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RECOVERY OF PLUTONIUM FROM SLAG AND CRUCIBLE FRAGMENTS BY LEACHING WITH NITRIC ACID

by

H. H. Hopkins, Jr.
Chemical Research Section
Separations Technology Division

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RECOVERY OF PLUTONIUM FROM SLAG AND CRUCIBLE FRAGMENTS BY LEACHING WITH NITRIC ACID

INTRODUCTION

The slag and crucible from each reduction run in the 235 Building metal production process retains approximately six grams of plutonium. The established plutonium recovery goal for this material is a minimum of 90%.(1) Proposed methods of dissolving this plutonium for recovery were:

A. High temperature hydrochlorination, (2) followed by dissolution in dilute acid.

B. Breakdown of separated crucible with molten potassium hydroxide, followed by dissolution of both crucible and slag in nitric acid. (3)

C. Total dissolution of crucible and slag in aluminum nitrate and nitric acid solution under reflux. (4) (5)

D. Leaching with nitric acid.

Method (A) works satisfactorily in the laboratory, but, due to the corrosive properties of hydrochloric acid, is unattractive for plant scale operation. Method (B) requires separation of the slag and crucible and treatment of each separately. A process such as (C) or (D) operating on slag and crucible together appears more desirable.

Method (C) involves a six hour treatment with boiling nitric acid.(5) After this treatment a silica residue remains which retains about 5% of the plutonium.(5) This plutonium may be recovered by separate treatment if desired.

This process (Method C) requires equipment capable of withstanding boiling nitric acid. At present a glass-lined dissolver is planned.(5)

Method (D) involves dissolution of the plutonium by leachings; only a fraction of the crucible dissolves. Some possible advantages of this process over method (C) are (1) rapidity, (2) no need for external heating, (3) lower acidity, and (4) lower temperature of operation. The latter two features should contribute to less corrosion of metallic equipment. The chief disadvantage of the leaching process is that a solid residue remains which would be difficult to analyze for plutonium without completely dissolving it.

Since the chemistry of processes (C) and (D) is similar, the choice of either for operation at Hanford Works should depend on the ease of operating and maintaining the necessary equipment. This consideration assumes both processes will be demonstrated to give high, reproducible recovery yields.

Treatment of the leaching solutions depends on the stage of the separations process to which the plutonium will be recycled. Recycling to the 224 or 231 Building may require some purification. Recycling to the 234 Building requires a higher degree of purification. Recycling to Redox feed streams could be done with no further treatment.

This report describes a leaching process derived from experiments on portions of slag and crucible from one reduction run. Also considered is one possible purification step resulting in a solution which can be recyled to the 224 Building.

SUMMARY

(A) Removal of encrusted iodine with reducing solution enables effective leaching.

(B) Three leachings with 4 $\underline{M}$ HNO_3 totalling 11 liters are effective in removing 99% of the plutonium from portions of slag and crucible.

(C) Approximately one-third of the crucible and one-half of the slag are dissolved in the leachings.

(D) Plutonium may be separated from the leachings by precipitation with ammonium hydroxide at a pH of 6. The plutonium is then redissolved in nitric acid to give a solution which may be recycled to the 224 Building.

(E) Filtration of the hydroxides is a slow step requiring filter aid. Therefore, solvent extraction appears more promising but remains to be worked out.

EXPERIMENTAL

A. Introduction

The slag from one reduction consists of approximately 550 g. of material, or about 230 g. calcium, 160 g. iodine, 150 g. fluorine and 6 g. plutonium. The fluorine is present as calcium fluoride, the iodine as calcium iodide and free iodine. About 50 g. of free calcium metal are present.(6)

The crucible consists of 1700 g. magnesium oxide, 30 g. silica and approximately 8 g. (or less) R_2O_3. Some of the slag and plutonium are encrusted on the crucible wall.

When a magnesium shipping container is opened, the slag is found as a hard solid cylinder, whereas the crucible consists of many pieces ranging from the size of sand particles to pieces several inches in diameter. After standing a few weeks in the laboratory atmosphere the cylinder of slag crumbles to a damp porous mass, as it is deliquescent.

This report treats of leaching crucible and slag from a full scale reduction. Thus the volumes, weights, and percentages reported here are for full scale operation on one crucible and its associated slag. The figures were obtained by applying scale-up factors to data on the behavior of small portions of slag, crucible, or both. Since the crucible pieces differ in size, shape, plutonium content, etc., a spread of values was obtained for each measurement, e.g., the percentage plutonium dissolved in the first leaching. The value adopted here as representative is that calculated from the total plutonium dissolved in the first leachings in all experiments and the total plutonium present in these experiments. The other data were obtained similarly.

