Classification changed to Unclassified with deletions
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RECOVERY OF PLUTONIUM FROM SLAG AND CRUCIBLE

By

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Chemical Research Section
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June 15, 1951

Declassified with deletions March 7, 1960.

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INTRODUCTION

In 234-5 operations, the reduction of plutonium tetrafluoride to metal leaves the plutonium in the slag and crucible. Methods for recovering this plutonium have been investigated at Los Alamos(1, 2) and at Hanford.(3) This report describes the experimental work at this site from October, 1950 through March, 1951.

The slag and crucible consists mainly of CaF_2, CaI_2, and sintered MgO. The recovery of plutonium from these materials requires (1) a dissolution step and (2) a separations step. The recovered plutonium must then be blended with that from regular plant production.

Conceivably either the dissolution step, the separation step, or both could be done by chemical operations now performed in the Bismuth Phosphate plant, or contemplated for the Redox plant. Thus, recovery might be accomplished by recycling slag and crucible or a solution thereof to one of the plants.

The main purposes of the present work are (1) to test dissolution methods and demonstrate them on a scale of a full size crucible, (2) to find and test separation procedures, and (3) to test the recycle of slag and crucible or solutions thereof to the Bismuth Phosphate or Redox Process.

These objectives have been partially achieved.

SUMMARY AND CONCLUSIONS

Three methods of preparing a nitric acid solution of slag and crucible and four methods of separating the plutonium have been investigated. The following conclusions have been drawn:

A. Slag and crucible can be dissolved satisfactorily by the Los Alamos method of total dissolution with nitric acid in the presence of aluminum nitrate. Leaching with nitric acid alone is unsatisfactory since plutonium recoveries are low unless most of the slag and crucible is dissolved, and since the resulting solutions are difficult to filter because of suspended fines.

B. Extraction of 99% of the plutonium from total dissolution salted with aluminum nitrate was achieved by three successive contactings with 1/10 volumes of 30% TBP-AMSCO 125-90W. Similar high extraction yields can be obtained from leaching solution if calcium nitrate is used as the salting agent. With aluminum nitrate as the salting agent emulsion formation occurs unless the leaching solution is digested with the aluminum nitrate for a considerable time, and then filtered.

C. The TBP-AMSCO phases contacted with leaching solutions salted with calcium nitrate must be scrubbed to remove calcium. Scrubbing also offers a convenient method for reducing the nitric acid concentration of the organic phase, if desired.

D. Stripping with three 1/10 volumes of 0.1 M hydroxylamine sulfate removes 99% of the plutonium from the 30% TBP-AMSCO, initially 0.1 M HNO_3.

E. Plutonium(III) oxalate, (which could be blended into 234-5 operations) can be precipitated from the aqueous strip solution. Solubilities as low as 22 mg/l have been obtained. If the extraction and stripping were done countercurrently instead of successively as in these experiments, this value would be equivalent to ca. 0.1% plutonium loss.

F. It is chemically feasible to recycle slag and crucible solution to the Redox IIA column in amounts up to at least 10% of IIAF by volume. (This test was run with leaching solution, although solution from the one-step dissolution process would be expected to behave similarly).

[redacted]

G. It is also chemically feasible to recycle nitric acid solution of slag crucible obtained in the presence of aluminum nitrate to the Product Precipitation step of the Second Decontamination Cycle of the Bismuth Phosphate Process. The behavior of small amounts of aluminum carried by the bismuth phos-

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Note in proof: It has been subsequently shown that it is possible to run solution from one step dissolution as IIAF.

phate in the Lanthanum Fluoride Concentration Cycle remains to be investigated.

EXPERIMENTAL

Considerable work was done simultaneously on the preparation of solution and on the separation methods. Consequently, the separations experiments were not all done on solutions of slag and crucible prepared by the best method. In this report the source of the solutions used will be described for each separations investigation.

Several investigations were conducted both on a test tube scale, and a "gallon" scale. The "gallon" scale runs employed a full size crucible and its associated slag. The data obtained in the test tube runs will be followed by the numbers measured in the "gallon" scale work. The latter work was performed in a nine foot gloved box fitted with stainless steel equipment (Figure 1).

A. Preparation of Solution

A typical full scale slag and crucible will have a composition similar to that presented in Table I.

Table I

COMPOSITION OF SLAG AND CRUCIBLE

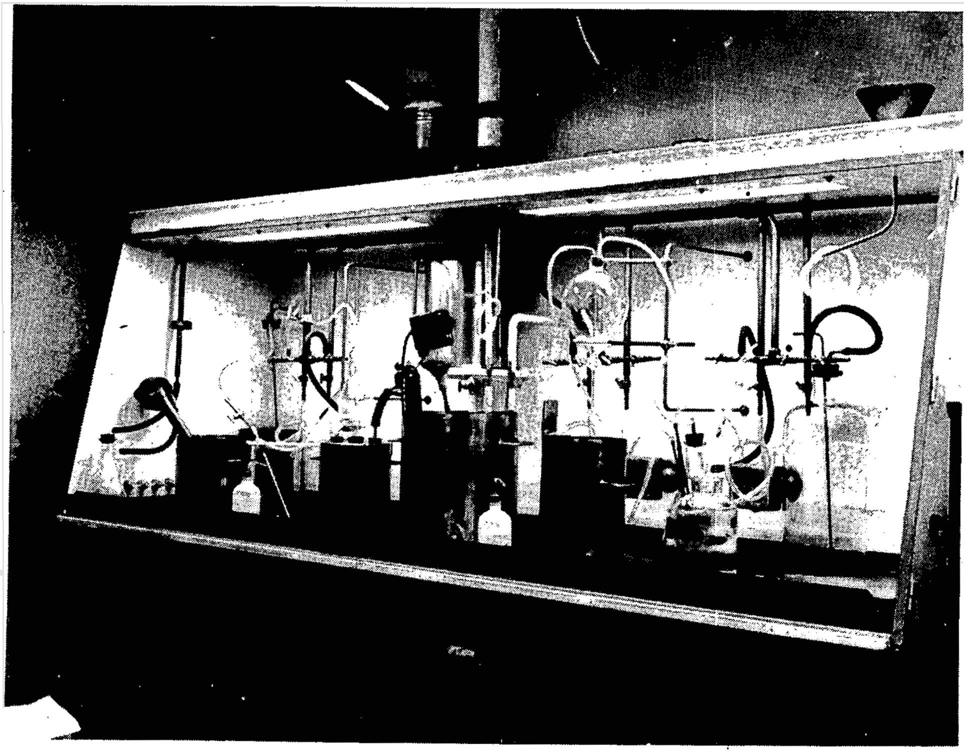
1600 g	MgO
310 g	CaF_2
185 g	CaI_2
50 g	Ca
30 g	SiO_2
6 g	Pu

Some of the iodine will be present as the free element.

To separate plutonium from the slag and crucible, these materials must be more or less completely dissolved. To prevent the formation of large amounts of free iodine by the action of nitric acid, the dissolution step is preceded by an iodine removal step.

The procedure described in the first report(3) called for a sodium hydrosulfite wash to remove iodine, followed by partial dissolution with nitric acid leachings. It will be seen in this report that on a scale of one full sized

Figure 1



GLOVED BOX FOR RECOVERY OF PLUTONIUM FROM SLAG AND CRUCIBLE

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crucible, leaching was not successful in dissolving the plutonium in a small number of leaches, and that emphasis shifted towards complete dissolution methods.

1. Iodine Removal Methods

a. Washing

Two experiments were carried out with slag and crucible from small (6 g Pu) reduction runs. Iodine removal consisted of washing the slag and crucible twice with 100 ml water containing 1 g $Na_2S_2O_4 \cdot 2H_2O$ (sodium hydrosulfite, J. T. Baker and Company) followed by a 100 ml water wash. The results are presented in Table II.

Table II

REMOVAL OF IODINE WITH $Na_2S_2O_4$ SOLUTION

(Small Reduction Crucibles)

Expt.	#1	#2
I_2 Initial (g)	2.38	2.33
I_2 in 1st $Na_2S_2O_4$ Wash (g)	2.08	1.96
I_2 in 2nd $Na_2S_2O_4$ Wash (g)	0.50	0.37
I_2 in H_2O Wash (g)	0.05	0.05
Total I_2 Removed (g)	2.63	2.38
Total % Pu Loss	0.94	0.38

Iodine removal was also tested by washing full size crucibles and slag. The treatment as proposed(3) called for a wash with three liters of solution containing 10 g $Na_2S_2O_4 \cdot 2H_2O$ and two washes with three liters of water per wash. The first run was made with the specified volumes but with 20 g $Na_2S_2O_4 \cdot 2H_2O$; the second, with 40 g. The washes were analyzed for plutonium. The analyses of nitric acid leachings of the slag and crucibles showed that the iodine had been effectively removed (Table III).

