SELECTIVE DISSOLUTION OF URANIUM
FROM FUEL FABRICATION SCRAP

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ABSTRACT

Uranium was preferentially dissolved from unsintered plutonium-uranium fuel fabrication scraps. Trace levels of dissolved plutonium were recovered by anion exchange. These processes were not applicable to sintered scrap containing solid solutions of $\text{PuO}_2\text{-UO}_2$ in which plutonium dissolved with uranium.

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INTRODUCTION

The Atlantic Richfield Hanford Company (ARHCO) has demonstrated the capability to recover plutonium and uranium from non-irradiated fuel scraps. Scrap with less than one weight percent plutonium was dissolved and processed in the Purex plant, whereas scrap with greater plutonium values was dissolved and processed in the Plutonium Reclamation Facility at Z Plant. Greater plutonium recovery rates could be achieved at Z Plant if the low-plutonium scrap could be enriched by selective uranium removal prior to plutonium dissolution.

The selective dissolution of uranium oxide in nitric acid was reported in earlier laboratory studies.^[1] L. E. Bruns recommended a flowsheet consisting of uranium dissolution with 6 to 12 molar nitric acid followed by anion exchange recovery of trace-dissolved plutonium.^[2] The following report presents a laboratory evaluation of the proposed flowsheet.

SUMMARY

An average of 72 wt% uranium was dissolved with 6M HNO₃; however, uranium dissolution was accompanied by 2 to 28 wt% plutonium dissolution depending on the form of the scrap. Pressed rods and oxide yielded 3% plutonium dissolution, whereas hood sweep fines yielded up to 17% plutonium dissolution. High-fired scrap containing UO₂-PuO₂ solid solution yielded 88% dissolution of plutonium.

Ninety-eight percent of the dissolved plutonium was recovered on anion exchange resin. Average resin feeds contained 0.03 g Pu/liter and 29 g U/liter compared with average

effluents of 0.003 g Pu/liter and 26 g U/liter. The resin was eluted with 1M HNO₃, yielding 100% U removal in 3 bed volumes (BV) and 97% Pu removal in 16 BV.

EXPERIMENTAL

EQUIPMENT

A 1000-ml Kimax distilling flask with three necks, each with 24/40 joints (Kimbel No. 26220), was used as a dissolver. A bulb-type Allihn condenser (Corning 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" 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-ml, round-bottom, table model Glas-Col heating mantle (Van Waters and Rogers 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 microns) quartz frit to support a Whatman #42 ashless filter (will collect 90 to 95% of particles 1 micron or larger). A 1-liter Pyrex filtering flask was used to collect the filtrate at a vacuum of 26" of mercury.

A glass column 45 mm ID x 30 cm long was packed with 250 cc (height:diameter ratio = 3.3) of 50 to 100 mesh Dowex 1X4/NO₃⁻ resin. Loading and eluting were both performed down-flow (room temperature and a 3 BV/hr flow rate).

PROCEDURES

Each run began by adding a charge (6 to 15 g) of scrap to 500 ml of nitric acid at room temperature. After 30 min of air sparging, 30 vol% of the acid was decanted and replaced,

together with a second charge of scrap. The first two runs were exceptions since 60 vol% was decanted and replaced each cycle. All cycles were 30 min in length.

The temperature of the initial nitric acid was 24 °C, but the exothermic dissolution reactions increased the temperatures to the 40 to 50 °C range. The temperature for Run 9 with sintered pellets was increased to between 90 and 95 °C before dissolution began. The sintered pellets contained about 20 wt% Pu whereas the scrap for Runs 1 through 8 contained 3 to 4 wt% Pu.

RESULTS AND DISCUSSION

DISSOLUTION

Six dissolution runs with non-sintered fuel fabrication scrap successfully demonstrated selective uranium dissolution by yielding approximately 75% U and 3% Pu dissolution (see Runs 1 through 6, Table I). Runs 7 and 8 with hood sweeps yielded approximately 80% U and 15% Pu dissolution which suggested the presence of a more dissolvable Pu material; *e.g.*, solid solution of $\text{PuO}_2\text{-UO}_2$. Run 9 with sintered pellets of solid $\text{PuO}_2\text{-UO}_2$ solution yielded 88% Pu and U dissolution. These observations indicated that selective uranium dissolution was feasible only in the absence of the $\text{PuO}_2\text{-UO}_2$ solid solutions.

The form of scrap affected dissolution rates. Broken pieces of pressed rods dissolved more slowly than oxide and thus required longer contact times. Longer contact times could be achieved by reducing feed rates, interspersing flushes during the run, or using a heel treatment as in Run 6.

