 with calcined run 1, etc.), the average difference between plutonium dissolution efficiencies was 13.7 percent, whereas the average difference between bulk dissolution efficiencies was 16.7 percent. One possible explanation for the efficiency differences may be that carbonaceous material in the uncalcined ash filtrate competes for the fluoride ion which is essential for the rapid dissolution of plutonium. Another explanation could be that the concentration of plutonium in the calcined incinerator ash feed was from 2 to 4 percent higher than that in the uncalcined feed.

5.1.2 ANION EXCHANGE

1. Plutonium loading capacity as a function of the calcium fluoride feed concentrations:
   No obvious correlation exists between the calcium fluoride feed concentrations and the plutonium loading capacities.

2. Plutonium loading capacity as a function of calcination: The plutonium loading capacity of the resin when processing filtrate generated from uncalcined incinerator ash was from one half to one quarter of the resin capacity when processing filtrate generated from calcined incinerator ash.

5.2 RECOMMENDATIONS

1. Continue the use of 0.35 M Fluoride in the dissolution feed: The best plutonium and overall bulk dissolution efficiencies were obtained with fluoride concentrations of 0.35 M and higher.

2. Do not add a fluoride complexing agent: The resin plutonium loading capacity for the filtrate generated from the calcined incinerator ash was comparable to that determined by Ryan, Bray and Wheelwright.[8] Therefore, it can be concluded that the fluoride had a minimal affect on the performance of the anion exchange resin under given conditions.

3. Recalcine virgin incinerator ash before dissolution: Based on information contained in this report, the recalcination of incinerator ash significantly increased dissolution efficiencies of both plutonium and overall bulk, and substantially increased anion exchange plutonium loading capacities.