Table III

IODINE REMOVAL BY $Na_2S_2O_4$ WASH

(Large Crucibles)

	1	2
Iodine present initially (g)	ca. 160	ca. 160
Iodine in leach solution (g)	0.001	0.020
Pu loss (mg)	0.11	0.590
Pu loss (%)	0.002	0.020

The iodine remaining after washing was reduced to the low value of Table III partially by volatilization during the leaching steps. The plutonium losses are satisfactorily low, although they are still significant from a waste disposal point of view.

The mechanical operability of washing full size slag and crucible was very poor. When the slag is treated with an aqueous solution, it crumbles, and considerable fines are suspended. These fines settled out in the early small scale experiments.(3) In the runs reported in Table II, the solution was filtered and considerable fines went through the filter, perhaps accounting for the plutonium loss. In the large scale runs the partially settled supernatant was filtered through a medium porosity sintered glass filter. This stopped the fines, but gave very slow filtration rates because of plugging of the filter with fines. A 50 sq. cm. filter passed at most about three liters of solution in an hour and was almost completely plugged at the end of the hour. Precoating with Cellite did not help. Coarser filter media, such as "D" porosity Micrometallic, passed the fines. Filtering out first the coarse particles and then the fines was even more objectionable; the coarse particles act as filter aids for the fines if not separated.

The solid-liquid separation is not impossible; it can be done by centrifugation and probably by using filter aid mixed in the slurry, or even by using a thick, fibrous coarse filter medium. The separation is difficult enough, however, to make iodine removal by volatilization look much more attractive.

b. Volatilization

Volatilization of the iodine from small reduction crucibles (6 g Pu) was accomplished by the method of Los Alamos.(2) This procedure consisted of placing slag and crucible in a round bottomed flask fitted with a reflux condenser and then adding 0.8 M $Al(NO_3)_3$ solution such that the weight of the aluminum nitrate 9-hydrate was six times the weight of slag. The mixture was air sparged for 15 minutes to insure removal of hydrogen. Concentrated nitric acid was added to make the final solution 5 M HNO_3, and hot water was run through the condenser. Upon the addition of the nitric acid the pink color of iodine soon became apparent. After air sparging for 45 minutes, the solution had a deep greenish hue indicating that all the iodine had been removed.

Several observations on iodine volatilization were made while dissolving crucibles which had been used for UF_4 reductions. While treating these crucibles with nitric acid under reflux, iodine came off rapidly in the first few minutes of boiling. In most of the experiments it collected just above the reflux line on the reflux condenser, and occasionally a little dropped back in. In the experiment in which uranium metal was dissolved along with the crucible, the vigorous current of nitrogen oxides swept the iodine through the condenser. It was concluded that it is necessary to steam distill the iodine out of the condenser, and hence the condenser must be heated, or at least not cooled, during the initial boiling with nitric acid.

c. Extraction

If iodine is not completely removed before the dissolution step, some will appear in the solution of slag and crucible. Such a solution was obtained, e.g., from the first three leachings of crucible Y-10-12-14 which were colored by iodine. These leachings were combined, salted with calcium nitrate and extracted with a 1/10 volume of AMSCO 125-90. This essentially removed the iodine color from the aqueous phase and turned the organic phase a deep purple indicating fairly complete extraction. The organic phase when analyzed for iodine showed less than 0.01 g/l, or less than 20 mg total. Three milligrams of plutonium were lost to this solution. Iodine removal by extraction is efficient, but volatilization appears easier.

2. Dissolution of Slag and Crucible

a. Partial Dissolution by Successive Leaches

Early leaching experiments have been previously reported.(3) The results of three recent small scale experiments are reported in Table IV.

Table IV

LEACHING OF PLUTONIUM FROM SLAG AND CRUCIBLE

Expt.	Weight Material (Grams)	4 $\underline{M}$ HNO_3 (ml per Gram)	% Pu 1st Leach	2nd Leach	3rd Leach	4th Leach	Leaches Combined
1	44	2.3	72.3	15.8	7.9	--	96.0
2	60	1.7	44.1	21.5	20.4	10.8	96.8
3*	50	2.0	2.2	30.2	54.4	9.4	96.2

* Experiment performed by W. H. Adams

The material for these runs was slag and crucible from small scale (6 g Pu) reductions. The contact times were 20 minutes. It is seen that ca. 96% of the plutonium was leached out in three or four leachings. Approximately half the total solids dissolved.

Leaching of the full size crucibles and slag was performed according to the following procedure: To each full size crucible and slag washed to remove iodine, add one liter of concentrated nitric acid, followed by three liters of water. Stir vigorously with a heavy stainless steel paddle, turning the pieces over and over. Every five minutes measure the temperature rise (due to heat of neutralization). When the temperature levels off (ca. 30-50 minutes, 70°), transfer the liquid to a measuring tank and filter. Successive leaches are accomplished in a similar manner but with smaller portions of acid (ca. 2/3 liter).

The plutonium was not successfully leached from full size crucible and slag; it was necessary to dissolve almost all the slag and crucible to dissolve ca. 99% of the plutonium. The lack of effectiveness of successive leaches is shown in Table V. The designation of combined leachings is also indicated.

Table V

PLUTONIUM IN SUCCESSIVE LEACHES (PER CENT)

(Full Size Crucible and Slag)

	Crucible			
Leach	I		II	
1	17.9	IA	64.9	IIA
2	33.5			
3	8.6		6.8	
4	12.9	IB	3.0	IIB
5	10.3		11.1	
6	10.0		12.8	
7	6.6		--	
Residue	0.2		1.4	

In the first crucible 40.0% of the plutonium remained after three leachings, in the second 28.3%. Leaching as carried out in these experiments is not a success.

From an operational point of view, the process was also unsuccessful. Stirring was difficult because the crucible pieces are heavy, sharp, and abrasive; they do not slide or roll over each other. It was necessary to turn the pieces over with a heavy stainless steel paddle. The grinding action removes the silica which is exposed as the magnesium oxide dissolves, and thus permits the reaction to proceed. A Lightnin' high speed propellor mixer did not produce the necessary action. An anchor stirrer or a drum mixer might work.

An even greater difficulty than the mixing was the solid-liquid separation. The fines of the previous iodine removal step were dissolved by the acid, but the silica released in dissolving the crucible plugged the filter just as badly as before. It took an hour to filter a three liter batch, and the filter (3 1/2" medium porosity sintered glass) had to be backwashed after every batch.

Another difficulty may be described as a control difficulty. In the leaching step, one is attempting to remove the plutonium by leaching with acid in the presence of a base, MgO. If the acid stays in contact with the base too long, the acid will all be neutralized, the pH will rise and the plutonium will be either adsorbed on the remaining crucible or precipitated as the hydroxide.

There was also difficulty from corrosion. A weld failed, valves leaked, and the tanks (Type 347 stainless steel) were etched after only two experiments. The leach solutions were green with chromium(III) ion. The corrosion products do not follow the plutonium through the extraction process, and hence corrosion is not serious from a contamination point of view, but the corrosion is serious from the point of view of damage to the equipment. The corrosion probably arises from the presence of fluoride ion and hydrofluoric acid from the calcium fluoride in the slag.

To alleviate certain of these difficulties one could add enough acid in one batch to dissolve all the slag and crucible, thus eliminating all but one filtration, and eliminating the control problem above. Also, by boiling the solution under reflux, the difficult stirring operation might be eliminated.

b. One-Step Dissolution

A "one-step dissolution" will mean the case in which all the acid required is added at once, as contrasted with "leaching" in which the acid is added successively in portions.

In studying the dissolution rate of crucibles it should make little difference whether the crucible had seen uranium or plutonium reductions. Since uranium reduction crucibles are more convenient to handle, several such crucibles were used in experiments on one-step dissolving of crucibles under reflux.

The nitric acid used was ca. 5 M, since with higher concentrations magnesium nitrate will precipitate from the final solution. Agitation was provided by gentle boiling. Under such conditions it took at least 24 hours to dissolve four gram pieces of crucible, even with 50% excess acid. The largest pieces found in full size crucibles are at least four times as thick as the four gram pieces used in these experiments, and it is estimated four days may be required to dissolve completely.

