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MASTER

RECOVERY OF PLUTONIUM FROM GRAPHITE

by

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THE DOW CHEMICAL COMPANY
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U. S. ATOMIC ENERGY COMMISSION
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CONTENTS

	Page
ABSTRACT.	iv
SUMMARY AND CONCLUSIONS	v
INTRODUCTION.	1
EXPERIMENTAL AND DISCUSSION	2
A. Graphite Burning.	2
B. Direct Leaching	5
1. Classification.	5
2. Nitric Acid Leaching.	6
3. Washing Techniques.	10
4. Solid-to-Liquid Ratios.	12
5. Needle-Gun Scarfings.	13
6. Dissolution of Graphite with 90% Nitric Acid.	14
7. Recommended Direct Nitric Acid Leaching Procedure	15
C. HYDROCHLORIC ACID LEACHING.	15

ABSTRACT

Several methods were investigated for recovering plutonium from graphite residues. These methods include ignition of graphite and recovery of the ash by dissolution, hydrochloric acid leach, fuming nitric acid leach, and nitric acid-fluoride leach. Of those investigated, the nitric acid-fluoride leach method was found to be the most efficient process for plutonium recovery.

SUMMARY AND CONCLUSIONS

A direct nitric acid-fluoride leach process was found to be most efficient for recovery of plutonium from graphite residues. Dissolution rates were dependent upon plutonium content in the graphite. The higher plutonium content graphite would yield higher rates; however, a second contact is necessary and washing procedures are more important. Conditions for using this process are as follows:

1. For graphite containing greater than 5% plutonium, a solid-to-liquid ratio of 200 grams per liter should be used. For graphite containing 1-5% plutonium, the ratio should be approximately 400 grams per liter; and for graphite containing less than 1%, the ratio may be 750 grams per liter.
2. The dissolver solution should be 12.5M nitric acid or greater and contain 0.1 to 0.3 moles per liter of fluoride ion. Both hydrofluoric acid and calcium fluoride were used in this study and no difference was noted in the form of fluoride used. Most of the dissolver solutions contained 0.25-0.3 moles of fluoride per liter.
3. Two hours at reflux temperature is adequate for optimum dissolution.
4. Graphite containing greater than 2% plutonium probably needs to be leached twice for maximum plutonium recovery. Material containing less than 2% plutonium will probably require one leach treatment.
5. The filter sludge after the final leach should be washed thoroughly. In this report, five wash volumes were required in a batch operation. Each wash volume was approximately equal to the weight of the sludge (e.g. 1-kg sludge would require 1 liter of wash). Although a water wash can be used if care is taken, a dilute acid wash is recommended for production operations.

6. The plutonium-rich leach solution required processing by anion exchange for both purification and concentration prior to subsequent processing steps (precipitation).

Other methods investigated were a burn-dissolve process, hydrochloric acid leaching, and fuming nitric acid leaching.

Ignition of the graphite requires oxygen and high temperatures. This in turn produces an ash which contains a highly refractory plutonium oxide. Leaching of this ash results in very low efficiencies in plutonium recovery.

Hydrochloric acid leaching appears to be rapid and efficient for freshly-used graphite where the plutonium has not yet oxidized. Hydrochloric acid is not recommended since the Rocky Flats facility is not equipped for handling chloride streams, and thus nitric acid systems are more desirable.

The fuming (90%) nitric acid leach was considered impractical as a production process. The main advantage was that this acid would destroy the graphite binder.

Attempts at upgrading the graphite by sieving were unsuccessful. Each sieve fraction contained significant quantities of plutonium which would require recovery. In addition, the sieve fraction containing the smallest particles (<200 mesh) was the most difficult to reduce to a discard level during leaching.

The graphite used was found to be nonhomogeneous and sampling errors in some instances were quite large. Graphite, which was originally assigned a plutonium value of 7%, was found to contain approximately 15% plutonium. The >28 mesh sieve fraction, which assayed at 0.5% plutonium, was found to contain 5-10% plutonium by leaching. Samples of filter sludges from each sieve fraction after one leach consistently indicated less plutonium present than that actually recovered by leaching.

Graphite containing >10% plutonium can be easily leached so that the residuals will contain 0.5% plutonium. Graphite containing 0.5% plutonium could be leached and reduced to <0.05% plutonium using the same conditions as described above. Leaching of low-level graphite is probably not very economical, and other processes should be considered for material containing <1% plutonium.

Calcining of the graphite prior to dissolution is not necessary since the plutonium probably exists in a finely-divided state and can be easily oxidized by boiling nitric acid.

