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RECOVERY OF PLUTONIUM-238 FROM SCRAP MATERIALS

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MASTER

PREPARED FOR THE U. S. ATOMIC ENERGY COMMISSION UNDER CONTRACT AT(07-2)-1

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RECOVERY OF PLUTONIUM- 238 FROM SCRAP MATERIALS

by

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Approved by

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April 1974

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ABSTRACT

Processes were developed and demonstrated for the recovery of ^{238}Pu from scrap from fuel form research, development, and production. The scrap materials studied were PuO_2 -Mo and PuO_2 - ThO_2 -Mo cermet, PuO_2 - ThO_2 and PuO_2 - ZrO_2 solid solutions, PuO_2 -Be, Pu metal, Pu-Zr alloy, and miscellaneous wastes containing iron oxides.

Metals and oxides, e.g., Mo, Be, and Fe, that interfere with PuO_2 dissolution in nitric acid containing fluoride ions are removed first. Molybdenum and its oxides are dissolved by 1.5M HNO_3 - 0.5M $\text{Fe}(\text{NO}_3)_3$ or solid $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. Beryllium metal is dissolved by 10M HNO_3 . Iron oxides are dissolved by 2M HNO_3 . Plutonium metal and Pu-Zr alloy are oxidized to obtain oxides. Plutonium oxide and its solid solutions are dissolved in 10 to 14M HNO_3 with 0.05 to 0.2M F^- ; aluminum is added to reduce corrosion of stainless steel. The plutonium is purified by anion exchange.

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RECOVERY OF PLUTONIUM-238 FROM SCRAP MATERIALS

INTRODUCTION

^{238}Pu is useful as a source of heat (to be used directly or converted to electricity) and of neutrons, produced by (α, n) reactions with beryllium or other light elements. For these uses, the free-flowing, fine-particle oxide powder produced by the Savannah River Plant (SRP) must be converted by chemical and/or physical techniques to the required physical form. Large quantities of contaminated ^{238}Pu (scrap) have been and are still generated at various AEC sites during research, development, and production of various components. SRP has built a facility to recover the ^{238}Pu from the scrap for reuse. This report describes the development of the chemical processes required for scrap recovery.

The new facility consists of a glove box train with equipment to receive shipping containers, prepare scrap for dissolution, and dissolve the scrap. The scrap solutions are processed either within the new facility or in a previously existing facility to recover and purify the ^{238}Pu by anion exchange. Because these facilities are constructed primarily of stainless steel, all process operations use nitrate or nitric acid systems; chemicals known to corrode stainless steel severely are avoided. The exception is that limited amounts of fluoride are used. Corrosion by fluoride is controlled by addition of Al^{3+} to complex the fluoride ion.

Although ^{238}Pu scrap inherently has an indefinite composition, the scrap received to this time can be grouped into the categories shown in Table I.

TABLE I

^{238}Pu Scrap Categories

$\text{PuO}_2\text{-Mo}$, $\text{PuO}_2\text{-ThO}_2\text{-Mo}$ cermet
High-Fired Mixed Oxides
 $\text{PuO}_2\text{-ThO}_2$
 Pu-Zr Alloy and $\text{PuO}_2\text{-ZrO}_2$
Cabinet Sweepings
Evaporator and Dissolver Sludge

DISSOLUTION OF SCRAP MATERIALS

The scrap to be recovered is principally $^{238}\text{PuO}_2$ mixed with various oxide or metal impurities, which may interfere with the dissolution of PuO_2 . Interfering oxides or metals must be removed by appropriate pretreatment before PuO_2 is dissolved.

Dissolution of any high-fired actinide oxide is difficult because dissolution proceeds from dislocations or imperfections in the surface of the crystals; high temperature treatment reduces the number of such imperfections. Nitric acid alone is not a good solvent for PuO_2 , but addition of fluoride ion at concentrations $>0.03\text{M}$ greatly increases the rate of dissolution. If cations that strongly complex fluoride (such as aluminum, zirconium, and molybdenum) are present, they must be removed or additional increments of fluoride added to dissolve PuO_2 completely.