The acid consumed in these experiments corresponded to an equivalent weight for crucible of 20.6 g as compared to 20.2 g calculated for MgO.

By use of concentrated acid in 100% excess the dissolving time could be reduced to twelve hours for four gram pieces. Uranyl nitrate or uranium metal had little effect on the dissolving rate; uranium metal in pieces equivalent in size to the crucible pieces was completely dissolved before the crucible was appreciably attacked. From these results it appeared that dumping slag and crucible into the dissolver of the bismuth phosphate plant would not result in complete dissolution during the present dissolver cycle.

Grinding the crucible to pass 20 mesh greatly increased the dissolution rate. About 99% of the ground material dissolved in seven minutes; a few of the large, more resistant particles lasted for one and a half hours. The crucible fragments never dissolved completely; there was always some silica left undissolved. Thus, it was difficult to determine when dissolution of the soluble portion of the crucible had been completed. This dissolution of ground crucible is not affected by the presence or absence of uranyl nitrate.

Grinding the crucibles presents something of a problem. The crucibles are almost as hard as china plates; they are brittle and can be easily shattered. However, it was possible to grind 400 g/hr in a mortar and pestle. Grinding is very effective in decreasing dissolution time, but this operation may be hazardous for plant operation.

Los Alamos(2) had reported that aluminum nitrate accelerated the dissolution of crucible pieces. The use of aluminum nitrate also promised to reduce the corrosion problem by complexing the fluoride. To test the dissolution rate three pieces of crucible were dissolved without grinding in the presence of aluminum nitrate. To 12.62 grams of crucible fragments were added 46 ml 0.84 M $Al(NO_3)_3$. After one-half hour digestion time, 68 ml concentrated HNO_3 were added. The crucible fragments dissolved in 3 1/2 hours' boiling, compared to 12 hours in the absence of aluminum nitrate for pieces of comparable size. The silica remaining in the flask appeared to be more crystalline than in the preceding experiments. The solution obtained by filtering this mixture had a volume of 88 ml and freezing point of 47°C.; when diluted back to 108 ml it had a freezing point of 21°C.

The details of a one-step dissolution procedure were available from work carried out at Los Alamos,(2) and the dissolution of slag and crucible from a small reduction run was completed using the Los Alamos procedure. The crucible weighed 46 g and the slag 6.5 g. Following the removal of iodine (Section III, A, 1, b), the mixture was refluxed for six hours. The solution was then filtered hot (80°C.) through a glass cloth filter and the small residue of silica was washed with 6 M HNO_3. The final solution contained 94.7% of the plutonium, while the silica retained 5.3%.

In summary, it is thought that the Los Alamos dissolution procedure for removing iodine and dissolving slag and crucible is the most efficient method. Presented below in Table VI is the solution composition expected when a full scale slag and crucible are dissolved according to the Los Alamos one-step procedure. Presented also is the composition of solution IA obtained from partial dissolution of slag and crucible by three leachings.

Table VI

COMPOSITION OF SOLUTION FROM ONE-STEP DISSOLUTION AND FROM LEACHING

(Full Size Crucible)

Solution:	One-Step Dissolution Calculated	Three Leachings (IA)* Experimental	Seven Leachings (I) Calculated
Volume	20. l	9.3 l	20. l
HNO_3	5.0 M	0.3 M	0.3 M
$Mg(NO_3)_2$	2.0 M	1.8 M	2.0 M
$Ca(NO_3)_2$	0.29 M	0.34 M	0.29 M
HF	0.4 M	0.12 M	0.4 M
$Al(NO_3)_3$	0.45 M	--	--
Pu	ca. 0.3 g/l	ca. 0.4 g/l	ca. 0.3 g/l
Pu recovery (%)	99.	60.	99.

* Concentrations measured in combined leachings (IA). The HF concentration was determined colorimetrically with zirconium alizarin indicator.

B. Separation of Plutonium by Precipitation

Precipitation of plutonium from slag and crucible solution was considered a possible separations method. The precipitation of the hydroxide from leaching solutions was previously described.(3) To summarize the difficulties, the precipitate carried 5% of the original magnesium and calcium, and the material was very difficult to filter. Although it might be possible to improve the properties and composition of the precipitate by homogeneous precipitation, the hydroxide method was considered unpromising. Precipitation of plutonium(IV) hydroxide from slag and crucible solutions containing aluminum would be very difficult. Thus the use of a hydroxide precipitation requires dissolution in the absence of aluminum nitrate, with the attendant corrosion and rate problems.

Precipitation of other compounds of plutonium e.g., iodate, peroxide, or phenylarsonate, from acid solution was deemed unattractive since there would be considerable plutonium loss in the large volume of supernatants. Alternatively, carrier precipitation might be employed to achieve high plutonium recovery, but this would require further processing to separate plutonium from the carrier.

C. Separation of Plutonium by Extraction with TBP (Tributyl Phosphate)

Solvent extraction of plutonium by TBP (tributyl phosphate) solutions appeared to offer promise as a process for the separation of plutonium from the non-extractable components of slag and crucible. A solvent extraction process using TBP as the organic solvent was especially attractive because of the possibility of obtaining large volume reductions. Reductions in volume were desirable since it was hoped to obtain a strip solution concentrated enough to permit a precipitation with high percentage recovery.

1. Extraction

The goal set in the extraction step was to obtain plutonium recoveries of 99% in three equilibrations using a volume ratio of aqueous to organic of 10:1 in each equilibration. To achieve this goal using leaching solution, a salting agent which would enable large plutonium distributions toward the organic phase was required. Because of the ability of aluminum to complex the fluoride ion present, thus giving large plutonium distributions toward the TBP phase, aluminum nitrate was the logical first choice as a salting agent. However, salting of leaching solution with aluminum nitrate and contacting with TBP solutions gave rise to the formation of interfacial emulsions. The results of Table VII show that aluminum nitrate salting gave plutonium distributions of the order desired, although emulsions were formed in every case.

The value E_a^o is defined as the equilibrium ratio of the concentration of a specified substance in the organic phase to its concentration in the aqueous phase.

Table VII

PLUTONIUM EXTRACTION FROM LEACHING SOLUTION WITH TBP

$Al(NO_3)_3$ Salting

$Al(NO_3)_3$ M	HNO_3 M	Organic Composition	Volume Ratio Aq:Org	E_a^o (Pu) for One Extraction
1.43	0.375	5% TBP-CCl_4	1:1	143
1.43	0.375	30% TBP-CCl_4	14:1	473
1.10	2.00	30% TBP-CCl_4	14:1	274
1.00	5.08	30% TBP-CCl_4	14:1	318
0.58	5.08	30% TBP-CCl_4	11:1	125
0.30	5.08	30% TBP-CCl_4	11:1	119
0.30	0.375	15% TBP-CCl_4	11:1	37
0.30	0.375	15% TBP-AMSCO 125*	11:1	37

* AMSCO - Naptha 125-90W, from American Mineral Spirits Company, Los Angeles, Calif.

The formation of emulsions appeared to be independent of the aluminum nitrate concentration, the diluent, and the TBP concentration. It was necessary, therefore, to search for an alternate salting agent which would give the high recoveries and volume reductions desired, without the formation of objectionable phases.

Formation of emulsions was avoided by the use of nitric acid as

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Table VIII

EXTRACTION OF LEACHING SOLUTION WITH TBP--EFFECT OF SALTING AGENT AND NITRIC ACID CONCENTRATION ON PLUTONIUM EXTRACTION

Aqueous Composition					Volume Ratio**	E_a^o (Pu)			% Pu Lost to Aqueous Waste
$Ca(NO_3)_2$ M	$Mg(NO_3)_2$ M	HF M	HNO_3 M	Organic Composition	Aq/Org	1st Extr.	2nd Extr.	3rd Extr.	
0.18	2.38	0.30	0.375	15% TBP-AMSCO 125	10:1	0.386	0.400	0.391	73.4
0.18	2.38	0.30	0.375	15% TBP-CCl_4	10:1	0.215	0.238	0.242	93.5
0.15	1.99	0.26	2.87	15% TBP-AMSCO 125	10:1	1.29	1.33	1.44	64.5
0.15	1.99	0.26	2.87	15% TBP-CCl_4	10:1	1.83	1.67	1.55	63.6
0.15	1.99	0.26	2.87	30% TBP-AMSCO 125	5:1	2.60	2.59	2.94	23.9
0.15	1.99	0.26	2.87	30% TBP-CCl_4	5:1	5.90	6.10	5.25	8.6
0.13	1.71	0.22	5.08	30% TBP-CCl_4	5:1	12.6	14.0	12.5	2.6
0.10 (Also 4.03 M NH_4NO_3)	1.38	0.18	5.08	30% TBP-CCl_4	12:1	11.9	16.0	13.9	1.8
0.11 (Also 1.01 M $Fe(NO_3)_3$)*	1.47	0.19	8.46	30% TBP-CCl_4	11:1	--	--	--	--

*Use of salting agent led to formation of third phase.

