2

conf-780819--1

MLM-2537(OP)

DECONTAMINATION OF HEPA FILTERS

J. W. Koenst, Jr., E. L. Lewis and D. F. Luthy
Mound Facility*
Miamisburg, Ohio 45342

Abstract

Mound Facility, during many years of plutonium-238 experience, has recovered over 150 kg of plutonium-238. Much of this material was recovered from HEPA filters or from solid wastes such as sludge and slag. The objective of this task was to modify and improve the existing nitric acid leaching process used at Mound so that filters from the nuclear fuel cycle could be decontaminated effectively. Various leaching agents were tested to determine their capability for dissolving PuO_2, UO_2, U_3O_8, AmO_2, NpO_2, CmO_2, and ThO_2 in mixtures of the following: HNO_3-HF; HNO_3-HF-H_2SO_4; and HNO_3-$(NH_4)_2Ce(NO_3)_6$. Adsorption isotherms were obtained for two leaching systems. In some tests simulated contaminated HEPA filter material was used, while in others actual spent glovebox filters were used.

The maximum decontamination factor of 833 was achieved in the recovery of plutonium-238 from actual filters. The dissolution was accomplished by using a six-stage process with $4\underline{N}$ HNO_3-$0.23\underline{M}$ $(NH_4)_2Ce(NO_3)_6$ as the leaching agent. Thorium oxide was also effectively dissolved from filter media using a mixture of nitric acid and ceric ammonium nitrate. Sodium carbonate and Na_2CO_3-KNO_3 fusion tests were performed using simulated PuO_2-contaminated filter media at various temperatures. Approximately 70 wt% of the PuO_2 was soluble in a mixture composed of 70 wt% Na_2CO_3-30 wt% KNO_3 (heated for 1 hr at 950°C).

Introduction

Efforts were directed toward determining the dissolution parameters of PuO_2, UO_2, and U_3O_8** in various leaching reagents. The reagents used were various concentrations of HNO_3, HNO_3-HF, HNO_3-HF-H_2SO_4, HNO_3-$(NH_4)_2Ce(NO_3)_6$, and HNO_3-H_2SO_4. Two types of plutonium dissolution tests were conducted with $8\underline{N}$ HNO_3. In the first test, PuO_2 was placed in $8\underline{N}$ HNO_3 at boiling temperature. In the other test, HEPA filter media contaminated with PuO_2 were added to boiling $8\underline{N}$ HNO_3. The dissolution rates of PuO_2 as measured by the alpha activity of the acid media were determined for each test; as shown in Figure 1, the apparent dissolution rate was less in the test using PuO_2-contaminated filter media. After 14 hr of heating, for example, there was a 3% difference (11% minus 8%) in dissolution rates. At this point, plutonium adsorption isotherms were developed to determine whether any of the dissolved plutonium was being adsorbed by the filter media.

---

*Mound Facility is operated by Monsanto Research Corporation for the U.S. Department of Energy under Contract No. EY-76-C-04-0053.

**The uranium oxides were depleted uranium-238, whereas the PuO_2 was a mixture of 80 wt% plutonium-238, 16 wt% plutonium-239, 2.5 wt% plutonium-240, 0.8 wt% plutonium-241, 0.2 wt% plutonium-242, plus small amounts of other actinides calcined at 750°C.

NOTICE

MN ONLY

PORTIONS OF THIS REPORT ARE ILLEGIBLE. It has been reproduced from the best available copy to permit the broadest possible availability.

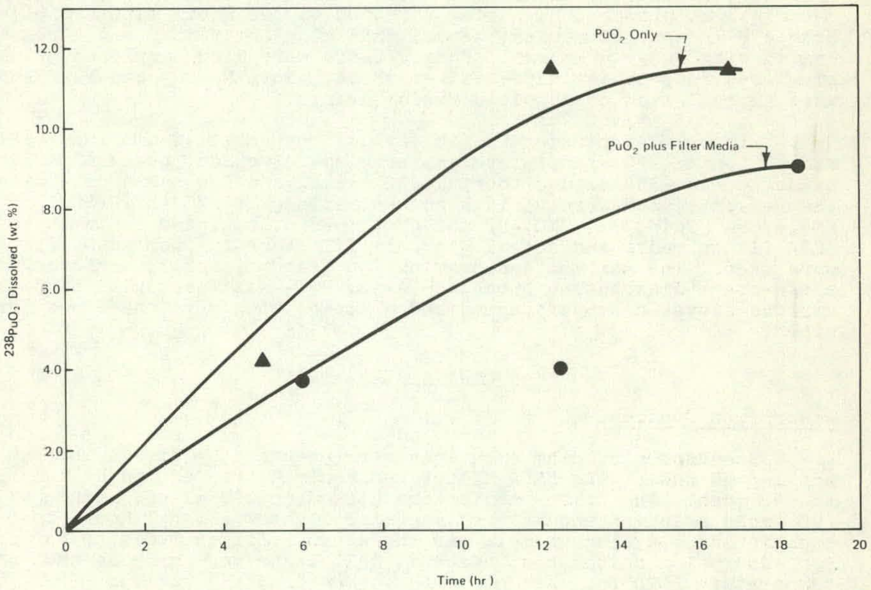

Figure 1 - Effect of filter media on dissolution rates of PuO_2 in boiling $8\underline{N}$ HNO_3.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

This is of great importance since the amount of adsorbed plutonium would limit the decontamination factor that could be achieved. Adsorption isotherms were determined for the Pu-HNO_3 and Pu-HNO_3-HF systems.

