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# RECOVERY OF PLUTONIUM FROM CARBON ANALYSIS RESIDUES

L. W. GRAY and N. W. McGAHEE

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# RECOVERY OF PLUTONIUM FROM CARBON ANALYSIS RESIDUES

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ABSTRACT

A method was developed for the recovery of plutonium from residues resulting from analyses of plutonium metal for carbon. The residue from each carbon analysis contains about 0.5 g of plutonium as high-fired $PuO_2$. By use of $2^P$ factorial experimental designs, recovery methods utilizing a variety of acids and conditions were investigated. The optimum recovery procedure was determined to be leaching of the crushed crucible and contents with a hot solution of 7M $HNO_3$ - 0.2M HF for about four hours. Dissolution of the crucible matrix is kept to a minimum by holding the leach solution to crucible residue ratio to about 2.5 mL/g of solids. Increasing this ratio to $\geq$10 does not improve the recovery of plutonium.

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## RECOVERY OF PLUTONIUM FROM CARBON ANALYSIS RESIDUES

### INTRODUCTION

During 1976, the Laboratories Department of the Savannah River Plant (SRP) installed and placed into service a *LECO** carbon analyzer to determine the carbon content of plutonium metal buttons. The procedure used is to add 500 ±2.0 mg of plutonium metal and 1 g of copper metal (used as a booster) to a *LECO* crucible. The crucible and contents are then heated to 900-1000°C in an oxygen atmosphere. In this temperature range the molten copper and plutonium begin to oxidize rapidly which further increases the temperature to 1300-1700°C. The carbon is oxidized to $CO_2$ and collected for analysis by the *LECO* analyzer.

The residue then consists of 20 to 22 g of crucible, about 0.55 g of high fired $PuO_2$ and about 1.25 g of CuO. Visual inspection of manually cracked crucibles reveals that the molten metals have penetrated from 2 to 8 mm into the crucible walls. By use of both a $2^3$ factorial experimental design and conventional experimental designs, an efficient recovery procedure has been determined. The procedure consists of leaching the crushed residue with a 0.2M HF - 7M $HNO_3$ solution for 3 to 4 hr. A leach solution to crucible residue ratio of about 2 mL/g of solids was found to be just as effective as a ratio of 10 mL/g. At a constant volume-to-solids ratio the recovery of plutonium increased by a factor of about 150 when the fluorine anion ($F^-$) concentration was increased from 0 to 0.1M. When the $F^-$ concentration was increased to 0.2M, the plutonium recovery increased by an additional factor of about 1.5. Further increases in $F^-$ content, however, had very little effect on plutonium recovery.

### EXPERIMENTAL PROCEDURE

The plutonium metal is weighed into the crucibles and kept constant within 0.2%; no further weighing or analyses of the plutonium in the crucible was performed. One or two crucibles with residues were ground to a coarse powder with a Tekmar Company A10 analytical mill; and all the material was used without further analysis. Plutonium contents of the solutions were determined with a computer-based multi-channel pulse height

* Brand name of LECO Corporation, 3000 Lakeview Avenue, St. Joseph, MI.

analyzer interfaced to a 1 cc germanium detector. The complete system was designed, fabricated, and programmed at Lawrence Livermore Laboratory.[1,2] Weights of leached residues were determined after drying at about 300°C.

## EXPERIMENTAL DESIGN

Two-level factorial experimental designs[3] were used to determine the best recovery conditions such as acid, acid concentration, solution-to-solid ratio, and leach time. To better define the recovery profile with time, these data were then used in conventional kinetic experiments. This was necessary because of the curvature of the data (a maximum in the experimental region) for the variables of time and HF concentration. Two-level factorial experimental designs permit estimation of the effects of several factors simultaneously. This is accomplished by making experimental runs at all combinations of the p-factors, with different levels per factor. Two-level factorial experiments are easy to design and analyze, and are readily adaptable to both continuous and discrete factors. The experiments also provide adequate prediction models for factor relationships that have no strong curvature (maximum or minimum) in the experimental region. For continuous variables the higher value is coded (+) and the lower values coded (-). The coding for a $2^3$ factorial design is given in Table 1; variable extremes are given in Table 2.