**Three successive extractions were made, each with the indicated volume ratio.

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Table IX

EXTRACTIONS OF LEACHING SOLUTION WITH $Ca(NO_3)_2$ SALTING

(Test Tube Scale)

Organic: 30% TBP-AMSCO 125

Aqueous Composition					E_a^o Values (Pu)			
$Ca(NO_3)_2$ M	$Mg(NO_3)_2$ M	HF M	HNO_3 M	Volume Ratio Aq/Org	1st Extr.	2nd Extr.	3rd Extr.	% Pu Lost to Aqueous Waste
1.54	1.29	0.16	2.95	14:1	26.9	21.6	21.3	6.6
2.13	1.26	0.15	2.86	7:1	36.9	39.7	31.0	1.5
3.29	1.16	0.14	1.67	10:1	77.3	29.0	14.3	0.8
3.51	1.23	0.15	1.15	10:1	75.3	36.1	19.1	0.4
3.45	1.25	0.15	1.15	14:1	78.3	29.2	46.6	1.9
3.49	1.21	0.15	1.14	10:1	79.8	26.1	24.2	1.5
3.42	1.19	0.15	1.14	5:1	76.0	24.6	18.0	0.3
3.34	1.21	0.14	1.14	10:1	79.7	22.6	20.0	0.8

Note: As in Table VIII successive extractions were made, each with the indicated volume ratio.

a salting agent for leaching solution, but the plutonium distributions were too low to give desired recoveries in three 10:1 extractions. Ammonium nitrate gave similar results, while the use of ferric nitrate as a salting agent again resulted in the formation of a third phase. The distribution ratios obtained using these salting agents are listed in Table VIII.

It was found that calcium nitrate at approximately 3 M gave effective salting and apparently reduced the fluoride ion activity permitting large plutonium distributions into the organic. Table IX presents the data obtained on a test tube scale with leaching solution. The high TBP concentration, 30%, was used in order to obtain as large a volume reduction as possible. Good phase separations were obtained. This might have been expected, as the emulsion forming material was probably silica, dissolved in the HNO_3-HF mixture formed by dissolving CaF_2 in the leaching acid, and reprecipitated in gelatinous form by ions forming a stable fluoride complex, such as aluminum or ferric ion.

Mention should also be made of the presence of americium remaining in the aqueous phase after three 1/10 extractions. Thus in the experiment in which 0.3% plutonium was not extracted (Table IX), analysis of the final aqueous phase indicated the residual activity to consist of 44,000 d/m/ml plutonium, and 38,800 d/m/ml americium. Throughout this report distribution values have been corrected for americium contributions, where significant.

Table X presents data obtained in the extraction of 15 liters of leaching solution salted with calcium nitrate.

Table X

EXTRACTION OF PLUTONIUM FROM LEACHING SOLUTIONS

($Ca(NO_3)_2$ Salting)

Solvent: 30% TBP in AMSCO 125.
Aqueous: Leaching solution plus $Ca(NO_3)_2$.

Run #		IA	IB	IIA
Concentration HNO_3, M		0.85	1.2	0.60
Concentration $Mg(NO_3)_2 + Ca(NO_3)_2$ in aqueous, M		4.7	4.2	4.0
Aqueous:solvent volume ratio		15	10	12
E_a^o (Pu)	1st extr.	103	102	37
	2nd extr.	60	18	33
	3rd extr.	57	35	12
% Pu lost to aqueous waste (Measured)		1.3	0.6	3.1
% Pu in 3rd Aqueous (Calc. from E_a^o (Pu)		0.5	0.8	3.3

The composition of solution IA from leachings (Section III, A, 2, a) was presented in Table VI. The nitric acid concentration was increased before extraction. When the salting agent, $Ca(NO_3)_2 \cdot 4H_2O$, was added, a volume increase of 55% was observed. It should also be pointed out that, on the basis of the calcium fluoride in the original slag, the total bound fluoride concentration was ca. 0.5 M, although a smaller amount is detected by analysis (Table VI).

The extractions were performed batchwise. Agitation was accomplished by a Lightnin' stirrer running for 30 minutes. Phases were separated after 5 minutes' settling. In Runs IA and IIA a solid material appeared at the interface. This was tentatively identified as CaF_2 which was reprecipitating for an unknown reason. In Run IA this precipitate carried 2 mg of Pu; in Run IIA (at lower acidity) 100 mg. Considerable nitric acid is extracted by the TBP-AMSCO-125 solution. The organic phases in Run IA were all about 1 M in HNO_3 in each of the three extractions. After extraction about half the residual activity in the aqueous phase was found to be americium.

Calcium nitrate is far from an ideal salting agent for the following reasons:

1. The process is designed to separate plutonium from calcium, among other things, and adding more calcium is going in the wrong direction.
2. When the calcium nitrate concentration is high enough for good salting, excessive calcium goes into the organic phase.
3. Solid material, believed to be calcium fluoride, forms on extraction.
4. Too much salting agent is required, which leads to
5. An excessive increase in volume when the salt is added.

Objections 1, 4, and 5 could be reduced, if not eliminated, by using stronger acid in the leaching step, thus increasing the concentration of salting agents, calcium and magnesium nitrate, increasing the concentration of plutonium in the leaching solution and decreasing volumes. A freezing point study would be required here to establish how much stronger acid might be used, as the acid strength allowable is limited by the freezing point of the leach solution. Scrub studies showed (Section III, C, 2) how the calcium in the organic phase might be reduced, answering the second objection. Since no immediate solution was seen to the problem of precipitation of calcium fluoride, and since the use of the more efficient aluminum nitrate might eliminate the scrub step, emphasis was shifted to treating the leach solution so it could be used with aluminum nitrate.

Los Alamos(2) reported that slag and crucible dissolved in the presence of aluminum nitrate under reflux and then filtered, could be contacted with TBP solutions without forming emulsions. It was thought here that leaching solutions heated in the presence of aluminum nitrate might be subsequently extracted without emulsion trouble. In order to test this possibility solid $Al(NO_3)_3 \cdot 9H_2O$ was added to a portion of leaching solution and the resulting solution was refluxed for a period of two hours (ca. 115°C.). The solution was filtered hot (80°C.) through a glass cloth filter, cooled and a portion subjected to a 30% TBP-AMSCO 125 extraction. The phases separated clearly and no objectionable emulsions formed, indicating a distinct difference between this solution and the original leach solution. The original leach solution and the solution obtained by the refluxing procedure were analyzed for silica content. The results of these analyses showed the silica content of the original leaching solution to be 8.21 g/l and the silica content of the refluxed and filtered solution to be 0.002 g/l. The great difference in silica content confirms that it is silica which is responsible for the formation of the thick emulsions observed in the earlier TBP extractions of leaching solution salted with aluminum nitrate.

In another experiment aluminum nitrate was added to a portion of leaching solution and the resulting solution heated at 80-90°C. After two hours the solution was filtered hot through a glass cloth filter and a portion contacted with 30% TBP-AMSCO 125. The formation of an emulsion was still observed, and the remaining solution was then heated an additional four hours at 80-90°C. The solution was again filtered and a portion was extracted with 30% TBP-AMSCO 125. Only a minute amount of scum was observed and clean phase separations were obtained.

Since heat treatment enabled clean phase separation on a small scale, eleven liters of leaching solution in a stainless steel pot were adjusted to 5 $\underline{M}$ HNO_3, 0.31 $\underline{M}$ $Al(NO_3)_3$ and heated for six hours at 95°C., then eighteen hours at 80°C. This treatment formed a galatinous precipitate of silica which was filtered onto a glass fiber filter cloth. The filtration was performed at 80°C. The solution passed through the filter very slowly due to the thick bed of silica. Approximately 500 ml of a gelatinous solid were obtained. This silica was heated under reflux for six hours with fresh nitric acid and $Al(NO_3)_3$. It then filtered well, giving a cake that drained. The cake volume, as broken up and removed from the filter, was about 200 ml. The filtrate from the first digestion was adjusted to 0.37 $\underline{M}$ $Al(NO_3)_3$ 5 $\underline{M}$ HNO_3, and extracted three times with 1/10th volumes of 30% TBP-AMSCO 125. The successive plutonium distribution coefficients were 36, 36, and 27. The plutonium left in the third aqueous was 0.8%.