RFP-598

INTRODUCTION

Plutonium metal may be fabricated by a casting and machining process. Plutonium metal is cast into a precoated graphite mold. This coating (calcium fluoride) minimizes, but does not prohibit, attack of the graphite by plutonium. When the graphite molds are broken away from the casting, small quantities of plutonium metal adhere to the mold surface. Although visible metal is stripped manually from the molds, significant quantities remain on the graphite after stripping. On molds which are used several times before discarding, plutonium metal penetrates into the pores of the graphite approximately 0.060 inch.

In early operations, attempts were made to remove plutonium from the graphite surfaces by using a small hand-grinder as a scarfing tool. This operation required an excessive amount of glove box space and operator time. In addition, a very fine dust was formed. This dust, which contained plutonium dioxide, would settle on clean graphite molds and recontaminate them. Consequently, many of the molds which were thought to be clean were found to contain recoverable quantities of plutonium and thus had to be reprocessed. Eventually, this method was abandoned and the used molds were stored for future processing. Many molds were found to contain little or no plutonium and were discarded. Samples taken from the dust of the scarfing operations indicated that the plutonium content was approximately 7%.

Improved techniques have been developed recently for removing the plutonium-contaminated layer of graphite. An "air-operated weld scaler" (needle gun) was found to remove the outer layer of graphite efficiently while at the same time minimizing the dust problem. This procedure, which will be reported elsewhere, produces graphite scarfings which contain approximately 1% plutonium. In order to upgrade these scarfings, a sink-float method is being developed. Upgrading these fines will probably simplify recovery problems by reducing the quantity of material which would have to be leached for plutonium recovery.

In this report, the following methods for recovering plutonium from graphite were investigated:

1. Burning the graphite and recovering the plutonium from the ignited residue by dissolving the ash. A similar method has been used successfully in our uranium recovery facility for several years. This method is straightforward and has been reported elsewhere⁽¹⁾. The graphite used in this burning study was H₄LM, a high-density non-porous graphite manufactured by The Great Lakes Carbon Company.
2. Physical disintegration of the graphite using fuming (90%) nitric acid. This process was found to be suitable as the head-end treatment for the Purex process when graphite-based fuel elements were being dissolved⁽²⁾.
3. Direct leaching of the graphite with either nitric acid solutions containing fluoride ion or dilute hydrochloric acid.

Each of the above was reviewed with respect to the ease in which the process could be adapted to plutonium recovery operations.

EXPERIMENTAL AND DISCUSSION

A. GRAPHITE BURNING

Attempts to burn chunks of H₄LM* graphite in a muffle furnace at 800°C were unsuccessful; however, when a stream of oxygen was directed at the graphite, it would ignite and burn. The burning temperatures, as observed by an optical pyrometer, were in the 1700°C range. When the oxygen stream was removed, combustion was not sustained at 800°C. After burning graphite in the furnace for approximately 2 hours, the stainless steel liner was burned out and burning tests were terminated. This particular furnace was rated for intermittent operating temperatures of 1000°C.

(1) "Oxidation of Graphite", The Industrial Graphite Engineering Handbook, National Carbon Company, Section 5D.03.01.

(2) Bradley, M. J., and Ferris, L. M., "Recovering Uranium From Graphite Fuel Elements", Ind. Eng. Chem., **53**, No. 4, 279-81(1961).

* A high-density non-porous graphite manufactured by The Great Lakes Carbon Company.

The difficulties encountered in making these laboratory experiments indicated that both design of equipment and finding acceptable materials of construction would be major problem areas for any processing facility. The fact that all off gases would require extensive filtering will make the problem more difficult. Experience at both Hanford and Rocky Flats has indicated that there are many problems still unsolved in the burning of easily-combustible wastes. Problems in operating a burning facility for graphite appeared to be even greater. Graphite is burned routinely in our uranium facility using oxygen. These furnaces are in hoods and the contamination problems are not as severe as with plutonium.

A few laboratory-scale runs were made to find how easily the graphite would burn and how easily plutonium could be recovered from the residues. Previous work indicated that incinerator ash could be leached with HNO_3 -HF and, under the proper conditions, complete plutonium recovery could be obtained⁽³⁾. The conditions for burning graphite, however, could produce a product from which it would be difficult to quantitatively recover plutonium.

In order to determine if this is true, 300 grams of plutonium metal were burned with 2000 grams of graphite in a muffle furnace. By simulating the burning process, we were able to obtain a known quantity of plutonium oxide. The average plutonium concentration in the graphite used for the leaching experiments was found to be 15%, but this will be discussed in Section B below.