The initial flowsheet suggested 12M HNO_3 , but further studies showed that 6M HNO_3 would do as well. Dissolution with 6M HNO_3 was similar to higher acidities and was more

TABLE I
DISSOLUTION DATA

Run	Type of Scrap	Run Conditions			% Dissolution			Dissolver Overflow		
		<u>HNO₃</u> <u>M</u>	<u>No. of</u> <u>Cycles</u>	<u>Wt of Charge</u> <u>per Cycle</u>	<u>Dissolved</u>	<u>U</u>	<u>Pu</u>	<u>Pu/liter</u> <u>g</u>	<u>U/liter</u> <u>g</u>	<u>H⁺</u> <u>M</u>
1	Oxide	12	5	6.5	85	77	3.5	0.013	14	11
2	Oxide	8	5	6.5	85	81	3.1	0.014	14	8.2
3	Oxide	10	10	10.	86	79	3.3	0.041	39	9.5
4	Oxide	6	5	10.	75	72	2.5	0.029	29	5.9
5	Pressed rods and oxide	6	10	15.	62	60	2.8	0.055	45	5.2
6	Pressed rods	6	10	15.	48	46	2.2	0.044	35	5.9
6 heel	No scrap added	6	8	0	36	34	1.8	0.044	29	6.0
7	Hood sweep fines	6	10	15.	70	79	14.	0.424	49	5.3
8	Hood sweep fines	6	10	15.	83	83	17.	0.49	53	5.4
9	Sintered pellets	6	5	15.	88	88	88.	8.8	25	5.9

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desirable as a feed for anion exchange recovery of dissolved plutonium.

The proposed plant feed rate of 400 g/30 liters/30 min will have to be modified according to the physical form of the scrap. With oxides, a processing rate of 900 g/30 liters/30 min was successfully achieved; but with the larger chunk-type scrap, such a high rate necessitated heel treatment (Run 6).

ION EXCHANGE RESIN LOADING

A 250-cc bed of 50 to 100 mesh Dowex 1X4 resin (Dow Chemical Company) recovered 98% of the Pu and only 4% of the U from 59 BV of feed (see Table II and Figure 1).

TABLE II
LOADING DATA BY RUN NUMBER

Run	BV	g/liter Feed			g/liter Effluent		% Recovery	
		Pu	U	, H ⁺	Pu	U	Pu	U
1	1-5	0.012	14	11.6	0.002	10	83	27
2	7-13	0.014	14	8.	0.002	9	85	36
3	14-20	0.041	39	9.2	0.002	31	96	20
4	21-24	0.029	29	5.8	0.008	25	73	13
5	25-31	0.055	45	5.6	0.006	43	89	4
6	32-38	0.044	35	6.0	0	35	100	0
6 heel	39-44	0.044	29	5.9	0.002	31	96	0
7	45-51	0.42	51	4.9	0.004	50	99	3
8	52-58	0.47	55	5.1	0.001	55	100	0
9	59	8.6	25	5.9	0.013	38	98	0
	60	8.6	25	5.9	3.3	27	80	0
	61	8.6	25	5.9	5.3	26	66	0
	62	8.6	25	5.9	6.1	28	56	0

The 250-cc bed loaded 5 g Pu at 50% Pu breakthrough. The introduction of hood sweeps and high-fired pellets in Runs 7, 8, and 9 yielded uncommonly high Pu values in the dissolver overflow stream to the ion exchange column. Thus 50% Pu breakthrough occurred about 60 BV whereas the trend of the

FIGURE 1
CUMULATIVE PERCENT LOADING

first six dissolver runs (1 to 45 BV) predicted 50% breakthrough no earlier than 450 BV (see Table III). Usually hood sweeps, high-fired pellets, and other scrap from which Pu readily dissolved would not be processed through the selective U step.

TABLE III
CUMULATIVE LOADING DATA PER 250 cc RESIN*

BV	Plutonium		Uranium	
	<u>g in Effluent</u>	<u>g Loaded</u>	<u>g in Effluent</u>	<u>g Loaded</u>
5	0.003	0.013	12	5
10	0.005	0.029	22	13
15	0.007	0.056	45	18
20	0.010	0.105	92	20
25	0.019	0.14	126	26
30	0.027	0.20	180	28
35	0.029	0.26	230	24
40	0.030	0.31	272	23
45	0.032	0.45	312	24
50	0.037	0.97	372	25
55	0.040	1.56	439	23
58	0.040	1.93	480	22
59	0.072	4.04	490	18
60	0.89	5.4	496	19
61	2.2	6.2	503	18
62	3.7	6.8	510	18

* 50% breakthrough at 5 g Pu loading.
Extrapolate 45 BV of ~0.45 g Pu to 450 BV loading of ~4.5 g Pu.

ION EXCHANGE RESIN ELUTION

One molar nitric acid at room temperature was passed through the resin bed with a flow rate of 3 BV/hr. Complete uranium removal was achieved within 3 BV (see Figure 2 and Table IV). Greater than 80% Pu removal was achieved with 8 BV of 1M HNO₃.

FIGURE 2
CUMULATIVE PERCENT ELUTION

TABLE IV
ELUTION OF DOWEX 1X4

<u>BV</u>	<u>g/liter Pu</u>	<u>g/liter U</u>
1	4.8	59
2	5.6	12
3	3.5	1
4	2.5	0.3
5	1.9	ND*
6	1.4	0.01
7	1.2	0.04
8	1.0	0.1
9	0.8	0.007
10	0.7	0.005
11	0.7	0.2
12	0.6	ND
13	0.5	0.002
14	0.4	0.002
15	0.3	0.007
16	0.3	0.002

* ND = nondetectable.

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