This experiment indicates that a heating treatment with strong nitric acid in the presence of aluminum nitrate will convert the silica to a filterable form. Since the precipitate is still somewhat difficult to filter, refluxing of the original slag and crucible is recommended. The silica so obtained is easy to filter.

Extraction of the solution obtained in a small scale run by the use of the Los Alamos one-step dissolution process proceeded quite satisfactorily (Table, XI, Experiment 75). No emulsion formation occurred and clean phase separations were obtained. The absence of emulsion formation was also observed in the case (Experiment 76) in which additional aluminum nitrate was added to the solution before the extraction. The results of the two experiments carried out are given in Table XI.

Table XI

PLUTONIUM EXTRACTIONS BY TBP

Organic: 30% TBP-AMSCO 125 at 1/10 volume per extraction
Three 10-minute equilibrations

	Aqueous Composition					E_a^o Values (Pu)			% Pu Lost to Aqueous Waste
Exp't	$Ca(NO_3)_2$ M	$Mg(NO_3)_2$ M	HF M	HNO_3 M	$Al(NO_3)_3$ M	1st Ex.	2nd Ex.	3rd Ex.	
75	0.14	1.92	0.25	5.00	0.16	132	55.1	45.0	1.1
76	0.14	1.94	0.25	1.97	0.97	213	121	67.2	0.1

Although the figures for the percentage plutonium in the final aqueous do not agree with those calculated from the distribution coefficients, the over-all extraction is satisfactory.

2. Scrubbing

An early analysis of strip solutions indicated the presence of ca. 3 g/l Ca (and Mg) in the organic phase which may be due to mechanical carry-over. In any case scrubbing appears to be needed, since at this time it is not known how much purification from calcium can be obtained in subsequent plutonium isolation steps.

One experiment tested the removal of calcium from the organic by scrubbing a cold organic with 1/10 volume of 1.00 M $Al(NO_3)_3$. From the data calcium has a distribution $E_a^o = 0.006$ between the systems 30% TBP-AMSCO 125 and 1 M $Al(NO_3)_3$. The value $E_a^o = 0.004$ was found for magnesium. Evidently calcium and magnesium can be readily removed from the organic by 1 M $Al(NO_3)_3$ scrubs.

Another reason for scrubbing is to remove most of the nitric acid which has extracted into the organic phase. Since it is hoped to obtain a volume reduction of a factor of three to five by stripping into a small volume of aqueous containing only a reducing agent, large amounts of nitric acid must first be removed. Of materials which would remove nitric acid from the organic in a scrub, water, sodium bicarbonate, ammonium carbonate, sodium carbonate and ammonium hydroxide were considered. If the plutonium tended to extract into the scrub, aluminum nitrate could be added to salt the plutonium back.

Table XII describes experiments on the removal of nitric acid from the organic phase by scrubbing and the distribution of plutonium under such scrubbing conditions. It is seen that use of a base and a salting agent reduce the acidity and still maintain a plutonium distribution highly favoring the organic.

Scrubbing of the combined organic phases resulting from the TBP extraction of solution from one-step dissolution was carried out using 1.75 M $Al(NO_3)_3$ solution and solid ammonium carbonate as the neutralizing agent. The results of these scrubbing runs also are given in Table XII.

Table XII

SCRUBBING DATA - SMALL SCALE EXPERIMENTS

Organic: 30% TBP-AMSCO 125
Scrub: As indicated

Scrub	Volume Ratio Org./Scrub	$E_a^o(Pu)$	% Pu Loss	M HNO_3 in Organic Before	M HNO_3 in Organic After
1.75 M $Al(NO_3)_3$	10:1	465	0.02	1.10	0.83
1.00 M $Al(NO_3)_3$	10:1	81	0.12	0.98	0.82
1.00 M $Al(NO_3)_3$	5:1	75	0.18	0.97	0.71
1.00 M $Al(NO_3)_3$ + solid $NaHCO_3$	5:1	134	0.19	0.86	0.10
1.00 M Na_2CO_3	10:1	4.7	2.10	0.97	0.77
H_2O	10:1	2.4	4.70	0.97	--
H_2O	5:1	3.2	5.70	0.97	0.51
1.75 M $Al(NO_3)_3$ + solid $(NH_4)_2\ CO_3$	10:1	57.3	0.53	1.14	0.26
" "	10:1	59.0	0.52	1.21	0.02

The organic phases from the gallon scale extractions were scrubbed with 1 M $Al(NO_3)_3$ solution to which solid sodium bicarbonate or ammonium carbonate was added. The solid was added while the organic was contacting the aqueous. Ammonium carbonate is a useful salt since the solution does not become basic locally. The data on these scrub runs are presented in Table XIII.

Table XIII

NEUTRALIZATION SCRUBBING OF ACIDIC TBP-AMSCO-125 (EQUILIBRIUM CONCENTRATIONS)

Run#	1A	1B	11A	11B
HNO_3 (organic) before Scrub M	1.06	1.1	0.7	1.05
Base	$NaHCO_3$	$(NH_4)_2CO_3$	$(NH_4)_2CO_3$	$(NH_4)_2CO_3$
Vol. Organic (ml)	2600	5600	4500	5000
Vol. Scrub (ml)	700	800	525	900
pH (aqueous)	0.8	0.1	2.3	0.8
HNO_3 (organic) M after Scrub	0.09	--	(0.01)*	--
$Al(NO_3)_3$ (aqueous) M	0.57	0.63	0.75	0.56
Salt from neutralization	3.9 M $NaNO_3$	7 M NH_4NO_3	6 M NH_4NO_3	5.6 M NH_4NO_3
E_a^o Pu	60	240	35	70

* Estimated from aqueous strip.

The pH data indicate a dependence of E_a^o on pH. In experiment 1A the plutonium concentration in the scrub was measured at pH's 0.8, 1.4 and 2.3. This concentration at pH = 2.3 was four times that at 0.8 and 1.4, indicating that pH = 1 is a safe final acidity in the scrub.

In summary, neutralization scrubbing is effective in removing acid from the organic with low plutonium loss. Whether one stage will reduce the calcium and magnesium concentrations sufficiently is unknown. This batch method was used because of its convenience in laboratory scale operation. Its possible adaptation to continuous operation, if needed, remains to be investigated.

3. Stripping

a. Test Tube Scale

Scrubbing data (Table XII) indicated that plutonium could not be readily stripped from the 30% TBP-AMSCO 125 merely by aqeuous solutions of low acidity. However, a reducing agent in the aqueous phase would reduce the plutonium(IV) in the aqueous to plutonium(III), and low E_a^o values should be obtained (good stripping).

Table XIV lists the results of stripping experiments testing the use of hydroxylamine on a test tube scale. In the case of experiment 46, in which the organic phase was 15% TBP-AMSCO 125, stripping with 0.1 M $NH_2OH \cdot HCl$ without neutralization of the nitric acid in the organic phase gave low E_a^o values and thus high plutonium recoveries; however, in experiment 58, in which the organic phase was 30% TBP-AMSCO 125 much higher E_a^o values and lower plutonium recoveries were obtained by stripping with 0.1 M $NH_2OH \cdot HCl$. The difference between the two experiments appeared to lie both in the amount of nitric acid which was present in the organic phases after the extraction step and the difference in TBP concentration. Experiment 52 was then carried out using the combination of 0.1 M $NH_2OH \cdot HCl$ as a stripping agent and 0.5 M $NaHCO_3$ to partially neutralize nitric acid in the organic phase. The lower E_a^o values obtained indicated that partial neutralization of the nitric acid in the organic phase was necessary before suitable plutonium recoveries could be obtained using three 10/1-organic/aqueous strips with 0.1 M $NH_2OH \cdot HCl$ as the stripping agent.