Chemical analysis of the ignited residue indicated that samples could not be completely dissolved, and thus no accurate plutonium values could be assigned to the ash. It was estimated that 10-15% of the starting material was still insoluble residue after boiling at reflux conditions for six hours with 15M HNO_3 -0.3M HF. X-ray diffraction data on the ignited oxide indicates that the major constituent is PuO_2 . The surface area was found to be 0.752

(3) Butler, F. E., Moseley, J. D., and Molen, G. F., Recovery of Plutonium from Incinerator Ash, The Dow Chemical Company, Rocky Flats Division, July 31, 1964, RFP-396.

square meters per gram. Oxides formed by calcination of $\text{Pu}(\text{C}_2\text{O}_4)_2$ at 400°C have a surface area of 20-60 square meters per gram, and oxides prepared by direct denitration of plutonium nitrate have a surface area of 5-10 square meters per gram⁽⁴⁾. The bulk density of the oxide was 2.78 g/cc and the tap density was 3-12 g/cc.

In our dissolution tests, the reagents used were 13M HNO_3 containing fluoride varying from 0 to 0.06M. The ash was treated for two hours at reflux conditions. The results from these experiments are found in Table I. For comparison purposes, completeness for

TABLE I
SOLUBILITY OF PLUTONIUM OXIDES PREPARED BY VARIOUS METHODS⁽⁵⁾

Method of Preparation	Residence Time for Calcination (hrs)	Maximum Calcination Temperature ($^\circ\text{C}$)	Percentage Pu Dissolved After 2 Hours Reflux				
			13M HNO_3 0 F ⁻ (%)	13M HNO_3 0.002M F ⁻ (%)	13M HNO_3 0.005M F ⁻ (%)	13M HNO_3 0.01M F ⁻ (%)	13M HNO_3 0.06M F ⁻ (%)
Pu Metal Burned with Graphite	—	1700	0.08	0.09	0.7	2	6
Denitrated $\text{Pu}(\text{NO}_3)_4$ (Activated with sulfate, prepared at Hanford.)	0.5	410	47.00	51.00	62.0	79	98
Denitrated $\text{Pu}(\text{NO}_3)_4$ (Not activated with sulfate prepared at Hanford.)	0.5	410	5.00	6.00	9.00	26	79
Denitrated $\text{Pu}(\text{NO}_3)_4$ (Prepared at Rocky Flats)	4.0	400	0.5	0.7	0.8	2	92
$\text{Pu}(\text{III})$ Oxalate (Prepared at Rocky Flats)	4.0	400	0.05	1.0	15.0	31	—
Pu Peroxide (Prepared at Rocky Flats)	4.0	1000	0.2	1.0	9.0	16	—

dissolution of oxides formed by denitration of plutonium nitrate and calcination of both plutonium peroxide and plutonium(IV) oxalate are given for the same conditions⁽⁵⁾. From these data, it was concluded that oxides formed from burning graphite are very refractory and that they would present difficult plutonium recovery problems, at least where nitrate solutions are required.

(4) Moseley, J. D., and Wing, R. O., Properties of Plutonium Dioxide, The Dow Chemical Company, Rocky Flats Division, August 24, 1965, RFP-503.

(5) Private Communication; J. D. Moseley to C. J. Pinamont, May 11, 1964.

Specific burning rates were not measured since equipment was not available for maintaining ideal conditions for burning.

As a result of the above work, although it was preliminary in nature, burning graphite did not appear to be an attractive process for plutonium recovery.

B. DIRECT LEACHING

Leaching by both nitric acid and hydrochloric acid was investigated. In this phase of the study, fines from the scarfing operations were used as feed material. In order to obtain a uniform feed, 5 kilograms of graphite were calcined in a muffle furnace at 400°C for four hours. This step was to insure that all plutonium was present as the oxide.

The weight loss from this operation was 160 grams, or -3.2%. This was probably due to both loss of adsorbed moisture on the graphite and the burning of combustibles, such as brush hairs and small pieces of paper.

1. Classification

After calcination, the graphite was passed through 1/4 inch and 28-, 48-, 100-, and 200-mesh screens. No material was retained by the 1/4-inch screen. Samples were then taken from each sieve fraction and analyzed for plutonium by the analytical laboratories. The results from these analyses are found in Table II. It was noted that the plutonium content varied with each sieve fraction, with the coarse material containing the least amount of plutonium and the fine material containing the most plutonium.