The use of these designs permits the estimation of factor effects more precisely than one-at-a-time testing because of the hidden replication included. Systematic error is kept at a minimum by replication of design points and randomization of the trials before running the trials. These designs do not give any estimate of curvature of responses on the experimental region. However, an estimate of the overall curvature (maxima or minima) can be obtained by obtaining data at a middle value of all factors. The severity of the curvature is estimated by the difference between the average of the design points and the average of the center points.

If a computed factor effect is larger (in absolute value) than the minimum-significant-factor effect, the experimenter can safely conclude that the true effect is nonzero. Similarly, if the curvature effect is larger than the minimum-significant-curvature effect, the experimenter can safely conclude that nonzero curvature is associated with at least one variable.

The factor effects computed represent the difference between response at the high and low levels of the factor. If the factor effect is divided by the difference of the high and low levels of the factors, the results will be the change in the response for a unit change in the factor.

TABLE 1

Two-Level Factorial Experimental Design

| *Trial* | *Factors*[a] *X1* | *X2* | *X3* |
|---|---|---|---|
| 1 | - | - | - |
| 2 | + | - | - |
| 3 | - | + | - |
| 4 | + | + | - |
| 5 | - | - | + |
| 6 | + | - | + |
| 7 | - | + | - |
| 8 | + | + | + |

a. X1 = HF or HCl concentrations, X2 = time, and X3 = volume of solution. The $HNO_3$ concentration was kept constant at 7M for the $HNO_3$-HF experiments. The amount of plutonium was kept constant at 0.5 g by using one crucible per experiment; the total mass of the crucible plus contents varied from 20 to 22 g.

TABLE 2

Variable Extremes for $2^P$ Experimental Designs

| *Variable* | *Experiments* *$HNO_3$-HF* *High(+)* | *Low(-)* | *HCl* *High(+)* | *Low(-)* |
|---|---|---|---|---|
| $HNO_3$, M | 7.0 | 7.0 | 0.0 | 0.0 |
| HF, M | 0.2 | 0.0 | 0.0 | 0.0 |
| HCl, M | 0.0 | 0.0 | 5.0 | 1.0 |
| Volume, mL | 250 | 50 | 250 | 50 |
| Time, hr | 4 | 1 | 4 | 1 |

The model underlying the two-level factorial is of the form

$$y = b_0 + b_1x_1 + b_2x_2 + \ldots b_px_p$$
$$+ b_{12}x_1x_2 + b_{13}x_1x_2 + \ldots b_{p-1,p}x_{p-1}x_p$$
$$+ \text{higher order interactions}$$

where

$y$ = predicted response

$x_j = \dfrac{\text{factor level - (Hi + Lo)/2, jth factor}}{\text{(Hi-Lo)/2}}$

$b_j$ = 1/2 (factor effect for $x_j$)

$b_{jj'}$ = 1/2 (interaction effect for $x_j$ $x_j'$)

## RESULTS

Analytical data for the experiments with $HNO_3$-HF solutions are given in Table 3 and shown graphically in Figure 1. A summary of the statistical data is given in Table 4. The data clearly show that the most significant variable is the HF concentration; the time of leaching is the next most significant variable; the volume of solution above a 2.5 mL per gram ratio is an insignificant variable. There is also an important interaction between the variables of time and HF concentration. There is, however, a significant negative curvature to the data indicating that there is a maximum associated with at least one of the two important variables, i.e. either HF concentration or time. Even though the data indicate an interaction between time and volume and a three-way interaction between HF concentration, time, and volume, one must be careful in interpretation of these two interactions because of this maximum in the data.