Experiments 64-C, 60 and 66-A tested stripping at various nitric acid concentrations in the organic phase. Experiment 66-A indicated that suitable recoveries could be obtained with 0.1 M $NH_2OH \cdot HCl$ when the nitric acid concentration in the organic was approximately 0.1 M. Experiments 64-A and 69 tested the rate of stripping from partially neutralized organic with 0.1 M $NH_2OH \cdot HCl$. These time studies indicated that at ca. 30 minutes the E_a^o is a minimum (stripping most complete). The data from Experiment 69 is plotted in Figure 2. Increasing the concentration of hydroxylamine hydrochloride from 0.1 M to 0.5 M decreased the first stripping E_a^o by a factor of two

Table XIV

STRIPPING DATA - SMALL SCALE

Exp't. No.	Organic Phase		Strip Composition	Strip Time (Min.)	Volume Ratio Org/Strip	E_a^o (Pu)			% Pu Stripped
	Composition	$\underline{M}$ HNO_3				1st Ext'n	2nd Ext'n	3rd Ext'n	
45	15% TBP-CCl_4	-	0.01 $\underline{M}$ HNO_3	10	8:1	0.240	0.173	0.074	89.3
46	15% TBP-AMSCO 125		0.01 $\underline{M}$ HNO_3 + 0.01 $\underline{M}$ $NH_2OH \cdot HCl$	15	10:1	0.061	0.009	0.006	99.8
58	30% TBP-AMSCO 125	0.97	0.1 $\underline{M}$ $NH_2OH \cdot HCl$	15	10:1	4.31	2.45	1.51	9.3
52	30% TBP-AMSCO 125	0.97	0.5 $\underline{M}$ $NaHCO_3$ + 0.1 $\underline{M}$ $NH_2OH \cdot HCl$	15	10:1	3.81	1.56	0.75	24.7
64-C	30% TBP-AMSCO 125	0.71	0.1 $\underline{M}$ $NH_2OH \cdot HCl$	20	10:1	1.29	1.08	0.56	30.5
60	30% TBP-AMSCO 125	-	0.1 $\underline{M}$ $NH_2OH \cdot HCl$	20	10:1	1.22	0.424	0.209	54.0
64-A	30% TBP-AMSCO 125	0.51	0.1 $\underline{M}$ $NH_2OH \cdot HCl$	5	2:1	0.106	-	-	75.4
				60	2:1	0.025	-	-	94.7
				270	2:1	0.077	-	-	84.8
				1440	2:1	2.17	-	-	11.1
69	30% TBP-AMSCO 125	0.094	0.1 $\underline{M}$ $NH_2OH \cdot HCl$	10	10:1	0.039	-	-	70.0
				20	10:1	0.027	-	-	77.9
				40	10:1	0.026	-	-	78.1
				60	10:1	0.029	-	-	77.1
				90	10:1	0.042	-	-	68.2
				120	10:1	0.135	-	-	35.1
66-A	30% TBP-AMSCO 125	0.098	0.1 $\underline{M}$ $NH_2OH \cdot HCl$	30	10:1	0.024	0.014	0.012	99.2
80	30% TBP-AMSCO 125	0.094	0.5 $\underline{M}$ $NH_2OH \cdot HCl$	30	10:1	0.012	0.010	0.016	99.4
70	30% TBP-AMSCO 125	1.1	0.1 $\underline{M}$ $(NH_2OH)_2 \cdot H_2SO_4$	30	10:1	0.100	0.010	0.010	99.0
75	30% TBP-AMSCO 125	0.26	0.1 $\underline{M}$ $(NH_2OH)_2 \cdot H_2SO_4$	30	10:1	0.143	0.046	0.012	97.8
72	30% TBP-AMSCO 125	0.094	0.1 $\underline{M}$ $(NH_2OH)_2 \cdot H_2SO_4$	30	10:1	0.012	0.006	0.009	99.9
76	30% TBP-AMSCO 125	0.02	0.1 $\underline{M}$ $(NH_2OH)_2 \cdot H_2SO_4$	30	10:1	0.012	0.025	2.33	97.3

692 28

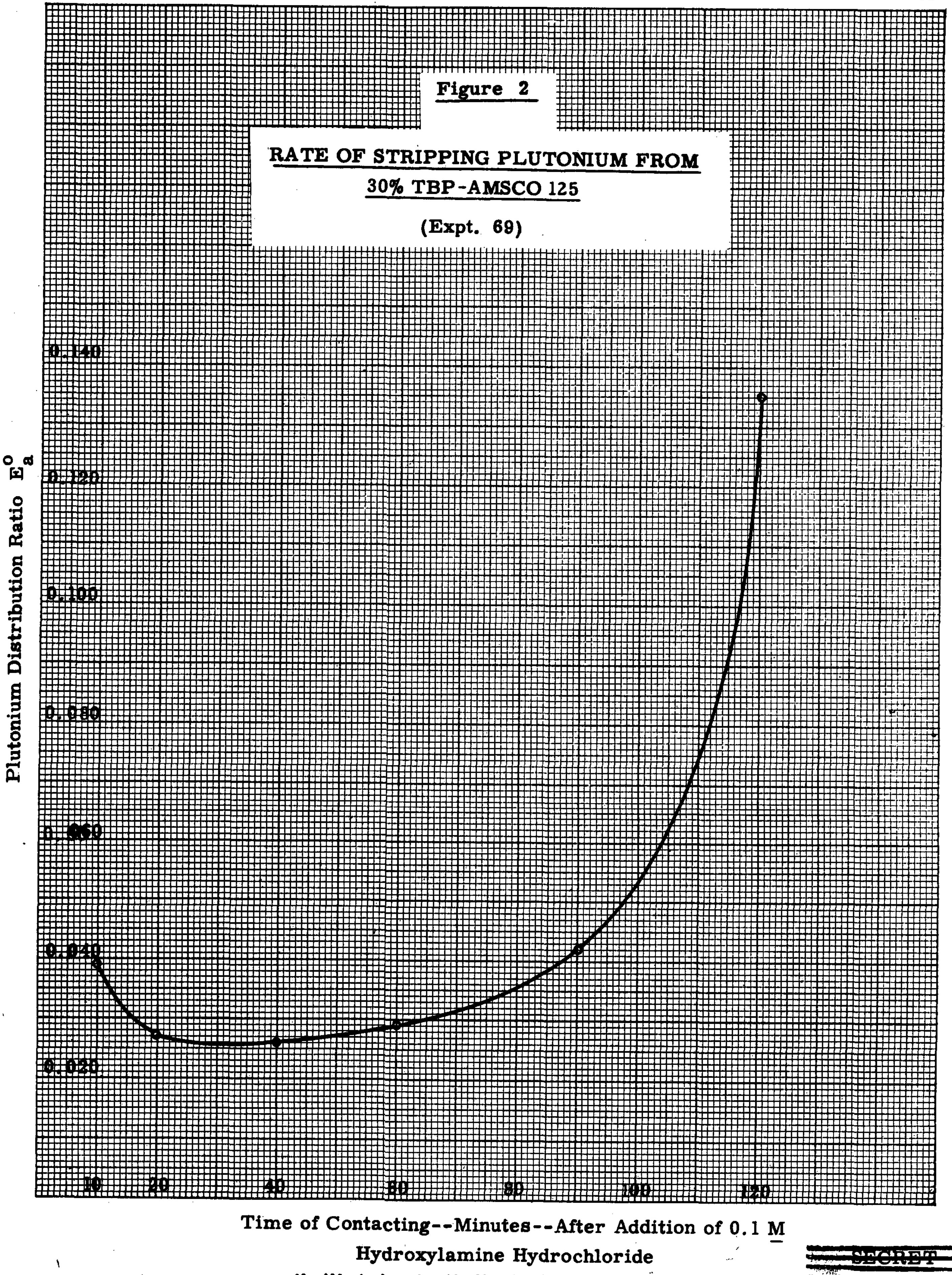

Figure 2

RATE OF STRIPPING PLUTONIUM FROM 30% TBP-AMSCO 125

(Expt. 69)

but did not affect the others appreciably (Experiment 80). Thus, over-all improvement was small.

Stripping experiments using 0.1 $\underline{M}$ $(NH_2OH)_2 \cdot H_2SO_4$ were also carried out. The results of experiment 70, in which unneutralized organic was used, indicated much lower E_a^o values than those obtained when using 0.1 $\underline{M}$ $NH_2OH \cdot HCl$ to strip unneutralized organic (Experiment 58). Even lower E_a^o values resulted upon neutralizing the organic phase to approximately 0.1 $\underline{M}$ HNO_3 and stripping with 0.1 $\underline{M}$ $(NH_2OH)_2 \cdot H_2SO_4$ as is shown by experiment 72.