To determine if these analyses were representative, 100-gram samples from each sieve fraction were leached with 12M HNO_3 -0.25M HF solutions. The quantity of plutonium recovered from each sieve fraction differed from the quantity expected using the direct plutonium sampling data. By calculating the total plutonium content using both sets of data, we find that the

TABLE II
COMPARISON OF PLUTONIUM VALUES FROM
DIRECT SAMPLING AND LEACHING SIEVED GRAPHITE

Mesh Size	>28 mesh	<28->48 mesh	<48->100 mesh	<100->200 mesh	<200 mesh
Sieve Fraction (weight percent)	36.9 %	10.4 %	11.4 %	13.2 %	27.9 %
Graphite Weight	1790 g	504 g	551 g	641 g	1354 g
Sampled Graphite Pu Analysis	0.548%	8.99%	11.1 %	18.2 %	35.6 %
Total Pu Content	9.8 g	45.2 g	61.3 g	116.3 g	480.6 g
Pu Analysis by Leaching	12.2 %	7.5 %	12.6 %	15.7 %	21.7 %
Total Pu Content	217.9 g	37.7 g	69.6 g	100.3 g	293.0 g
Difference	+208.1 g	-7.5 g	+8.3 g	-16.0 g	-189.6 g

Pu Content by Analysis = 713.2 g
Pu Content by Leaching = 718.5 g

difference between sampling directly and leaching is small (713 g vs 718 g). The total plutonium content in the graphite is 14.6%. This graphite had been assigned a value of 7% based on sampling data obtained several years ago (1957-58). We feel that this new value is more representative.

2. Nitric Acid Leaching

Optimum conditions for leaching plutonium from graphite were then determined. Butler, Moseley, and Molen⁽³⁾, in their work on recovering plutonium from incinerator ash, found that a reflux time of 2 hours was best when dissolving with 12M nitric acid containing 0.4M fluoride ion. They also found that the solid-to-liquid ratio was important. A high ratio gave high plutonium concentrations but the insoluble heels required further treatment. A low ratio would usually give a heel which could be discarded, but the plutonium concentration was low. In view of these findings, we used a ratio of 100 grams of graphite per 0.5 liters of acid and a reflux time

(3) Butler, F. E., *loc. cit.*, p 3.

of 2 hours. The fluoride ion concentration was varied from 0 to 1M since we felt that this was the only parameter which was uncertain. Since calcium fluoride is used as a mold coating, we thought that possibly no fluoride would be required. Unfortunately, this was found not to be true. The results for leaching each of the sieve fractions are found in Table III. In all of these leaching experiments,

TABLE III
EFFECT OF FLUORIDE ION CONCENTRATION ON PLUTONIUM RECOVERY

Run No.	Reagent Concentrations	>28 mesh	<28->48 mesh	<48->100 mesh	<100->200 mesh	<200 mesh
1	0 Fluoride					
	Pu Recovered	9.63 g	9.59 g	9.95 g	14.99 g	10.00 g
	Pu Remaining	0.42 g	0.53 g	0.89 g	1.10 g	2.28 g
2	0.005M Fluoride					
	Pu Recovered	11.74 g	6.45 g	11.56 g	13.96 g	20.22 g
	Pu Remaining	0.45 g	0.70 g	0.54 g	2.10 g	4.35 g
3	0.05M Fluoride					
	Pu Recovered	11.34 g	9.91 g	13.93 g	14.51 g	18.32 g
	Pu Remaining	0.41 g	0.68 g	0.53 g	1.00 g	2.88 g
3A	0.075M Fluoride					
	Pu Recovered	4.70 g				
	Pu Remaining	0.14 g				
3B	0.1M Fluoride					
	Pu Recovered	2.20 g				
	Pu Remaining	0.14 g				
3C	0.3M Fluoride					
	Pu Recovered	4.00 g				
	Pu Remaining	0.14 g				
3D	0.4M Fluoride					
	Pu Recovered	5.40 g				
	Pu Remaining	0.24 g				
4	0.5M Fluoride					
	Pu Recovered	20.22 g	5.78 g	11.52 g	16.18 g	25.82 g
	Pu Remaining	0.51 g	0.31 g	0.32 g	0.88 g	0.89 g
5	1M Fluoride					
	Pu Recovered	6.02 g	4.47 g	12.90 g	12.53 g	22.10 g
	Pu Remaining	0.41 g	0.19 g	0.85 g	1.10 g	1.55 g

Run Conditions: 100 grams graphite in 500 mls 12M HNO_3 .
Boil at reflux for 2 hours.
Runs 3A-3D - leached 3 times.

both HF and CaF_2 were used as fluoride sources. No differences were noted in using these reagents for a fluoride source.