After dissolution, the plutonium-containing solutions can be adjusted to 7.5M HNO_3 , and the plutonium recovered and purified by anion exchange using "Dowex"* 1-X4 or 21K anion exchange resins.¹

CERMETS

Cermet scrap is generated in a process in which PuO_2 or $\text{PuO}_2\text{-ThO}_2$ is coated with molybdenum metal and heated to 1500°C in a graphite die lined with tantalum foil, to form a disk. This disk is removed from the die and machined to shape. The machinings constitute the largest portion of scrap from this process, although reject or broken disks may be included. The ^{238}Pu content of this scrap is about 50 wt %. Analyses have shown that principal impurities other than molybdenum are tantalum and carbon.

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*Registered trademark of the Dow Chemical Co.

Little plutonium is dissolved during repeated treatment of cermet with fresh portions of hot nitric acid-fluoride ion mixtures when molybdenum is present. Thus, the molybdenum must be removed before PuO_2 dissolution. Molybdenum metal does not dissolve readily in acids, but it can be oxidized to molybdenum trioxide (MoO_3). The trioxide has a low solubility in acid and forms molybdic acid (H_2MoO_4), which can polymerize to form precipitates insoluble in both acid and base. The trioxide is, however, readily soluble in base (forming molybdates), and polymerization in acid is prevented by the addition of ferric ion (forming complexes) or phosphate ion (forming molybdophosphates). Therefore, molybdenum can be readily dissolved after oxidation to MoO_3 .

The three possibilities for oxidation of molybdenum are: solution oxidation, air oxidation at elevated temperatures, and fusion with oxidants. All three methods were tested. Solution oxidation was found to be the best method. In this method, cermet scrap (PuO_2 -Mo or PuO_2 - ThO_2 -Mo) is processed by first removing molybdenum with 1.5M HNO_3 - 0.5M $\text{Fe}(\text{NO}_3)_3$ solution, solid $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, or saturated ferric nitrate solution, and then dissolving the PuO_2 or PuO_2 - ThO_2 in 11 to 14M HNO_3 - 0.05 to 0.2M KF.

Solution Oxidation

In tests summarized in Table II, attempts were made to remove molybdenum from cermet by oxidation with nitric acid alone and dissolution of the resulting MoO_3 in sodium hydroxide. Complete removal of molybdenum by this procedure was not reproducible, due to occasional formation of insoluble polymolybdic acids. Dissolutions of plutonium from the residue with nitric acid-fluoride ion was complete only when prior removal of molybdenum was complete. Thus, the procedure was not considered suitable for plant operation.

TABLE II

Dissolution of PuO₂-Mo Cermet Scrap after Oxidation of Molybdenum with Nitric Acid²³⁹Pu = 50.6 ± 1.1 wt %

Mo = 17.2 ± 9.6 wt %

Test	Sample Wt., g	Solvent		Dissolution Time, hr	% Pu Dissolved
		Composition	Volume, ml		
1	5.20	2M HNO ₃	56	1	----
		10.5M HNO ₃ - 0.03M KF - 0.17M Al ³⁺	160	2	3.5
		10.5M HNO ₃ - 0.035M KF - 0.19M Al ³⁺	100	2.5	0.82
		10.5M HNO ₃ - 0.035M KF - 0.19M Al ³⁺	300	2	2.9
		10.5M HNO ₃ - 0.035M KF - 0.037M Al ³⁺	100	2	.25
		4M NaOH	100	0.5	.09
		10.5M HNO ₃ - 0.07M KF - 0.027M Al ³⁺	100	2	27.1
2	5.35	2M HNO ₃	56	0.5	----
		2M NaOH	74	0.5	.11
		10.5M HNO ₃ - 0.05M KF - 0.01M Al ³⁺	100	4	20.8
		10.5M HNO ₃ - 0.05M KF - 0.01M Al ³⁺	100	2	28.4
		10.5M HNO ₃ - 0.064M KF - 0.027M Al ³⁺	100	4	20.9
3	5.10	2M HNO ₃	56	1	----
		4M NaOH	47	0.5	1.7
		10.5M HNO ₃ - 0.10M HF	80	3.2	57.6
		10.5M HNO ₃ - 0.15M HF	165	2.5	42.5
4	2.25	2M HNO ₃	56	1	----
		4M NaOH	50	0.5	0.6
		10.5M HNO ₃ - 0.10M HF	80	2.25	86.9
		10.5M HNO ₃ - 0.15M HF	85	2.5	20.3
5	5.20	2M HNO ₃	56	0.5	----
		1M NaOH	50	0.5	.16
		10.5M HNO ₃ - 0.1M KF - 0.024M Al ³⁺	150	2	71.1
		10.5M HNO ₃ - 0.1M KF - 0.024M Al ³⁺	100	2	27.4

Condensation of H₂MoO₄ to form polymolybdic acids will not occur in acid solution if sufficient ferric ion is present to form the soluble ferrimolybdate complex. Tests with molybdenum powder showed that molybdenum oxidizes and dissolves completely in 1 to 2M HNO₃ containing at least 0.4M ferric ion. This solvent not only prevents formation of polymolybdic acids, but it also dissolves the dark red precipitate that forms in nitric acid.