To determine which of the two significant variables showed a nonlinear response, conventional kinetic experiments were carried out with the variables time and HF concentration. The percent plutonium recovery data with respect to these two variables is given in Table 5 and shown graphically in Figure 2. It is evident from the data in Figure 2 that there is curvature to both of these variables.

At the completion of the kinetic experiments, the remaining solids were collected, dried at about 300°C, and weighed. Data for the percent of the total material dissolved are given in Table 6. A maximum of about 15% of the total material was dissolved after three hours.

TABLE 3

Raw Analytical Data for the $HNO_3$-HF Experiments

| *$2^3$ Factorial Design Points*[a] | *Observed Recovery, g* | *Mean* | *Variance* |
|---|---|---|---|
| 1 | 0.0007; 0.0005 | 0.0006 | $2 \times 10^{-8}$ |
| 2 | 0.2350; 0.2600 | 0.2475 | $3.13 \times 10^{-4}$ |
| 3 | 0.00055; 0.0025 | 0.0015 | $1.90 \times 10^{-6}$ |
| 4 | 0.4605; 0.4500 | 0.4552 | $5.51 \times 10^{-5}$ |
| 5 | 0.0025; 0.0025 | 0.0025 | 0.00 |
| 6 | 0.3600; 0.4950 | 0.4275 | $9.112 \times 10^{-3}$ |
| 7 | 0.0030; 0.0000 | 0.0015 | $4.500 \times 10^{-6}$ |
| 8 | 0.4500; 0.4250 | 0.4375 | $3.125 \times 10^{-4}$ |
| 9 | 0.3690; 0.2730<br>0.3600; 0.3750 | 0.3442 | $2.294 \times 10^{-3}$ |

a. Design Points 1 through 8 are given in Tables 1 and 2; Design Point 9 is the center point of Points 1 through 8.

TABLE 4

Results of a Statistical Data Analysis for the $HNO_3$-HF Experiments

| *Factor* | *Factor Effect Value* |
|---|---|
| $S_{pooled}$[a] | 0.03894 |
| (MIN)[b] | 0.04283 |
| HF | +0.39040[e] |
| Time | +0.05440[e] |
| HF-Time | +0.05450[e] |
| Volume | +0.04105 |
| HF-Volume | +0.04010 |
| Time-Volume | -0.04990[e] |
| HF-Time-Volume | -0.04895[e] |
| (MIN C)[c] | 0.05246 |
| Curvature[d] | -0.14750[e] |

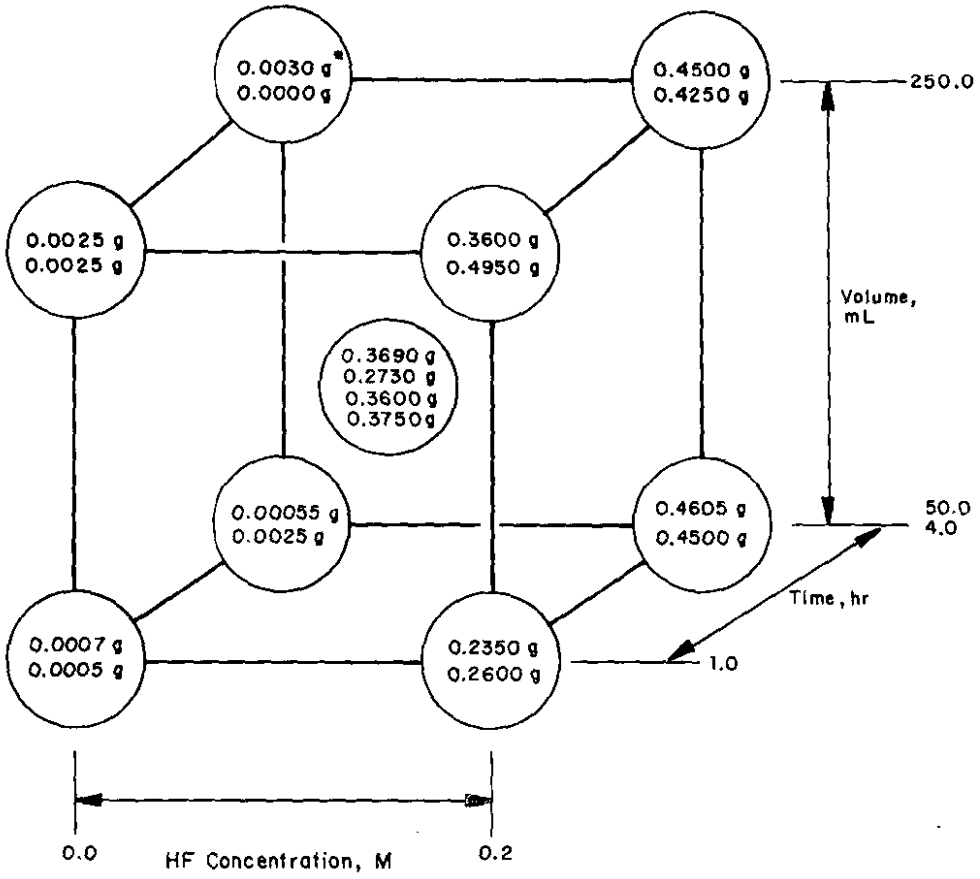
a. $S_{pooled}$ = standard deviation; $S^2_{pooled}$ = pooled variance

