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BATCH DISSOLUTION OF INCINERATOR ASH

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BATCH DISSOLUTION OF INCINERATOR ASH

INTRODUCTION

Plutonium recovery from incinerator ash was initially demonstrated on a production-scale at Los Alamos.⁽¹⁾ Similar processes have been used at Hanford⁽²⁻⁴⁾ and Rocky Flats.⁽⁵⁻⁹⁾ The pertinent dissolution criteria are summarized below:

- Optimum dissolution solution: nitric acid with fluoride.
- Four-tenths to six-tenths molar fluoride was essential.
- Nine to 15.8M nitric acid molarity.
- Temperature: 100 to 130 °C.
- Multiple contacts with fresh portions of dissolving solution were required to achieve quantitative plutonium recovery (>99.0 percent).
- Greater than 80 percent plutonium dissolution occurred within the first 15 minutes of each contact.

The purpose of this study was to evaluate dissolution variables using current incinerator ash. A secondary purpose was to determine the effect of reburning on ash dissolution.

SUMMARY

Optimum dissolution conditions were found and demonstrated. Plutonium recovery ranged from 95 to 100 percent using HNO₃-0.3M CaF₂ at 100 °C. Plutonium dissolution could be obtained as readily with 5M HNO₃ as with 10M HNO₃ provided the fluoride was 0.6M. Plutonium dissolution was more than 80 percent complete within 15 minutes; longer contact times yielded trace or no additional dissolution. The number of multiple contacts required for greater than 99 percent plutonium recovery varied

from 2 to 4, depending on the plutonium content of the ash.

Solids dissolution ranged from 40 to 70 volume percent using the same conditions which yielded greater than 95 percent plutonium recovery. When ash was reburned prior to chemical treatment, solids dissolution ranged from 60 to 95 percent. Reburning alone yielded a 20 volume percent and a 15 weight percent reduction in the three out of four cans of ash studied.

EXPERIMENTAL

EQUIPMENT

A 1000-milliliter Kimax distilling flask with three necks, each with 24/40 joints (Kimble Catalog No. 26220), was used for a dissolver. A bulb-type Allihn condenser (Corning Catalog No. 2440) with a drip tip 24/40 joint was placed in one neck. A thermometer tube attached to a 24/40 joint was placed in a second neck. An open tube through a 24/40 joint, angled to reach within 1/2 inch of the flask bottom, was placed in the third neck to provide a means of air agitation.

The flask was heated with a 335 watt, 1000 milliliter, round bottom, table model, GLAS-COL heating mantle (Van Waters and Rogers Catalog No. 33752-125). This style of heating mantle was self-supporting and provided uniform heat to the dissolver.

Solids were collected using a 600-ml Buchner funnel with a medium porosity (10 to 15 micron) quartz frit. A one-liter Pyrex filtering flask was used to collect the filtrate at a vacuum of 26 inches of mercury.

Ash was reburned using a 4-inch diameter, quartz slip joint cylinder with end frits and a crucible furnace (Hoskins), operated at 400, 600, or 800 °C. Air was passed through the quartz vessel at 0.3 ft³/min. Higher rates tended to pack the

ash against the upper frit with a resultant pluggage.

PROCEDURES

All dissolution tests were carried out with 500 milliliters of dissolving solution in the one-liter dissolver. Thirty grams of Z Plant incinerator ash were used in each test to achieve a solid to liquid ratio of 60 grams per liter. The dissolving solution was composed of 5M HNO_3 -0.3M CaF_2 heated to boiling. All contacts were agitated by air sparging. At the end of the dissolution period, solids were allowed to settle so that only the solution would be decanted. Fresh dissolving solution was then added for the next contact.

The completion of plutonium dissolution was determined by gamma counting the dissolver residues with an NaI(Tl) detector. Residues with very few plutonium gamma counts indicated essentially 100 percent plutonium removal into solution. The gamma count of dissolver residues was compared with the initial gamma count of the ash to determine the relative degree of plutonium dissolution. In most cases several tests with nearly complete plutonium removal established a plutonium value to be associated with a particular ash and thereafter enabled dissolution values to be calculated on a percent basis.