The utility of ferric ion in dissolving PuO₂-ThO₂-Mo cermet scrap is shown in Table III. In Tests 1 to 3 with cermet powder, the heel from the previous dissolution was left in the dissolver. Test 4 was made using a crushed piece of cermet disk that was passed through a 100-mesh screen. Without crushing, dissolution is very slow. The tests show that at least two dilute nitric acid washes must be used to remove ferric ion sufficiently, so that it does not interfere with PuO₂ dissolution. The nitric

acid-ferric ion solution must be boiled at least one hour to dissolve the molybdenum; the washes must be boiled half an hour to obtain efficient removal of residual molybdenum. A minimum of 40 ml of solvent must be used per gram of scrap, or about 80 ml per gram of ^{238}Pu .

TABLE III

Dissolution of $\text{PuO}_2\text{-ThO}_2\text{-Mo}$ Cermet Scrap after Oxidation of Molybdenum with $1.5\text{M HNO}_3 - 0.5\text{M Fe(NO}_3)_3$

Test	Sample Wt, g	Solvent		Dissolution Time, hr	% Pu Dissolved
		Composition	Volume ml		
1	5	$1.5\text{M HNO}_3 - 0.5\text{M Fe(NO}_3)_3$	100	2	0.5
		1.5M HNO_3	100	1	0.3
		$13.5\text{M HNO}_3 - 0.05\text{M KF}$	100	2.5	9.6
		$13.5\text{M HNO}_3 - 0.05\text{M KF}$	100	3	19.2
2	5	$1.5\text{M HNO}_3 - 0.5\text{M Fe(NO}_3)_3$	100	2	0.7
		1.5M HNO_3	100	1	0.02
		1.5M HNO_3	100	0.25	0.005
		$13.5\text{M HNO}_3 - 0.05\text{M KF}$	100	2	15.3
		$13.5\text{M HNO}_3 - 0.05\text{M KF}$	100	2	16.0
		$13.5\text{M HNO}_3 - 0.05\text{M KF}$	100	2	14.7
3	5	$13.5\text{M HNO}_3 - 0.05\text{M KF}$	100	2	15.9
		$1.5\text{M HNO}_3 - 0.5\text{M Fe(NO}_3)_3$	200	2	.75
		1.5M HNO_3	200	0.5	.02
		1.5M HNO_3	200	0.5	.008
		$13.5\text{M HNO}_3 - 0.05\text{M KF}$	200	2	22.9
		$13.5\text{M HNO}_3 - 0.05\text{M KF}$	200	5	33.0
4	2^a	$13.5\text{M HNO}_3 - 0.05\text{M KF}$	200	3	44.0
		$1.5\text{M HNO}_3 - 0.5\text{M Fe(NO}_3)_3$	100	3	----
		1.5M HNO_3	100	0.5	----
		1.5M HNO_3	100	0.5	----
		$13.5\text{M HNO}_3 - 0.1\text{M KF}$	100	3	86.3
		$13.5\text{M HNO}_3 - 0.1\text{M KF}$	100	3	8.7

a. Sample of disk crushed.

Oxidation and dissolution of molybdenum in cermet scrap by ambient temperature reaction with solid $\text{Fe(NO}_3)_3 \cdot 9\text{H}_2\text{O}$ or saturated ferric nitrate solution was also tested. The PuO_2 or $\text{PuO}_2\text{-ThO}_2$ was dissolved in concentrated nitric acid with fluoride ion catalyst (after removal of the molybdenum). Solid $\text{Fe(NO}_3)_3 \cdot 9\text{H}_2\text{O}$ or saturated solutions of $\text{Fe(NO}_3)_3$ oxidized molybdenum rapidly at ambient temperatures, yielding a clear solution of molybdenum as the ferrimolybdate complex. The solution was stable, but a precipitate formed on evaporation. Test results with these reagents are shown on Table IV. Sufficient ferric nitrate must