B. Laboratory Study of Leaching Procedure

1. Removal of iodine

A wash with a reducing agent removes the cake of iodine which adheres to the inner surface of the crucible. The wash also removes iodide ion which would otherwise be converted to free iodine in the leaching step. Washing also wets the hard cylinder of slag, causing it to crumble so that the texture of the slag is sandy.

The wash consists of treatment with three liters of solution containing 10 g. $Na_2S_2O_5$ followed by two treatments with three liters of water. Removal of the wash liquid is easily accomplished with a dip stick. The plutonium loss in the washing step is 0.1%.

2. Leaching

An effective leaching mixture is obtained by adding three liters of water to the washed slag and crucible, then adding one liter of concentrated nitric acid. In laboratory experiments on a one liter scale, the heat of mixing results in an initial temperature of about 45°C. The mixture must be stirred vigorously as the slag and crucible are dense and tend to pack on the bottom of the container. The temperature of the mixture rises to 90°C. over a ten minute period due to the heat of neutralization of MgO. After fifteen minutes the acidity is less than 1 M. The solids are allowed to settle from the solution and the supernatant is removed with a dip stick. The solids are now rinsed rapidly with 500 ml of 4 M HNO_3 to dissolve the film of iron and plutonium hydroxides which has adsorbed on the pieces of MgO. This liquid is added to the first leaching.

A second leaching is performed in the same manner. A third leaching is performed with one-half the above volume of acid, i.e., two liters. The three leachings contain 99% of the plutonium, about one-third of the crucible and one-half the slag. An analysis of the leachings of 400 g. of crucible and slag (experiment 8) indicated that the composition of the expected 11 liters of leachings from a large crucible and slag is:

Al^{+++}	0.006	g./l.	Mg^{++}	30	g./l.
Ca^{++}	15	g./l.	Pu^{++++}	0.5	g./l.
Fe^{+++}	0.08	g./l.	F^-	3	g./l.
H^+	0.8	g./l.			

The fluoride and iron concentrations are expected to be larger in a run performed in steel equipment.

The small amount of silica which is present is removed by filtration through a bed of filter aid as each leaching is removed from the pot. This material is washed with hot concentrated nitric acid.

Some free iodine is usually formed when the nitric acid is first added to the slag and crucible. It rapidly volatilizes from the hot solution.

If the leachings are stirred longer than fifteen minutes, the acidity falls and the reaction stops. The initial acidity of 4 $\underline{M}$ was fixed on the basis that more concentrated acid could dissolve enough MgO to yield a supersaturated solution at room temperature. Also the reaction mixture would heat to the boiling point.

The experimental data from which the leaching procedure was deduced are presented in Table I. The experiments used portions of washed crucible and slag from reduction run X-10-3-31. In the first experiments contact times and acid strengths were varied from the above conditions. However, experiments #6 through #9 approximate the conditions fairly closely.

Considering all experiments, it is noted that 98.7% of the plutonium was removed in three leachings, despite variations of conditions. In the last four experiments, using the proposed leaching process, 99.4% was removed.

Further leachings dissolve little plutonium. The remaining few tenths of a per cent seem to be deeply embedded in the crucible and cannot be removed by leachings. Complete dissolution takes at least 15 hours at 90°C.

3. Purification

Early in this project it was thought that a hydroxide precipitation of plutonium from the appropriately buffered leaching solution would separate plutonium from calcium and magnesium so that after redissolution the plutonium could be recycled to the 224 Building. The present belief is that it is preferable to use a solvent extraction purification step leading to recycle to the 234 Building. This report covers the early work on the hydroxide precipitation.