In experiments 1 through 5, the graphite was leached only once. In experiments 3A through 3D, the graphite was leached three times. From these experiments it appears that a fluoride ion concentration of approximately 0.1M-0.3M is optimum for plutonium dissolution. This is based on the sludge analysis. Although the 0.07M fluoride ion concentration looks more attractive in Table III, we found that the third leach still assayed 3 grams Pu per liter, while for the 0.1M fluoride, the Pu concentration in the third leach was 0.6 grams per liter. The large difference in plutonium content, especially in the >28 mesh and <200 mesh sieve fractions, are indicative of non-homogeneity of plutonium in the graphite. Because of this, we used the final sludge analysis to determine the completeness of plutonium removal.

Since we had differences with plutonium content in the raw graphite, we were uncertain of the true plutonium content remaining in the sludge. We leached the sludge from Runs 1 through 5 three more times, using fresh nitric acid for each batch. The fluoride ion concentration was held constant at 0.5M for the first two and the last leach contained no fluoride ion. The results of these subsequent leachings are found in Table IV. The data presented are the overall recovery figures from several leachings for each mesh size, e.g., the sludges from each sieve fraction were combined. Runs 1 and 5 and Runs 2 and 3 were combined. The results shown in Table IV are the sum total of these two leachings plus Run 4, which was run by

TABLE IV
EFFECT OF ADDITIONAL LEACHINGS ON GRAPHITE SLUDGE

Sludge	>28 mesh	<28>48 mesh	<48>100 mesh	<100>200 mesh	<200 mesh
Pu Content (by analysis)	2.20 g	2.41 g	3.13 g	6.18 g	11.95 g
1st Heel Leach Pu Recovered	3.01 g	4.24 g	6.54 g	7.85 g	9.07 g
2nd Heel Leach Pu Recovered	0.97 g	0.92 g	6.69 g	1.62 g	5.43 g
3rd Heel Leach Pu Recovered	0.37 g	0.71 g	1.21 g	0.53 g	1.76 g
Total Pu Recovered	4.34 g	5.87 g	14.44 g	10.00 g	16.26 g
Sludge Pu Content (by analysis)	0.35 g	0.38 g	0.88 g	1.41 g	1.83 g
Total Pu	4.69 g	6.25 g	15.32 g	11.41 g	18.09 g
Difference:					
Pu Recovered - (Pu in Starting Sludge)	+2.49 g	+3.84 g	+12.19 g	+5.23 g	+6.14 g

itself. Data for these runs are presented in Table III. Note that in every case, more plutonium was recovered than the original sludge sample analysis indicated. This indicates that the original analysis is probably in error. The most probable error is due to sampling. These data also indicate that quantitative recovery of plutonium from graphite is more difficult when the particle size is smaller. This is probably due in part to difficulties which would be expected in washing finer particles.

Table V summarizes the data from Tables III and IV. Although these data indicate that three contacts are required for 97%

TABLE V

PERCENT PLUTONIUM DISSOLVED FROM GRAPHITE

	>28 <u>mesh</u>	<28->48 <u>mesh</u>	<48->100 <u>mesh</u>	<100->200 <u>mesh</u>	<200 <u>mesh</u>
1st Contact	92.6 %	85.3 %	79.6 %	86.3 %	84.2 %
2nd Contact	97.4 %	95.3 %	88.3 %	95.7 %	92.1 %
3rd Contact	98.9 %	97.4 %	97.2 %	97.7 %	96.9 %
4th Contact	99.5 %	99.1 %	98.8 %	98.3 %	98.9 %

plutonium recovery, we think that probably two contacts would be sufficient. The varying dissolution conditions used for the first contact (Table III) probably resulted in less than optimum dissolution in some contacts.

The next step was to determine if a shorter dissolution time could be used. Samples were taken at measured time intervals from 500 ml of 15M HNO_3 -0.25M CaF_2 containing 100 grams of <200 mesh graphite. From our previous work, the plutonium content should be between 21.7% and 35.6%, as indicated in Table II. Three experiments were performed. In each, the solution was heated to 90°C before the graphite was added. In observing each of these runs, it was noted that the brown NO_2 fumes did not appear until a little over 15 minutes of

digestion had taken place. The data also indicated that rapid dissolution did not take place until after a 15-20 minute digestion period. These data are summarized in Table VI.

From these data, it appears that most of the dissolution takes place during the first hour. During the second hour, we are unsure whether further dissolution occurred or whether the higher Pu concentration is due to evaporation. It appears, however, that for batch dissolution, dissolution for two hours at reflux temperature is desirable.