TABLE IV

Dissolution of PuO₂-ThO₂-Mo Cermet Scrap after Oxidation of Molybdenum with Solid Fe(NO₃)₃·9H₂O

<i>Test</i>	<i>Sample Wt, g</i>	<i>Solvent</i>		<i>Time, hr</i>	<i>% Pu Dissolved</i>
		<i>Quantity</i>	<i>Composition</i>		
1	5	5 g	Fe(NO ₃) ₃ ·9H ₂ O	0.2	----
		100 ml	1M HNO ₃	0.5	.17
		100 ml	1M HNO ₃	0.5	.77
		200 ml	13.5M HNO ₃ - 0.05M KF	2	41.0
		200 ml	13.5M HNO ₃ - 0.05M KF	2	30.2
2	5	6 g	Fe(NO ₃) ₃ ·9H ₂ O	0.2	----
		4 ml	H ₂ O		
		100 ml	1M HNO ₃	1	.85
		100 ml	1M HNO ₃	1	.03
		200 ml	13.5M HNO ₃ - 0.05M KF	3	34.6
		200 ml	13.5M HNO ₃ - 0.05M KF	3	32.6
		100 ml	13.5M HNO ₃ - 0.05M KF	2	25.2
		100 ml	13.5M HNO ₃ - 0.05M KF	2	14.1
3	5	6 g	Fe(NO ₃) ₃ ·9H ₂ O	0.2	----
		4 ml	H ₂ O		----
		100 ml	1M HNO ₃	1.0	.25
		100 ml	1M HNO ₃	0.5	.24
		100 ml	1M HNO ₃	0.5	.06
		200 ml	13.5M HNO ₃ - 0.05M KF	2.5	41.7
		100 ml	13.5M HNO ₃ - 0.05M KF	3	11.9
4	5	9 g	Fe(NO ₃) ₃ ·9H ₂ O	0.2	----
		100 ml	1M HNO ₃	0.25	.54
		100 ml	1M HNO ₃	0.25	.03
		200 ml	13.5M HNO ₃ - 0.05M KF	3	43.8
		200 ml	13.5M HNO ₃ - 0.05M KF	12	28.3
		200 ml	13.5M HNO ₃ - 0.05M KF - 0.025M Al ³⁺	11	12.9
		100 ml	13.5M HNO ₃ - 0.05M KF	4	4.6
5	5	9 g	Fe(NO ₃) ₃ ·9H ₂ O	0.5	----
		100 ml	1M HNO ₃	0.25	.72
		100 ml	1M HNO ₃	0.25	.07
		2 g	Fe(NO ₃) ₃ ·9H ₂ O	0.75	----
		200 ml	13.5M HNO ₃ - 0.05M KF	6	37.4
		200 ml	13.5M HNO ₃ - 0.05M KF	6	60.4
		100 ml	13.5M HNO ₃ - 0.05M KF	3	4.5
6	5	9 g	Fe(NO ₃) ₃ ·9H ₂ O	0.5	----
		100 ml	1M HNO ₃	0.25	.83
		100 ml	1M HNO ₃	0.25	.04
		2 g	Fe(NO ₃) ₃ ·9H ₂ O	1	----
		200 ml	13.5M HNO ₃ - 0.05M KF	6	62.1
		200 ml	13.5M HNO ₃ - 0.05M KF	6	36.6
		100 ml	13.5M HNO ₃ - 0.05M KF	6	4.2
7	5	9 g	Fe(NO ₃) ₃ ·9H ₂ O	0.5	----
		100 ml	1M HNO ₃	0.25	.86
		100 ml	1M HNO ₃	0.25	.43
		2 g	Fe(NO ₃) ₃ ·9H ₂ O	1	----
		200 ml	13.5M HNO ₃ - 0.05M KF	6	70.2
		200 ml	13.5M HNO ₃ - 0.05M KF	6	20.3

be used to completely remove molybdenum, preventing interference with PuO_2 dissolution. Best results were obtained using a second addition of ferric nitrate after washing out the initial ferri-molybdate solution. Molybdenum dissolution was equally good with solid ferric nitrate hydrate or a saturated solution of ferric nitrate.