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Table I

LEACHING OF CRUCIBLE X-10-3-31 WITH NITRIC ACID

Exper. No.	Crucible (g)	Slag (g)	Pu (g)	Vol. HNO_3 in Leaching Sol'n. Ml. Per Gram Solids		% Pu Removed in Leachings			% Pu in Residue
				1st Leach	2nd (and 3rd) Leach	1st Leach	2nd Leach	3rd Leach	
1	150	0	0.11	1.2 ml. 8 M	0.7 ml. 4 M	76	9	14	1
2	150	45	0.54	2 ml. 3 M	0.8 ml. 5 M	83	3	9	5
3	200	0	0.24	2 ml. 4 M	2 ml. 4 M	92	4	1	3
4	175	0	0.07	1.7 ml. 6 M	1.7 ml. 4 M	83	5	-	12
5	0	63	0.20	6 ml. 4 M	1.5 ml. 4 M	93	6	-	1
6	200	0	0.05	1.5 ml. 4 M	1.5 ml. 4 M	78	14	1	7
7	0	180	0.51	4.5 ml. 4 M	2.5 ml. 4 M	94	4.6	1	0.4
8	300	100	2.1	2 ml. 4 M	1.5 ml. 4 M	90	9	0.6	0.4
9	400	200	1.7	2.1 ml. 5.5 M	0.7 ml. 5.5 M	82.5	14.6	2.1	0.7
TOTAL	1575	588	5.5	-	-	82.4	13	3.3	1.3

The composition of the solution obtained from leaching has been described above. Ammonium nitrate and ammonium hydroxide are added to provide an ammonium ion concentration of 1 M and pH of 6. The ammonia must be added very slowly with vigorous agitation; otherwise local precipitation of magnesium occurs. Total volume of the slurry is about 12 liters. The hydroxide precipitate settles to a volume of three liters. The supernatant may be decanted and washing conducted in like manner. This process is very slow; about 12 hours is required for the settling.

Filtration of the hydroxide reduces the volume of the precipitate to 400 ml. However, filtration is also very slow; filtering through a 6" sintered glass funnel with a filter bed required three hours. The resulting cake is about one inch thick. A wash with an ammonium nitrate solution is recommended.

The filtration process can be greatly accelerated by use of Celite filter aid. A minimum of 150 g. is stirred into the slurry immediately before filtration; the filtration time is reduced to approximately one hour.

The one-inch cake of hydroxide is dissolved by the addition of 150 ml. of hot concentrated nitric acid. After this is passed through the filter, 50 ml. of hot nitric acid is contacted with the filter bed to remove adsorbed plutonium.

The resulting plutonium solution has a volume of 600 ml. On the basis of small scale experiments, the composition of this solution is expected to be:

Al^{+++}	0.1	g. /l.	La^{+++}	0.2	g. /l.
Ca^{++}	13	g. /l.	Mg^{++}	30	g. /l.
Fe^{+++}	13	g. /l.	Pu^{++++}	10	g. /l.

The amount of iron present in a large scale treatment may be different from this figure since the reaction vessels will be of steel instead of glass.

The above value for the Fe^{+++} concentration is not consistent with that reported for the leaching solutions. This inconsistency will be cleared up in later work.

4. Equipment

For the leaching process a stainless steel pot with a power

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anchor stirrer is needed. The pot could be mounted on a swivel to enable easy dumping of leached residues. For small scale demonstrations a beaker and paddle are used.

Supernatants are removed by a dip stick leading to an evacuated drum which serves as storage and mixing tank.

Filtration of the leachings is performed on a 6" coarse porosity filter covered with an eighth inch bed of filter aid. Filtration of the hydroxides requires a larger filter to minimize the time required.