In view of the results of experiments 70 and 72, experiments 75 and 76 were performed to define more exactly the optimum acidity for stripping. A comparison of the over-all stripping results indicates this optimum acidity to be about 0.1 $\underline{M}$. At higher nitric acid concentrations the initial strip has an unfavorably high distribution ratio presumably due to the salting effect of nitric acid. At lower acid concentrations the later strips have unfavorably high distribution ratios presumably due to incomplete reduction of Pu(IV) to Pu(III).

b. Gallon Scale

Organic phases from the extraction of leaching solution with 30% TBP-AMSCO were scrubbed to remove nitric acid and then were stripped with hydroxylamine hydrochloride solution. Agitation was maintained for twenty minutes in stainless steel equipment. Phase separation was satisfactory. The data from these runs is presented in Table XV.

Comparison of the E_a^o values with those obtained in test tube experiments (Table XIV 66-A) shows that stripping was less effective on the larger scale. The acid concentration in the organic was lower than the optimum value as explained above in section (a).

The fourth E_a^o value obtained in run IIA indicates that hydroxylamine sulfate may be more effective than chloride for stripping plutonium out of the organic. This was also borne out in the test tube scale runs.

Table XV

STRIPPING PLUTONIUM FROM 30% TBP-AMSCO 125 WITH HYDROXYLAMINE SALTS

(Gallon Scale)

Volume Ratio per Stage: Organic:Aqueous::10:1

Organic Phase	IA 2600 ml.			IB 5600 ml.			IIA 4500 ml.			IIB 5000 ml.	
	$NH_2OH \cdot HCl$			$NH_2OH \cdot HCl$			$NH_2OH \cdot HCl$			$(NH_2OH)_2 \cdot H_2SO_4$	
Extraction	pH	M	E^{o}_{a} (Pu)	pH	M	E^{o}_{a} (Pu)	pH	M	E^{o}_{a} (Pu)	M	E^{o}_{a} (Pu)
1st	0.6	0.2	0.4	1.5	0.2	0.26	1.15	0.2	0.3	0.1	0.023
2nd	0.6	0.1	0.02	1.1	0.1	0.02	0.7	0.2	0.1	0.1	0.0080
3rd	0.7	0.1	0.13	0.7	0.1	0.02	--	0.2	0.06	0.1	0.0054
4th	--	--	--	--	0.1	0.02	0.7	0.1*	0.005	0.1	--
Pu remaining in organic phase (%)		2.4			0.7			0.9		0.1	

*0.1 M Hydroxylamine sulfate used.

Table XVI presents a summary of plutonium losses in the recovery of plutonium from leach solutions of full size slag and crucibles. Also presented are percentage losses for the extraction, scrubbing, and stripping steps, and an average figure for the losses of the same step performed on the test tube scale.

Table XVI

LOSS OF PLUTONIUM IN TBP SEPARATION PROCESS

(Leaching Solutions)

Extraction Volume Ratio per Stage: Organic:Aqueous::1:10

Scrub and Stripping Volume Ratio per Stage: Organic:Aqueous::10:1

Solution	Gallon Scale Runs				Average of Test Tube Runs
	IA	IB	IIA	IIB	
Extraction (3 stages)	2.0%	0.6%	3.5%	1.2%	0.7%
Extraction (4 stages)	0.3	--	--	0.3	--
Scrub (1 stage)	0.6	0.1	0.5	0.3	0.25
Stripping (3 stages)	1.7	--	11.0	0.2	0.8
Stripping (4 stages)	--	0.7	1.2	--	--
Recovery through Extraction, Scrub, Strip	97.4	98.6	94.8	99.2	98.2

Thus, fair recovery of plutonium was obtained in all cases. Extraction losses can be reduced further by the use of another stage. Stripping losses can be cut to 0.2% by use of hydroxylamine sulfate instead of hydrochloride.

It may be mentioned that the final plutonium solution recovered from two full size crucibles and slag, consisted of 5200 ml of a blue solution, 1.5 g/l Pu(III) and approximately 0.1 molar hydroxylamine (hydrochloride and

and sulfate). The strip solution from Runs IA, IB, and IIA were combined and analyzed together, and the strip solution from IIB analyzed separately. The analytical results are given in Table XVII.

Table XVII

ANALYSES OF FINAL STRIP SOLUTION

Source		IA, IB, IIA	IIB
Constituent	Method		
Pu, g/l	Radio-assay	1.70	0.825
HNO_3, g/l	Titration	11.6	36.1
Al, %*	Colorimetric	3	1.2
Al, %	Spectroscopic	100	20
Ca, %	Spectroscopic	200	5
Mg, %	Spectroscopic	10	2
La, %	Spectroscopic	1	L 1
Na, %	Spectroscopic	20	L 1

* % = parts per hundred parts plutonium
L = less than

The spectroscopic analyses were run under difficulties, as the samples submitted were small and the distribution of impurities abnormal. This is probably the source of the discrepancy between the colorimetric and spectroscopic aluminum determination, and makes all the spectroscopic determinations no more than determinations of order of magnitude.

That the aluminum is higher in the first case than in the second is almost surely due to carry-over in the scrub step, since aluminum nitrate was used as a salting agent in the second case. This carry-over might also explain the higher magnesium and lanthanum contents of the first sample. The higher calcium content of the first sample is probably due to use of calcium nitrate as a salting agent, and the higher sodium content to the use of sodium bicarbonate as a neutralizing agent.

Thus Run IIB was a successful separation process. In this case 99.2% of the plutonium was recovered and 99.98% of the associated "impurities" was removed. Even in the less favorable case, 99.5% of the "impurities" were removed.

4. Precipitation of Plutonium(III) Compounds from Strip Solutions

Preliminary investigations of a suitable process for precipitating plutonium from the hydroxylamine strip solution have been directed at precipitating plutonium(III) oxalate, since this procedure presents a way of directly coupling the strip solution to the present 234-5 process.

The first precipitations were carried out by addition of 0.35 M $H_2C_2O_4$ to portions of hydroxylamine strip solution from gallon scale experiments. The solubility of the precipitate was studied as a function of both time and final nitric acid concentration. The results obtained are given in Table XVIII.

Table XVIII

PRECIPITATION OF PU(III) OXALATE FROM STRIP SOLUTION

Composition of Strip Solution:
0.176 M HNO_3
1.95 g/l Pu
2.91 g/l NH_2OH
Precipitant: 0.35 M $H_2C_2O_4$

	Solubility of Pu, g/l			
Final HNO_3 M	30 mins.	1 hr.	2 hrs.	4 hrs.
0.1	0.031	0.032	0.039	0.047
0.2	0.025	0.027	0.027	0.026
0.5	0.022	0.022	0.023	0.034
1.0	0.10	0.09	0.11	0.15

The observed solubilities are in fair agreement with those reported for plutonium(III) oxalate(5), but the color of the precipitates obtained was gray, not the characteristic blue-green of plutonium(III) oxalate, and the precipitates appeared to be contaminated with some substance, probably calcium, (see Table XVII). It has been possible, however, to obtain the blue-green oxalate from strip solution from small scale extraction experiments, and the prospects of being able to utilize the precipitation of plutonium(III) oxalate as a means of coupling to 234-5 operations still appear to be good.

D. Separation of Plutonium by Recycle to the Redox Process

In considering recycle to Redox there appeared to be three logical places to introduce the material into the process. First, solid slag and crucible could be added directly to the dissolver. There were, however, two objections to this plan; (1) the large amounts of iodine evolved during the dissolution of the slag and crucible would appreciably shorten the life of the silver reactors, and (2) the time required to dissolve the crucible would lengthen the time cycle of the dissolver, thus decreasing production. Grinding of the crucible fragments would obviate this latter trouble. Difficulties of this nature prohibited further consideration of adding slag and crucible to the dissolver.

Recycling a solution to the cross-over oxidizer and then to the Redox IIA Column appears considerably less complicated. At this point in the Redox process a solution of slag and crucible would be combined with a solution of similar composition, i.e., a highly salted aqueous plutonium solution which is almost free of uranium and fission products. Also the modifications in equipment needed to introduce the dissolved slag and crucible might be much easier to make in this relatively cold column. Recycling to the IIA column would necessitate separate dissolving and filtering facilities and the construction of facilities for adding the dissolved material.