RESULTS

Those dissolution variables which were studied to permit selection of optimum dissolution conditions were:

- Fluoride molarity and source of fluoride.
- Nitric acid molarity.
- Temperature.
- Contact time.
- Number of contacts.

FLUORIDE MOLARITY

Fluoride levels were varied from 0.0 to 0.6M to find the effect on plutonium dissolution in an ash-nitric acid system. Complete plutonium dissolution was achieved with 0.6M fluoride (see Table I).

TABLE I
EFFECT OF FLUORIDE ON PLUTONIUM DISSOLUTION

<u>Fluoride*</u> <u>Molarity</u>	<u>Plutonium Dissolved (Relative Percent)</u>		
	<u>1st Contact</u>	<u>2nd Contact</u>	<u>Summation</u>
0.0	5	3	8
0.2	42	22	64
0.6	69	31	~100

* Dissolver solution: 10M HNO₃.

SOURCE OF FLUORIDE

Comparison of NaF, HF, and CaF₂ revealed no significant differences in dissolution properties (see Table II). Calcium fluoride possessed the advantages of being non-toxic and of providing added salting strength to subsequent solvent extraction processes.⁽¹⁰⁾

TABLE II
COMPARISON OF FLUORIDE COMPOUNDS

<u>Fluoride*</u> <u>Molarity</u>	<u>Plutonium Dissolved (Relative Percent)</u>		
	<u>1st Contact</u>	<u>2nd Contact</u>	<u>Summation</u>
0.6M HF	63	31	94
0.6M NaF	70	28	98
0.3M CaF ₂	65	35	~100

* Dissolver solution: 10M HNO₃.

NITRIC ACID MOLARITY

Nitric acid molarities of 10 and 5M each with 0.6M fluoride were studied since these concentrations corresponded to the usual initial and final acid levels of plant dissolver operation. Four tests with 5M HNO₃ yielded an average of 2.82 grams plutonium recovered, while four tests with 10M HNO₃ yielded an average of 2.88 grams of plutonium recovered. Considering the inhomogeneity within a single can of ash, there appeared to be no significant difference between the use of 5 or 10M HNO₃ with 0.6M fluoride.

TEMPERATURE

The temperatures of all dissolutions were in the range of 95 to 105 °C with the exception of one test at 80 to 90 °C. The lower temperature resulted in reduced plutonium dissolution (see Table III) and reduced solids dissolution.

TABLE III

EFFECT OF TEMPERATURE ON PLUTONIUM DISSOLUTION

<u>Temperature*</u> <u>°C</u>	<u>Plutonium Dissolved (Relative Percent)</u>		
	<u>1st Contact</u>	<u>2nd Contact</u>	<u>Summation</u>
80 to 90	35	26	61
95 to 105	66	34	100

* Dissolver solution: 5M HNO₃-0.3M CaF₂.

CONTACT TIMES

Ash was contacted with fresh dissolving solution for periods of two hours each. In every case the majority of dissolution occurred within the first hour (see Table IV). The second hour of each two-hour contact produced only 3 to 4 percent of the total plutonium dissolved.

TABLE IV
EFFECT OF CONTACT TIMES ON PLUTONIUM DISSOLUTION

Run* No.	Plutonium Dissolved (Relative Percent)			
	Contact No. 1		Contact No. 2	
	1st hour	2nd hour	1st hour	2nd hour
1	70	2	27	1
2	78	2	19	0
3	61	7	32	0
4	72	1	27	0
5	38	7	49	6
6	63	0	31	6
7	66	6	24	3
8	80	1	18	1
9	64	6	24	6
10	58	8	31	3
Average	65	4	28	3

* Dissolver solution: 5M HNO₃-0.3M CaF₂.

The study of contact times was extended to evaluate plutonium dissolution at 15-minute intervals. Without exception the majority of plutonium dissolution occurred within 15 minutes of each fresh dissolvent addition (see Table V). After the first 15-minute interval, the plutonium dissolution rate was 2 percent every 15 minutes.