Air Oxidation

Tests were made of air oxidation of molybdenum at 500 to 650°C with molybdenum metal powder mixed with thorium oxide supported on a quartz frit in a 6-mm quartz tube. Air was pulled through the column by vacuum applied below the frit. Heating for 1/2 hr, 1 hr, and 2 hr gave incomplete oxidation of molybdenum in each case, as measured by the molybdenum removed by hot caustic treatment of the powder. Heating a crucible of ThO_2 -Mo powder for 4 to 6 hr at 550 to 600°C in static air gave better results.

In tests with $^{238}\text{PuO}_2$ -Mo cermet (Table V), removal of molybdenum was incomplete after heating at 550°C for 4 hours and dissolving in 1M NaOH. The small amount of plutonium dissolved in successive nitric acid-fluoride ion treatments is indicative of the presence of excessive, residual MoO_3 . The second test with oxidation at higher temperature for a longer time gave only slightly better results. Longer heating times and higher temperatures were not tested because sublimation and transport of MoO_3 would occur.

TABLE V

Dissolution of PuO_2 -Mo Cermet Scrap after Air Oxidation of Molybdenum

Oxidation

<u>Sample Wt., g</u>	<u>Temp., °C</u>	<u>Time, hr</u>	<u>Solvent</u>	<u>Time, hr</u>	<u>% Pu Dissolved</u>
3.06	550	4	1M NaOH	0.5	0
			1M NaOH	0.5	0
			13.5M HNO_3 - 0.05M KF - 0.0025M Al^{3+}	2.5	19.0
			13.5M HNO_3 - 0.05M KF - 0.0025M Al^{3+}	2.5	26.2
			13.5M HNO_3 - 0.05M KF - 0.0025M Al^{3+}	2.5	16.8
3.5	625	6	1M NaOH	0.5	0.01
			1M NaOH	0.5	0
			13.5M HNO_3 - 0.1M KF - 0.005M Al^{3+}	2.5	19.9
			13.5M HNO_3 - 0.1M KF - 0.005M Al^{3+}	2.5	52.9

Fusion

Mound Laboratory has treated cermet scrap by fusing it with a mixture of potassium nitrate-potassium hydroxide, crushing the cooled melt, and leaching with water to remove K_2MoO_4 , KNO_3 , and KOH .² After removal of molybdenum, PuO_2 is dissolved in hot concentrated nitric acid with fluoride ion as catalyst. Two fusion tests were relatively successful (Table VI), but long times were required to dissolve the melt. In addition, in tests with molybdenum powder alone, numerous sparks and considerable frothing were observed during the initial stages of fusion. The sparking was considered a possible safety hazard, so no further work was done.

TABLE VI

Dissolution of PuO_2 -Mo Cermet Scrap after Fusion with Potassium Nitrate-Potassium Hydroxide

<u>Sample</u> <u>Wt., g</u>	<u>Solvent</u> <u>Composition</u>	<u>Quantity</u>	<u>Time,</u> <u>hr</u>	<u>% Pu</u> <u>Dissolved</u>
2.5	KNO_3 -450°C	3 g	0.25	----
	0.1M KOH	200 ml	2.5	0.04
	13.5M HNO_3 - 0.05M KF	200 ml	3	62.3
	13.5M HNO_3 - 0.05M KF	100 ml	4	11.5
1.8	KNO_3 - 600°C	3 g	1	----
	0.1M KOH	200	2.5	1.56
	13.5M HNO_3 - 0.05M KF	200	3	69.1
	13.5M HNO_3 - 0.05M KF	100	4	16.1

PLUTONIUM OXIDE-THORIUM OXIDE SOLID SOLUTION

Most of the PuO_2 - ThO_2 solid solution³ scrap contains 1 to 4% ThO_2 . The remainder contains from 8 to 50% ThO_2 and was formed by heating PuO_2 and ThO_2 mixtures to >1500°C during research and development on ^{238}Pu fuel forms.

The tests in Table VII show that PuO_2 -4% ThO_2 is easily dissolved in 13.5M HNO_3 - 0.05M KF. When thorium dissolves, it complexes fluoride ion and retards corrosion of the stainless steel dissolver. The remainder of the scrap, which contains more thorium and was heated to higher temperatures, will require additional fluoride to obtain equivalent dissolving rates.