The feasibility of this recycle has been investigated by diluting leaching solution with IIAFS solution to various dilution ratios, and then measuring the plutonium distribution ratios on contacting the resulting solutions three times with equal volumes of hexone. The organic phases were combined and stripped once with an equal volume of 0.01 $\underline{M}$ HNO_3. No evidence of emulsion formation was observed at any of the dilution ratios investigated. The results of these experiments are listed in Table XIX.

Table XIX

HEXONE EXTRACTIONS OF PLUTONIUM FROM LEACHING SOLUTION AFTER DILUTION WITH IIAFS SOLUTION

Aqueous: Leaching solution (0.375 M HNO_3, 0.21 M HF, 0.13 M $Ca(NO_3)_2$, and 1.70 M $Mg(NO_3)_2$) diluted with IIAFS solution to volume ratio indicated.

Organic: Hexone (0.5 M HNO_3)

Three equal-volume equilibrations

Dilution Ratio IIAFS/Leach Solution Volume	1st Ex.	2nd Ex.	3rd Ex.	E_a^o Stripping	% Pu in Final Aqueous
10:1	6.25	6.24	5.38	0.014	0.4
25:1	6.28	6.66	4.78	0.013	0.4
50:1	6.29	6.50	4.97	0.014	0.3
10:1*	6.21	5.86	4.91	0.009	0.4

* This experiment carried out with leaching solution obtained by W. H. Adams in stainless steel equipment.

Experiments of this type have not been carried out with solution prepared by the one-step dissolution method; however, similar distribution coefficients are expected.

Thus recycle to the IIA column appears to be a satisfactory method of recovering plutonium from solutions of slag and crucible.

The third method of processing slag and crucible thru the Redox plant would be to feed a solution of slag and crucible without dilution, either as IIAF when no normal IIAF is available, or as IIIAF if the third plutonium cycle were not needed. Table XX shows that recoveries are good in such operations. In these experiments, emulsions were noted in two cases, similar to those observed in TBP extraction of leaching solution salted with aluminum nitrate (section III, C, 1). These emulsion difficulties can probably be overcome by dissolving the slag and crucible in the presence of aluminum nitrate as was done in the TBP studies.

Note in proof: This expectation has been confirmed by countercurrent batch extraction studies in which satisfactory plutonium recoveries were obtained without emulsification.

Table XX

EXTRACTION OF PLUTONIUM FROM LEACHING SOLUTION BY HEXONE

Aqueous: Leachings of slag and crucible from small scale (6 g Pu) reductions. (0.375 $\underline{M}$ HNO_3, 0.21 $\underline{M}$ HF, 0.13 $\underline{M}$ $Ca(NO_3)_2$, 1.70 $\underline{M}$ $Mg(NO_3)_2$, and 1.43 $\underline{M}$ $Al(NO_3)_3$)

Organic: Hexone (0.5 $\underline{M}$ HNO_3)

Three equal-volume equilibrations

E_a^o Values (Pu)*			
1st Extr.	2nd Extr.	3rd Extr.	% Pu in Final Aqueous
45	ca. 9	ca. 1	0.1
39	ca. 6	ca. 1	0.1

*Analytical difficulties necessitate reporting only approximate values of the extraction coefficients.

E. Separation of Plutonium by Recycle to the Bismuth Phosphate Process

Recycle to the Bismuth Phosphate Process is attractive because separations facilities already exist. Three points in the Bismuth Phosphate Process were considered for the introduction of slag and crucible: (1) the dissolver, (2) the bismuth phosphate product precipitation of the second decontamination cycle, and (3) the lanthanum fluoride by-product precipitation in the concentration cycle.

Consideration of the dissolver appeared unfeasible due to the results discussed in Section III, A, 2, on the dissolution rate of crucibles under reflux,

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and due to the problems arising from the volatilization of large amounts of iodine. Introduction of slag and crucible past the dissolver would, of course, necessitate construction of a separate dissolving facility and an introduction line. A bismuth phosphate product precipitation should separate the plutonium from calcium and magnesium. One experiment tested recycle to the bismuth phosphate product precipitation step of the second decontamination cycle. The data are presented in Table XXI. Bismuth phophate precipitations were made with simulated plant solutions. The control run contained 30 mg/l Pu, the cold run contained simulated slag and crucible solution at 1/80 volume, and the last run contained "hot" slag and crucible solution at 1/80 volume. The solution for the third run was prepared by the Los Alamos one-step dissolution procedure. The figures indicate that plutonium carrying was unaffected by the slag and crucible solution within experimental error and that separation from magnesium, calcium and aluminum was very good. Thus, recycle of slag and crucible solution to this step appears very promising.

Table XXI

RECYCLE OF SLAG AND CRUCIBLE SOLUTION TO $BiPO_4$ PRODUCT PRECIPITATION

Component Of Slag And Crucible	Per Cent Carried on $BiPO_4$		
	Control	Cold Simulated Slag And Crucible Solution 1:80	Hot Simulated Slag And Crucible Solution 1:80
Pu	99.2 %	--	99.0 %
Ca	--	0.07 %	--
Mg	--	0.2	--
Al	--	0.7	--

The behavior of slag and crucible solution in the lanthanum fluoride by-product precipitation step is not clear. Equilibrium data indicate that calcium and magnesium fluorides may partially precipitate in this step, or in the lanthanum fluoride product precipitation. Experiments are being performed to investigate this point.

PROGRAM

It has been shown that either a TBP extraction process, recycle to the Redox plant, or recycle to the Bismuth Phosphate Process should recover the plutonium from slag and crucible solution obtained according to Los Alamos one-step dissolution method. A number of questions remain to be answered before any of these processes could be installed.

In the dissolving procedure, a silica residue is filtered off, then washed with nitric acid. Los Alamos proposes to recover any plutonium retained by this residue by hydrofluorinating the silica, and dissolving the resulting residue for recycle through solvent extraction. It may prove possible to discard this residue at Hanford since the recovery goal here is 90% or better(4), and since it is unlikely that the silica will consistently retain 10% of the plutonium. The decision to recover such plutonium should be based on an economic consideration.

Our TBP solvent extraction studies were performed batchwise. It is hoped to test countercurrent performance, utilizing a continuous three or four stage countercurrent batch extraction process for separating the plutonium from the dissolved crucible and slag material. Such a process involving extraction of a solution 5 $\underline{M}$ in HNO_3 and 0.45 in $Al(NO_3)_3$ with an organic phase 30% TBP-AMSCO 125, should enable a ten to one volume reduction. To remove impurities a scrub stage is planned, also countercurrent, but whether this will be with a solution or with pure water remains to be investigated.

Stripping with hydroxylamine (sulfate) is also visualized as countercurrent. One problem may be the large concentration of nitric acid in the organic phase, which may hinder stripping in the countercurrent stripping stages. It is hoped to avoid the acid neutralization procedure by use of a one to one countercurrent scrub with water which will remove much of the acid. Stripping countercurrently with one-quarter volumes of hydroxylamine sulfate solution should result in a final strip solution of 500 ml. per original crucible, containing <u>ca</u> six grams of plutonium.

Coupling of the strip solutions with the metal production steps will involve purity testing, as it is not known what the fate of small amounts of impurities, e.g., calcium, magnesium and aluminum will be in 234-5 Building chemistry.

It should be shown that these materials cannot build up in process solutions through a recycling procedure.

It would be attractive to end a solvent extraction process with a solution pure enough and concentrated enough to blend directly into the oxalate precipitation step. It is planned to study the efficiency of scrubbing impurities out of the organic phase. If scrubbing proves ineffective, extraction with lower concentrations of TBP should be tried in the hope that the extraction coefficients of impurities would be decreased much more than those of plutonium.

A TBP extraction process, as has been outlined above, should provide the groundwork for the recovery of plutonium from other sources of waste besides slag and crucible.

Recycling to Redox IIAF has been shown to be possible as judged by the distribution coefficients. At present a batch countercurrent demonstration is planned.

Investigation of recycle to the Bismuth Phosphate Process has only been touched upon. Further studies are planned on introducing slag and crucible solution to the bismuth phosphate product precipitation steps of the second decontamination cycle with emphasis on the ultimate fate of small amounts of calcium, magnesium and aluminum which follow the precipitate. Recycle to the first bismuth phophate precipitation step would recontaminate the plutonium with fission products. However, the improved separation from calcium and magnesium gained in two carrying steps might overcome the objection. Recycle to the lanthanum fluoride by-product and to the product precipitation steps will also be tested.

To summarize: It appears that a separate solvent extraction facility can recover the plutonium from slag and crucible. Also, recycle to either the Redox or Bismuth Phosphate plants will work.

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