TABLE V
EFFECT OF FIFTEEN-MINUTE CONTACT TIMES
ON PLUTONIUM DISSOLUTION

Contact*	Plutonium Dissolved (Relative Percent)				
	0-15 min	15-30 min	30-45 min	45-60 min	Total/hr
1	28	2	3	0	33
2	27	3	3	3	36
3	28	1	0	2	31
Totals	83	6	6	5	~100
Average	28	2	2	2	33

* Dissolver solution: 5M HNO₃-0.3M CaF₂.

NUMBER OF CONTACTS

Ash from three different cans was dissolved using 5M HNO_3 -0.3M CaF_2 at 100 °C. The number of one-hour batch contacts required to achieve 95 to 100 percent plutonium recovery was dependent on the type of ash (see Table VI).

TABLE VI
EFFECT OF PLUTONIUM CONCENTRATION OF ASH
UPON DISSOLUTION RATE

Wt% Pu in Ash	Plutonium Dissolved* (Relative Percent)				Cumulative
	1st Contact	2nd Contact	3rd Contact	4th Contact	
3-5	69	31	-	-	~100
8-11	34	43	18	5	~100
15-23	70	20	10	0	~100

* Dissolver solution: 5M HNO_3 -0.3M CaF_2 .

REBURNED ASH

The presence of partially burned material in some ash suggested that complete burning would yield less carbonaceous residues after dissolution. Aliquots from four different cans of Z Plant incinerator ash were reburned. While the incinerator feed for these ashes appeared to be about 50 vol percent paper and 50 vol percent plastic, the physical appearance and the plutonium content of the final ash varied (see Table VII).

Reburning ash to a constant weight at 400, 600, or 800 °C yielded losses which appeared to be independent of reburn temperatures (see Table VIII). The average weight loss of the first three ashes was approximately 15.0 percent regardless of reburn temperature. Reburn volume and weight losses appeared to fluctuate according to the individual ash and presumably the completeness to which the ash was originally burned in the incinerator. The fourth batch of ash was obviously the best burned as determined by its very fine consistency. This batch

yielded the lowest volume and weight losses upon reburning.

TABLE VII
CHARACTERIZATION OF FOUR BATCHES OF ASH

<u>Batch</u>	<u>Incinerator Feed</u>	<u>Wt% Pu</u>	<u>Ash</u>
			<u>Physical Appearance</u>
1	Unknown	8-11	Homogeneous fines
2	50 vol% plastic 50 vol% paper	15-23	Homogeneous, slightly coarser fines
3	50 vol% plastic 45 vol% paper 5 vol% asbestos	3-5	Non-homogeneous, coarse mixture of charcoal chunks and fines, fibers
4	50 vol% plastic 50 vol% paper	3	Homogeneous, very fine

TABLE VIII
PERCENT VOLUME AND WEIGHT LOSS DURING ASH REBURN

<u>Batch</u>	<u>Percent Volume Loss</u>			<u>Percent Weight Loss</u>		
	<u>400 °C</u>	<u>600 °C</u>	<u>800 °C</u>	<u>400 °C</u>	<u>600 °C</u>	<u>800 °C</u>
1	27	20	18	18	20	13
2	8	18	33	12	15	16
3	-	21	-	-	11	-
4	-	3	-	-	5	-

Reburning ash had an insignificant effect on plutonium recovery (see Table IX). Comparison of plutonium removal from once-burned and reburned ash indicated a similar degree of completeness.

Reburning increased chemical dissolution of solids from 55 ±15 volume percent to 80 ±15 volume percent. Dissolution of solids appeared to occur for the most part within 15 minutes; multiple contacts were necessary to achieve maximum solids dissolution.

TABLE IX
COMPARISON OF PLUTONIUM GAMMA COUNTS
BEFORE AND AFTER ASH DISSOLUTION*

Ash	Pu Gamma Counts/min			
	Ash No. 1		Ash No. 2	
	Before	After	Before	After
Once burned	2793	<10	5144	<10
Reburned				
400 °C	2181	78	7845	149
600 °C	3602	23	4900	13
800 °C	3186	<10	6196	12

* Dissolver solution 5M HNO₃-0.3M CaF₂.

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