TABLE VII

Dissolution of PuO_2 - 4 wt % ThO_2 Solvent = 13.5M HNO_3 - 0.05M KF

<u>Sample Wt, g</u>	<u>Dissolution Time, hr</u>	<u>Volume, ml</u>	<u>% Pu Dissolved</u>
5	3	200	70.2
	3	100	3.7
5	3	200	91.7
	3	100	6.5

SWEEPINGS

Scrap labelled "sweepings" is obtained from periodic cleaning of glove boxes. Sweepings are processed by dissolving iron and other easily soluble oxides with 2M HNO_3 . PuO_2 is dissolved in 10.5M HNO_3 - 0.1M KF - 0.025M Al^{3+} .

Samples of high and low ^{238}Pu content were tested, as shown in Table VIII. Analyses of the two samples tested show the scrap is primarily oxides of iron, chromium, nickel, titanium, and silicon, with varying amounts of other metal oxides. The ^{238}Pu content varies from 0.1 to 17%. In the tests, 60 to 70% of the sweepings, which included some metallic plutonium, were dissolved with 5M HNO_3 . Iron was the major non-plutonium component of the residue, with minor amounts of silicon and copper. After subsequent treatment with 10.5M HNO_3 - 0.05M KF - 0.004M Al^{3+} , about 5% of the initial solids remained. The solids contained tin, silver, silicon, titanium, and iron, with negligible ^{238}Pu . Initial treatment with 2M HNO_3 removed the contaminating oxides just as efficiently and dissolved less plutonium than 5M HNO_3 .

SCRAP CONTAINING BERYLLIUM

Scrap containing beryllium contains either Pu-Be alloy or PuO_2 -Be mixtures. The Pu-Be alloys are actual (α, n) neutron sources with very high neutron emission rates and can be handled only in small quantities in the unshielded SRP recovery facility. The PuO_2 -Be scrap is a mixture of PuO_2 with beryllium particles of $>250 \mu\text{m}$ diameter, compacted into stainless steel cylinders and retained by a disk, spring, and cap, all of brass. This PuO_2 -Be is partially fused in the containers and cannot be removed easily by mechanical means.

TABLE VIII

Dissolution Of Sweepings

²³⁸ Pu in Sample, wt %	Sample Wt, g	Solvent		Contact Time, hr	²³⁸ Pu Dissolved, %
		Composition	Volume, ml		
0.5	35.8	5M HNO ₃	450	3.5	27.9
		10.5M HNO ₃ — 0.05M KF— 0.004M Al ³⁺	200	2.5	69.8
16	10	2M HNO ₃	200	1	8.3
		10.5M HNO ₃ — 0.1M F ⁻ — 0.025M Al ³⁺	200	2	65.6
		10.5M HNO ₃ — 0.1M F ⁻ — 0.025M Al ³⁺	100	2	26.0

Beryllium and brass were dissolved in 10M HNO₃ while purging with air or nitrogen to prevent accumulation of flammable concentrations of hydrogen. PuO₂ was dissolved by >10M HNO₃ with 0.08M KF and 0.005M Al³⁺ (Table IX). In the first test, PuO₂-Be was mechanically removed from the cylinder and treated with 1M HNO₃. After refluxing for 1 hour, the solution was cooled, concentrated nitric acid was added to 10.5M, and the solution was refluxed again for 3 to 4 hours. The residue was removed and was shown by emission spectrographic analysis to be plutonium. In addition to plutonium and beryllium, the solution contained nickel at approximately the same concentration as beryllium. In a second test, the stainless steel cylinder, brass cap, and PuO₂-Be not removed for use in Test 1 were placed in the dissolver with the residue from Test 1. Brass and beryllium were dissolved in 10M HNO₃, and PuO₂ was dissolved in nitric acid containing fluoride ion. There was no residue in this test. The third test used an unopened cylinder and was similar to the second test. However, all the PuO₂ did not dissolve with only one nitric acid-fluoride treatment.

The dissolver was purged with nitrogen during the tests because brass and beryllium could evolve hydrogen during dissolution. The gases evolved during dissolution of brass and beryllium were analyzed because there is little information in the literature on the composition of these gases. In these tests, brass bolts and pure beryllium wire were dissolved by similar procedures, as follows.