TABLE VI

DISSOLUTION RATE-PLUTONIUM FROM GRAPHITE
100 g 200 mesh graphite-500 ml 12M HNO₃-0.25M F⁻

Sample Time	No. 1 Pu g/l	No. 2 Pu g/l	No. 3 Pu g/l
0	0	0	0
5 minutes	1.5	-	0.64
10 "	3.5	7.6	0.98
15 "	1.4	14.6	3.2
20 "	27.3	23.3	19.9
25 "	40.0	36.1	30.5
30 "	46.7	42.8	37.1
45 "	55.0	48.0	42.8
60 "	56.3	50.6	46.4
90 "	63.8	53.0	48.4
Filtrate	70.5	71.3	60.0
Vol. Solution (liters)	0.345	0.350	0.390
Pu Recovered (grams)	24.3	21.4	23.4
Vol. Wash Solution (liters)	0.169	0.350	0.350
Pu Content (grams)	5.1	5.3	4.7
Total Pu	29.4 g	26.7 g	28.1 g
Pu Content Sludge g/g	2.7×10^{-2}	2.7×10^{-2}	2.3×10^{-2}

The total plutonium recovered, after washing the sludge thoroughly, averaged 28 grams. This would give a plutonium content of 28%, which is within the values given in Table II. From this, we can again only surmise that the sampling of raw graphite is extremely difficult. The amount which is recovered from each run varies considerably.

3. Washing Techniques

Since we had found by experience that the washing of filter sludges is important for removal of as much Pu as possible, we decided to study the effectiveness of our washing techniques. The filter sludges from the runs described in Table VI were used. The sludges probably contained from 60-80 grams of solids. In the first, 25 ml of 0.5M HNO₃ were used for each wash. The technique used was to slurry the graphite with the wash solution and then filter through a sintered glass

funnel. An acid wash was used in order to prevent hydrolysis of plutonium. The second and third runs were the same, except that 50 ml of dilute acid were used for each wash. The data are summarized in Table VII. These data indicate that a 50-ml

TABLE VII
EFFECT OF WASHING GRAPHITE SLUDGE AFTER ONE LEACH
Sludge from 100 g of <200 mesh of leached graphite used in each run

Wash No.	Run No. 1 Wash = 0.5M HNO ₃				Run No. 2 Wash = 0.92M HNO ₃				Run No. 3 Wash = 0.12M HNO ₃			
	Pu Conc. g/l	Vol. ml	H ⁺	Total Pu g	Pu Conc. g/l	Vol. ml	H ⁺	Total Pu g	Pu Conc. g/l	Vol. ml	H ⁺	Total Pu g
1	62.3	23.3	14.0	1.44	48.4	50	10.9	2.42	43.0	50	10.5	2.15
2	41.9	23.8	9.4	1.00	26.3	50	6.5	1.32	32.5	50	7.6	1.62
3	36.6	23.6	8.2	0.86	15.4	50	3.9	0.77	11.5	50	2.7	0.58
4	36.0	23.6	7.4	0.85	7.7	50	2.4	0.38	4.5	50	1.1	0.22
5	20.7	24.2	5.0	0.50	4.1	50	1.7	0.20	1.9	50	0.45	0.09
6	11.3	25.2	3.5	0.28	2.3	50	1.3	0.11	0.59	50	0.22	0.03
7	6.0	25.0	2.6	0.15	1.4	50	1.1	0.07	0.14	50	0.09	-
Total Pu g				5.1				5.3				4.7
% of Total Recovered				17.4%				19.9%				16.7%
Sludge Analysis g/g				2.7x10 ⁻²				2.7x10 ⁻²				2.3x10 ⁻²

wash is more desirable than a 25-ml wash and that five to seven washes are required. In scaling this up to a production process, possibly additional wash volumes would be required. We estimate that the total wash volume ratio should be greater than 5 liters per kilogram of filter sludge.

In subsequent work, we found that by using a volume of wash equal to the weight of the filter sludge (e.g. 1 kg solids require 1 liter of solution) for each washing, the number of washes required is approximately five. This is indicated in Table IX in the hydrochloric acid leaching work. Possibly the volume of wash solution may be reduced by reusing low level washes.

4. Solid-to-Liquid Ratios

To determine if the 200 grams of solids per liter solution ratio is optimum, a series of tests were performed varying the graphite ratio. The ratio was varied from 25 grams to 200 grams of graphite in 200 ml of solution. The graphite was washed five times, each with 50 ml of dilute acid before sampling. The results of this work are found in Table VIII. With one leach, a

200-grams graphite per liter of solution appears to give a discardable filter sludge. The inconsistency for the 125 g/l data cannot be explained at this time. Possibly fluoride was omitted from the dissolver solution.