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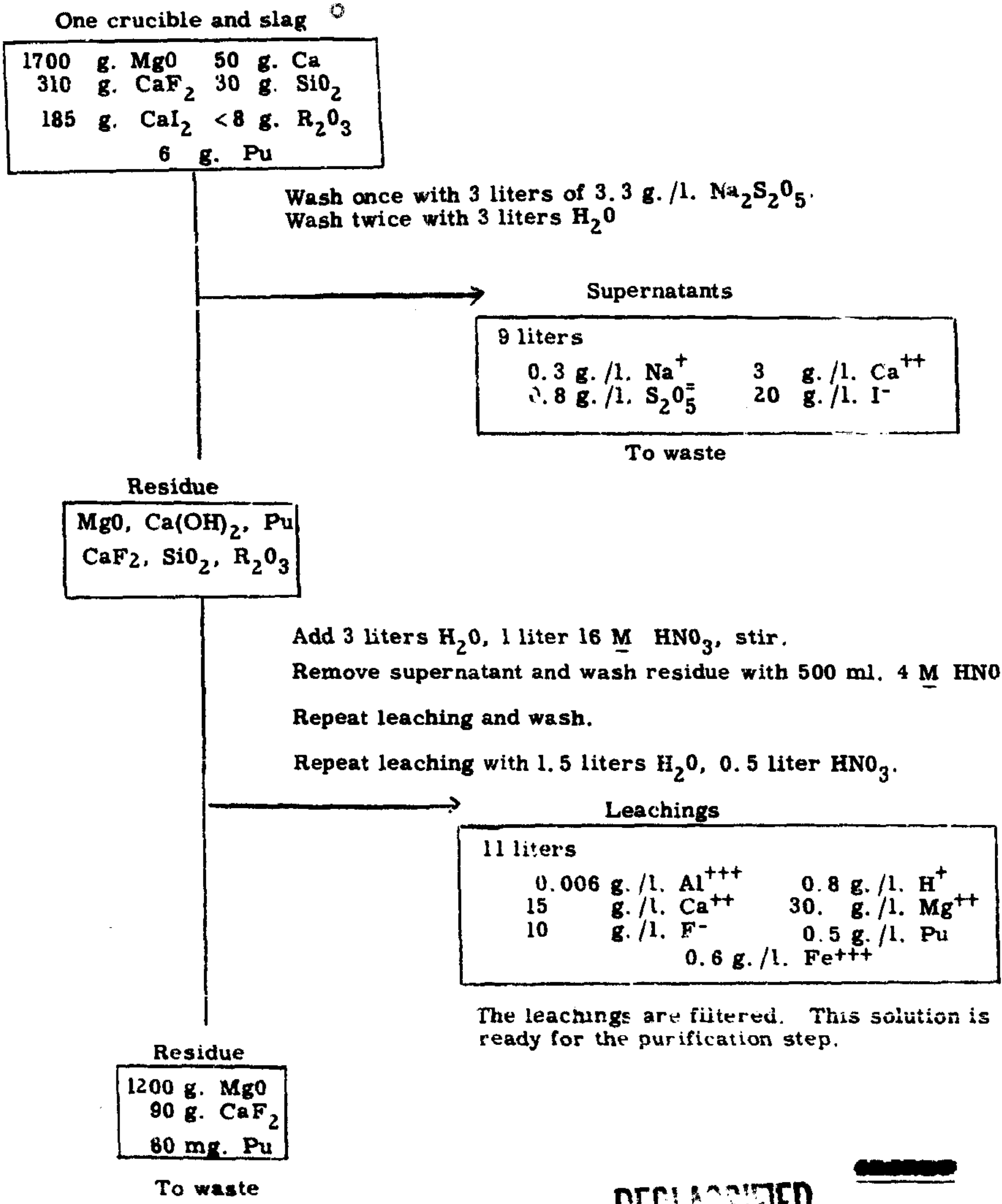
C. Proposed Leaching Process



One crucible and slag

1700 g.	MgO	50 g.	Ca
310 g.	CaF_2	30 g.	SiO_2
185 g.	CaI_2	< 8 g.	R_2O_3
6 g.	Pu		

Wash once with 3 liters of 3.3 g./l. $Na_2S_2O_5$.
Wash twice with 3 liters H_2O

Supernatants

9 liters

0.3 g./l.	Na^+	3 g./l.	Ca^{++}
0.8 g./l.	$S_2O_5^=$	20 g./l.	I^-

To waste

Residue

MgO, $Ca(OH)_2$, Pu
CaF_2, SiO_2, R_2O_3

Add 3 liters H_2O, 1 liter 16 M HNO_3, stir.

Remove supernatant and wash residue with 500 ml. 4 M HNO_3.

Repeat leaching and wash.

Repeat leaching with 1.5 liters H_2O, 0.5 liter HNO_3.

Leachings

11 liters

0.006 g./l.	Al^{+++}	0.8 g./l.	H^+
15 g./l.	Ca^{++}	30. g./l.	Mg^{++}
10 g./l.	F^-	0.5 g./l.	Pu
0.6 g./l.	Fe^{+++}		

The leachings are filtered. This solution is ready for the purification step.

Residue

1200 g. MgO
90 g. CaF_2
80 mg. Pu

To waste

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The above flow sheet is based on analyses of the leachings and knowledge of the composition of the original slag and crucible. The values for Al^{+++}, Ca^{++}, H^{+}, Mg^{++} and Pu are from direct analyses. The value for F^{-} is from a difference calculation. The value for Fe^{+++} is obtained from several measurements of the Fe^{+++} concentration in final plutonium solutions processed from leachings.

PROGRAM

Since the hydroxide precipitates are hard to handle and the step does not achieve purification from iron and aluminum, purification by solvent extraction is under investigation by W. W. Schulz. This step should provide a high purity product which might be recycled within the 234 Building.

Demonstration of leaching on a full crucible scale is planned for the near future.

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