Two hundred ml of HNO_3 was placed in a reaction vessel fitted with a reflux condenser and gas collection bulb. Nitric acid concentrations tested were 1M, 5M, and 10M; 0.01M hydrofluoric acid (HF) was added for the beryllium tests. The metal was added, the system was purged with nitrogen, and the mixture was heated to start the reaction. HF was added at this point in tests with beryllium. When the reaction was about half complete, the vessel was purged with nitrogen, and a sample was collected. In tests with 10M HNO_3 , enough gas was produced that no purge was necessary. Hydrogen and nitrous oxide (NO) in the off-gas were measured by gas chromatography. Gases from beryllium dissolution in 10M HNO_3 - 0.1M HF were also measured by mass spectrometry.

TABLE IX

Dissolution of PuO_2 -Be Scrap

<u>Test</u>	<u>Sample Wt., g</u>	<u>Solvent Composition</u>	<u>Plutonium Dissolved, g</u>	<u>Beryllium Dissolved, g</u>
1	2.45	1M HNO_3	----	----
		10.5M HNO_3	0.042 ^a	1.09
2	---- ^b	10M HNO_3	0.054	1.58
		11.3M HNO_3 -		
		0.08M KF -		
		0.005M Al^{3+}	0.179	0.26
3	---- ^b	10M HNO_3 -	----	----
		0.08M KF -		
		0.005M Al^{3+}	0.429 ^a	3.83

a. Solids remained consisting of PuO_2 only.

b. Weight of initial sample unknown; dissolved in cylinder.

Brass dissolved readily in high concentrations of nitric acid, yielding <0.0001 mole of hydrogen per mole of gas evolved. Alloying zinc with copper alters its dissolution behavior, so that almost no hydrogen is obtained. Brass may, therefore, be dissolved without hazard.

Massive beryllium metal, like aluminum, is resistant to acidic dissolution due to the formation of an inert and impervious BeO film on the surface.⁴ Therefore, beryllium dissolves slowly in nitric acid, but the rate is greatly increased in the presence of HF.⁵ Two modes of dissolution are possible:

Test dissolutions with HNO₃-HF mixtures demonstrated that both reactions do occur, with 12 mol % of the evolved gas being hydrogen, and the remainder NO. The H₂-to-NO ratio did not change with nitric acid concentration. For each mole of gas produced, 1.44 mole of beryllium is consumed.

The test results and dissolution rate data in Reference 5 were used to determine gas purge rates necessary to avoid explosive H₂ mixtures, from the general equation:

$$\text{purge}(\ell/\text{min at STP}) = 4.97(\ell/\text{g Be dissolved}) \times R(\text{g}/\text{cm}^2\text{-min}) \times A(\text{cm}^2)$$

where R is rate of dissolution from Reference 5, and
A is the surface area.

PLUTONIUM OXIDE-ZIRCONIUM OXIDE SOLID SOLUTION

PuO₂-ZrO₂ solid solution scrap is obtained from oxidized Pu-Zr alloy and also from mixtures of PuO₂ with ZrO₂. Tests were conducted with samples of oxidized alloy.

PuO₂-ZrO₂ is dissolved by 10M HNO₃ - 0.1M KF. Zirconium in solution very strongly complexes fluoride ion;⁶ therefore, excess fluoride ion must be added to provide free fluoride ion for catalyzing PuO₂ dissolution. Thus, 0.1M KF with no aluminum was used in the tests shown in Table X. These tests demonstrate that at least 90% of the PuO₂ can be dissolved if >40 ml of solvent are used per gram of scrap, and that any residual PuO₂ can be dissolved with a second HNO₃-KF contact. One test with material containing only 1 to 2% PuO₂ in ZrO₂ microspheres demonstrated that, although the plutonium could be dissolved, the high-fired ZrO₂ would not go into solution and had to be discarded as a solid.

TABLE X

Dissolution of $\text{PuO}_2\text{-ZrO}_2$ ScrapConditions: 3 hr in boiling 10M HNO_3 - 0.1M KF

<u>Test</u>	<u>Sample Wt., g</u>	<u>Solvent Volume, ml</u>	<u>% Pu Dissolved</u>
1	5	100	67.7
		200	27.2
2	5	200	99.5
		100	0.5
3	5	100	66.8
		100	17.7
		200	0.3
4	2.1	170	95.8
		85	4.2

PLUTONIUM METAL AND ALLOYS

Plutonium metal scrap is expected to be a small portion of the total scrap processed; however, there is a significant amount of Pu-Zr alloy encapsulated for heat sources. Of the various scrap categories, plutonium metal or plutonium alloy probably constitutes the greatest processing hazard. The most serious accident would be spontaneous ignition of metal or alloy in a container upon opening. In addition to plutonium metal and some of its alloys, a few other plutonium compounds, such as hydride and substoichiometric oxides, are flammable. A study⁷ of the oxidation characteristics of these plutonium materials showed that a peak temperature of 1350°C is possible with 200 to 350 g quantities, although sparks or flames may not be visible.