TABLE VIII
EFFECT OF GRAPHITE RATIO TO 200-ml HNO₃

Graphite grams/liter	Filtrate vol. ml ^a	Pu g/l	Total Pu	Residue Analysis % Pu
1000	675	46.0	31.0	5.07%
750	720	34.6	24.9	1.92%
500	680	25.1	17.1	6.22%
375	700	13.3	9.3	4.19%
250	600	14.9	8.9	0.69%
125	440	2.23	1.0	19.90%

* Includes wash solutions.

In analyzing the data from Table VIII, higher plutonium concentrations can be obtained by increasing the amount of graphite per unit volume; however, it is necessary to leach the graphite more than once. For these tests, 12.6M HNO₃ and 0.25M fluoride were used. Previously we concluded that additional leaching is necessary; however, it is possible that adequate washing procedures are all that is required.

For low-level graphite (<1% Pu), a ratio of 750-grams graphite per liter can be used with one leach. The results are found in Table IX. Washing of this low-level graphite three times appears to be sufficient.

TABLE IX
LEACHING OF LOW-LEVEL GRAPHITE

Pu Assay = 0.433% Weight = 150 g Graphite
Run Conditions - 2 hr. leach with 12.5M
HNO₃-0.25M CaF₂

	<u>Pu g/l</u>	<u>Vol.</u>	<u>Total Pu</u>
Leach Solution	2.96	200	0.59
Wash 1	0.13	150	0.02
Wash 2	0.19	150	0.03
Wash 3	0.05	150	-
Wash 4	0.01	125	-
Wash 5	0.003	150	-
Wash 6	0.001	150	-
Wash 7	0.004	125	-
Wash 8	0.004	100	-
Wash 9	0.001	125	-
			0.64 g Pu Recovered

5. Needle-Gun Scarfings

During the middle stages of this program, it was found that a "needle gun" did an excellent job of removing the outer layer from the graphite molds and yet dusting was minimized. This prevented contamination of the molds once they are cleaned up. A sieve analysis on these scarfings is as follows:

> 35 mesh	- 34.0%
35- 48 mesh	- 22.6%
48- 65 mesh	- 15.9%
65-200 mesh	- 22.4%
<200 mesh	- 5.0%

This compares favorably with particle size of the graphite from the other process where the <200 mesh fraction accounted for 27.9% of the graphite.

The graphite from the needle gun contains a lower percentage plutonium. Analyses varied from 0.3% to 4% plutonium as compared to 15% plutonium in the previous scarfings. In leaching this material, recovery rates were not as high as previously found. The filter sludge remaining after leaching was found to contain from 0.01% to 0.5% plutonium. Thus, it appears that the percent recovery is dependent upon the initial plutonium concentration in the feed. As an example, if the

initial plutonium concentration is 30%, the filter sludge can be reduced to 0.5%; if the initial concentration is 0.5%, the filter sludge may only be 0.05% plutonium.

The lower percentage plutonium in the graphite now being produced via the needle gun probably means that the solid-to-liquid ratio can be increased from 200-grams graphite per liter to approximately 400 grams per liter. This higher ratio can be used for graphite containing 1-5% plutonium. For graphite containing less than 1%, a ratio of 750-grams graphite per liter of solution may be used. It should be emphasized that these higher solid-to-liquid ratios probably require additional washing. Recovery of plutonium from low-level graphite (<1%), by direct leaching, is probably not economical. We estimate that the total volume for each kilogram of graphite would be approximately 8 liters. For 1% material, this would average approximately 1.2 g Pu/liter. Other methods, such as heavy liquid separation, are probably necessary to upgrade the graphite prior to dissolution. Design of large equipment for recovery of plutonium from graphite is not feasible due to criticality considerations. Although in general the plutonium concentrations will be low, because of errors in sampling, it is possible that a few batches will contain sufficient plutonium to present criticality hazards.

6. Dissolution of Graphite with 90% Nitric Acid

It was found that fuming nitric acid (90%) would decompose the binder in the graphite. The resultant material was 10-20 mesh in size after a 2-hour treatment. This method was abandoned without too much further work when a needle gun was found to do an efficient job in removing the outer layers of graphite which are contaminated with recoverable quantities of plutonium. Many thousands of gallons of fuming nitric acid would have been required if this process were to be used. A ratio of 200 grams of graphite in one liter of fuming nitric acid was used in the work.