b. (MIN) = minimum significant factor effect

c. Calculated significant factors and interactions

d. (MIN C) = minimum significant curvature

e. Curvature = maxima or minima in the data




* *Grams Pu recovered from a Pu charge.*

FIGURE 1. Factorial $2^3$ Design Data for $HNO_3$-HF Leach of Plutonium from *LECO* Crucible Residues

TABLE 5

Kinetic Data for $HNO_3$-HF Leaching of *LECO* Crucible-$PuO_2$ Residues

| *Experiment* | *HF, M* | *Time, hr* | *Pu Recovery, %* |
|---|---|---|---|
| A | 0.1 | 0.75 | 16.4 |
| | | 1.50 | 36.4 |
| | | 3.00 | 51.9 |
| B | 0.2 | 0.75 | 44.4 |
| | | 1.00 | 50.0 |
| | | 1.50 | 59.1 |
| | | 3.00 | 83.3 |
| | | 4.00 | 95.0 |
| C | 0.3 | 0.75 | 47.7 |
| | | 1.50 | 68.2 |
| | | 3.00 | 85.6 |

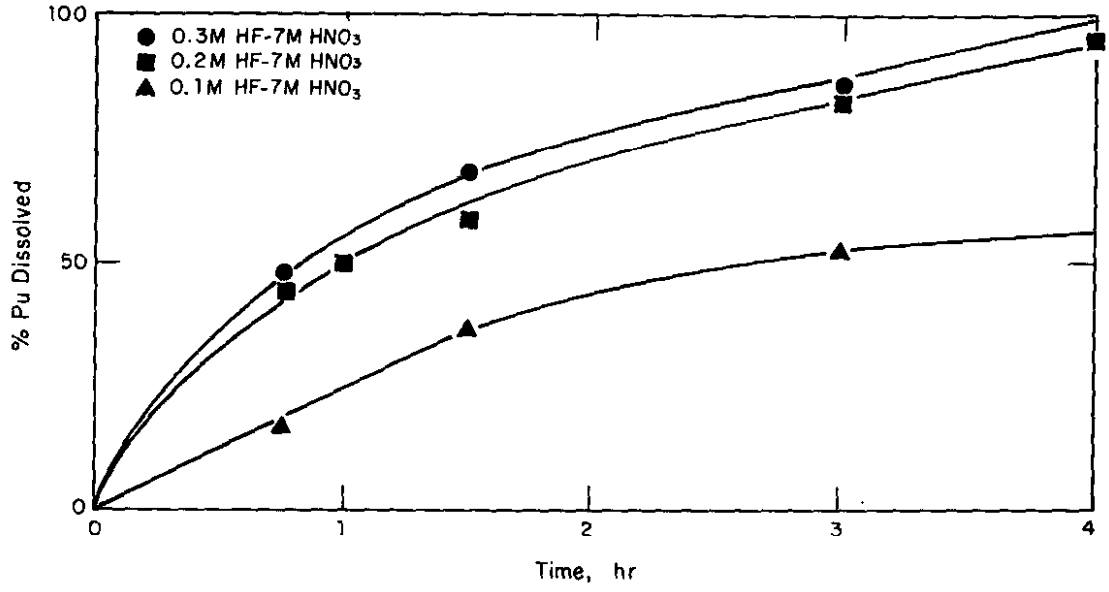



FIGURE 2. Dissolution of Plutonium from *LECO* Crucible Residues as a Function of Time and HF Concentration

TABLE 6

Dissolution of the Crucible Matrix

| *Experiment* | *HF, M* | *Time, hr* | *Total Solids Dissolved, %* | *Crucible Dissolved, %* |
|---|---|---|---|---|
| A | 0.1 | 3.0 | 11.3 | 2.6 |
| B | 0.2 | 3.0 | 14.6 | 6.0 |
| C | 0.3 | 3.0 | 16.2 | 7.6 |

Analytical data for the experiments with HCl are given in Table 7. Because only a maximum of about 0.8% of the plutonium was recovered, further experimentation and data reduction were not undertaken.

TABLE 7

Raw Analytical Data for HCl Experiments

| *$2^3$ Factorial Design Points* | *Observed Recovery, mg* | *Mean* | *Variance* |
|---|---|---|---|
| 1 | 0.050; 0.000 | 0.025 | 0.00125 |
| 2 | 1.950; 0.800 | 1.375 | 0.66125 |
| 3 | 0.000; 0.900 | 0.450 | 0.40500 |
| 4 | 3.450; 3.900 | 3.675 | 0.10125 |
| 5 | 0.000; 0.000 | 0.000 | 0.00000 |
| 6 | 0.000; 0.700 | 0.350 | 0.24500 |
| 7 | 0.010; 0.000 | 0.005 | 0.00005 |