It has been reported that Pu-Zr alloy can be dissolved safely in $\text{HNO}_3\text{-HF}$ acids, but only if the fluoride-to-zirconium ratio is kept greater than 4 to 1 to deactivate any potentially explosive metal phases.⁸ Thus, the preferred method for re-processing Pu-Zr alloy is oxidation to $\text{PuO}_2\text{-ZrO}_2$, followed by dissolution in mixed $\text{HNO}_3\text{-HF}$ acids. Pu-Zr alloy oxidizes more slowly than plutonium metal below 300°C, but the rates of oxidation are identical above 300°C.⁹ Mound Laboratory has shown that self-heating in air causes slow oxidation.¹⁰ Therefore, oxidation of plutonium metal and alloy can be conducted safely in a container placed in a metal box that has a lid and is partially filled with magnesia sand. The sample is allowed complete access to air unless the reaction becomes too vigorous,

in which case the lid is closed to slow or stop oxidation. Combustibles should be absent from the glove box where the oxidation is conducted. No laboratory tests were made at SRL because properly sized Pu-Zr samples were not available for recovery.

No laboratory tests were made because of the large size of the Pu-Zr capsules available for recovery.

ANION EXCHANGE RECOVERY OF ^{238}Pu FROM SOLUTIONS CONTAINING MOLYBDENUM AND BERYLLIUM

Recovery of plutonium by anion exchange from waste solutions has been in general practice for many years.¹ Such waste solutions contain numerous components, and, in general, the concentrations are low enough not to affect the absorption of the plutonium nitrate complex. However, molybdenum and beryllium are present at significant concentrations in the solutions from dissolving certain ^{238}Pu scrap materials. The absorption of the plutonium nitrate complex from solutions containing the molybdate and/or the beryllium ions has not been reported in the literature; however, our tests showed that molybdate or beryllium ions do not interfere with anion exchange recovery of plutonium, and that prior removal of these impurities is not required.

Twenty bed volumes of solution containing 0.02M MoO_4^{2-} and/or 0.02M Be^{2+} in 7M HNO_3 were passed through a column of "Dowex" 1-X4 (50 to 100 mesh) anion resin, and the effluents were analyzed for each ion. The concentrations of molybdate and/or beryllium in the influent and effluent streams were almost identical, indicating no absorption of these ions by the anion resin.

Absorption of plutonium on anion exchange resin in the presence of molybdate and/or beryllium was tested with two solutions, one containing 1.96 g/l ^{238}Pu plus 0.07 g/l Mo in 7.5M HNO_3 , and the other containing 1.96 g/l ^{238}Pu plus 0.05 g/l Be^{2+} in 7M HNO_3 . Each solution was passed through "Dowex" 1-X4 (50 to 100 mesh) anion resin, and the effluent was analyzed for $^{238}\text{Pu}^{4+}$, MoO_4^{2-} , and Be^{2+} . The ^{238}Pu was eluted with 0.35M HNO_3 , and also analyzed for ^{238}Pu , MoO_4^{2-} , and Be^{2+} . The results (Table XI) indicate that neither MoO_4^{2-} nor Be^{2+} interferes with the absorption or elution of ^{238}Pu ; neither contaminates the ^{238}Pu product.

TABLE XI

Anion Exchange of ^{238}Pu in Presence of MoO_4^{2-} and Be^{2+} "Dowex" 1-X4 (50-100 Mesh) - 7.5M HNO_3

<u>Test</u>	<u>Solution</u>	<u>Bed Volumes</u>	<u>% ^{238}Pu</u>	<u>ppm (relative to ^{238}Pu)</u>	
				<u>Mo</u>	<u>Be</u>
1	Feed	50	100	35,000	---
	Wash	3	0.5	NA ^a	---
	Eluate	5	99	>400	---
2	Feed	50	100	---	25,000
	Wash	3	1	---	NA ^a
	Eluate	5	96	---	2

^aNA = Not Analyzed

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