7. Recommended Direct Nitric Acid Leaching Procedure

In summary, for nitric acid leaching, we recommend the following:

- a. The solid-to-liquid ratio should be 200 grams of graphite per liter of solution for graphite containing 5% Pu or greater. A ratio of 750 g/l can be used for graphite containing 1% Pu. It is possible that 400 g/l can be used for 1-5% Pu graphite.
- b. The leaching solution should be 12.5M HNO_3 containing 0.1-0.3M fluoride ion. Either HF or CaF_2 may be used.
- c. Dissolution time should be two hours at reflux temperature.
- d. Although one leaching apparently recovers the major portion of the plutonium, two leachings would be more desirable. Thorough washing of the filter sludge is necessary for maximum plutonium removal. For a batch operation using graphite containing 1% Pu or greater, a minimum of five washes are necessary. Each wash volume is to be equal to the weight of the sludge (e.g. 1 kilogram of sludge requires 1 liter of solution). The sludge should be stirred during each wash. For graphite containing less than 1% Pu, one leach and three washes are sufficient.
- e. The wash solution should always be a dilute acid to prevent plutonium hydrolysis. The filtrate from the final wash should contain less than 1 g Pu/l.
- f. Sampling of the graphite, either before or after leaching, does not necessarily give a true plutonium value for the batch.

C. HYDROCHLORIC ACID LEACHING

Since graphite which had been used recently contains mostly plutonium metal or plutonium intermetallics, an HCl leaching procedure was attempted. Again, the graphite scarfings were screened. We did not sample the sieve fractions since we felt that the answers would not be representative of the batch. Instead, the whole fraction was leached with 7M HCl. After leaching, the washed filter sludge was sampled. Results from

these experiments are found in Table X. In this table, the plutonium content for each sieve fraction is calculated using

TABLE X

NET WEIGHT AND Pu CONTENT FOR EACH SIEVE FRACTION

<u>Mesh Size</u>	<u>>28 mesh</u>	<u><28->48 mesh</u>	<u><48->100 mesh</u>	<u><100->200 mesh</u>	<u><200 mesh</u>
Sieve Fraction (wt. %)	29.4 %	7.4 %	21.9 %	18.8 %	22.4 %
Graphite Weight	597 g	151 g	446 g	382 g	456 g
g Pu Recovered	111.6	24.3	66.1	43.4	61.9
g Pu in Sludge	9.7	0.9	1.4	2.0	11.8
% Pu Calc.	20.6 %	16.7 %	15.1 %	11.9 %	16.2 %
Filter Sludge Pu Content	2.58%	0.78%	0.46%	0.67%	3.44%

Average Pu Content = 15.6 %

the recovery figures. The filter sludge in each of these runs varied from 0.4% to 3.6% Pu. The average plutonium content for this graphite was 15.6%.

From these data it appeared that sieving of the graphite gave no advantage to recovering plutonium. In order to insure this was correct, another run was made using unsieved graphite. To 500 ml of 6M HCl, 500 grams of graphite were added. The reaction appeared to be complete in 15 minutes. The solution was then filtered and washed five times with 0.3M HCl. Results from this experiment are found in Table XI. It appears that HCl can be used to affect quantitative recovery

TABLE XI

from graphite scarfings, provided that graphite is fresh and little or no oxide is present. The filter sludge from this experiment averaged 0.85% plutonium. Since our present metal production recovery streams are not equipped for

LEACHING OF 500 g GRAPHITE WITH 500 ml 6M HCl

<u>Solution</u>	<u>Vol. Filtrate (liters)</u>	<u>Pu g/l</u>	<u>Total Pu Grams</u>
6M HCl	0.340	143.0	48.6
Wash 1	0.500	43.3	21.6
Wash 2	0.550	11.6	6.4
Wash 3	0.490	3.08	1.5
Wash 4	0.505	1.01	0.5
Wash 5	0.500	0.49	0.2

Total Pu Recovered (grams) 78.8
 Graphite - % Pu = 15.8%
 Filter Sludge - Pu Content = 0.85%

handling chloride solutions, we performed some oxalate precipitations on the chloride solution. This solution contained both the leach and washes, and assayed at 38.6 g Pu/l with an acidity of 1.95.

Oxalate precipitations of plutonium from the solution with no valence adjustment resulted in filtrates containing 0.3 to 0.4 g Pu/liter even when the solution was heated prior to precipitation. When hydroxylamine was added to ensure that only trivalent plutonium was present, the filtrate at room temperature was 5.16×10^{-2} g Pu/liter and at 70°C was 1.84×10^{-2} g/l. The filtrate was then diluted and passed through a cation column where the plutonium absorbed and the effluent was discarded.

Since it is possible that the oxalate cake contains appreciable amounts of chloride ion, it may be advantageous to load the plutonium directly onto a cation column, wash with water, and elute with 6M HNO_3 . Previous experience in plutonium processing indicated that effluents from cation columns would contain less than 1×10^{-2} grams plutonium per liter.

If a chloride recovery process is available, HCl dissolution should be considered since plutonium oxide, which is not highly refractory, is soluble in HCl solutions.