| 8 | 0.800; 1.950 | 1.375 | 0.66125 |
| 9 | 0.600; 0.000; 0.000 | 0.200 | 0.12000 |

## CONCLUSIONS

Plutonium can be recovered from *LECO* carbon analysis residues when copper is used as the booster by leaching with a solution of 7M $HNO_3$ - 0.2M HF. The $PuO_2$ associated with the CuO dissolves fairly rapidly. The $PuO_2$ which diffused into the walls of the crucible during the time of the analysis requires dissolution of the crucible matrix. Therefore, the crucible must be crushed before leaching.

Because the recovery depends upon good solvent-solid interaction, the recovery vessel should have the maximum practical surface-to-depth ratio, be fitted with a condenser, and have provisions for agitation. A crude dissolver for leaching 10 crucibles could be made from the bottom 1/3 of a 4L stainless steel beaker. If a condenser of sufficient cooling were fashioned for this cut-off beaker to keep the solution at a hard-boil, mechanical agitation would not be necessary. If the condenser did not have sufficient cooling capacity, mechanical agitation would be necessary.

The procedure for using this crude dissolver is to grind 10 crucibles with residues (~210 g total mass) in an analytical mill. (The crucibles grind better if cracked into two or more pieces before dropping them into the mill.) This charge is added to 500 mL of 7M $HNO_3$ - 0.2M HF and fast refluxed for about 3.5 hours, and then filtered. After filtering, the solids are washed with $HNO_3$-HF solution. The plutonium-laden solution and washings are then combined and the percentage of plutonium recovered is determined. On a laboratory scale (using 2 crucibles), the combined solution contains an average of 95% of the plutonium charged.

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