Efforts were also directed toward the determination of dissolution parameters in various reagents of PuO_2* and PuO_2-UO_2** solid solution. The reagents used were various concentrations of HNO_3-HF-H_2SO_4, HNO_3-HF, HNO_3-$(NH_4)_2Ce(NO_3)_6$, and HNO_3-H_2SO_4. In one series of tests, simulated contaminated HEPA filter media was used. This material was prepared by mixing shredded filter media with actinide oxides. In another series, actual HEPA glovebox filter media contaminated with PuO_2 were used. Fusion tests were also completed using simulated PuO_2-contaminated filter media. Both Na_2CO_3 and Na_2CO_3-KNO_3 were investigated as possible fusion agents.

Dissolution parameters (in various reagents) of americium-241 and plutonium-239 oxide mixtures, uranium-233 oxide, neptunium-237 oxide, curium-244 oxide, thorium-232 oxide, and PuO_2 were determined. The reagents used were various concentrations of HNO_3-HF-H_2SO_4, HNO_3-$(NH_4)_2Ce(NO_3)_6$, HNO_3-HF and HNO_3. Both simulated contaminated HEPA filter media and actual glovebox filter media from spent filters were used. The maximum decontamination factor was 833, achieved using a six-stage dissolution process. Also, PuO_2 was fused with $NaCO_3$ at various elevated temperatures, and a dissolution percentage was determined.

Experimental Work

Adsorption Studies

Standard plutonium solutions were prepared by dissolving PuO_2 in boiling 8N HNO_3. The HEPA filter media were shredded and ball-milled to <40 mesh. The filter media were placed in 100 ml of the prepared PuO_2-acid solution and stirred magnetically for several hours to reach equilibrium. A blank sample was run without filter media to correct for adsorption on the test beakers. All tests were made at ambient temperature (∿20°C).

Figure 2 shows the adsorption of plutonium on filter media in different acids. The ordinate is x/m, where x = milligrams of plutonium-238 adsorbed and m = milligrams of filter media. The abscissa is C, which is the concentration of the solution in equilibrium with the

---

*The uranium oxides were depleted uranium-238, whereas the PuO_2 was a mixture of 80 wt% plutonium-238, 16 wt% plutonium-239, 2.5 wt% plutonium-240, 0.8 wt% plutonium-241, 0.2 wt% plutonium-242, plus small amounts of other actinides calcined at 750°C.

**The uranium was uranium-238 while the plutonium was 85.0 wt% plutonium-239, 12.0 wt% plutonium-240, 1.7 wt% plutonium-241, 0.75 wt% plutonium-238, plus small amounts of other actinides.

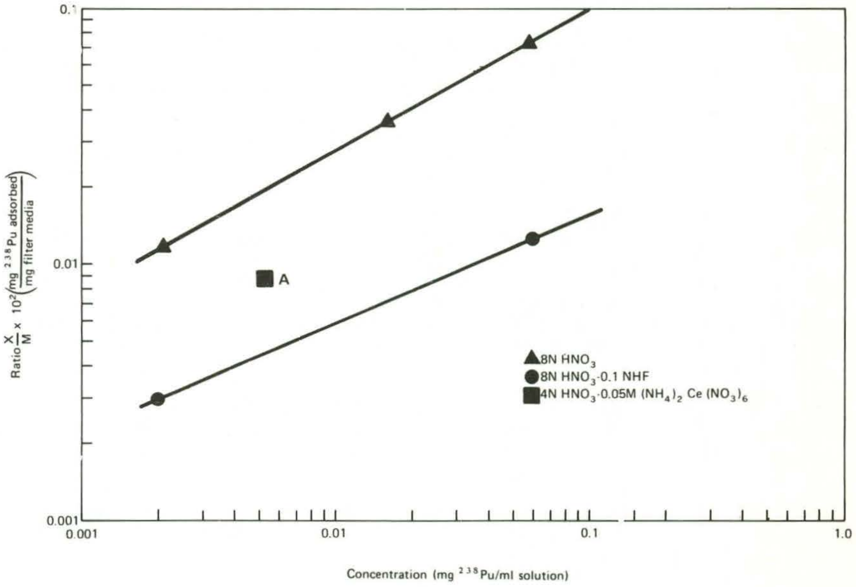

Figure 2 - Adsorption of ^{238}Pu on filter media at ambient temperature (∿20°C) in different acids.

filter media (expressed in milligrams of plutonium-238 per milliliter of solution). The Freundlich equation relates x/m and C as follows:

$$x/m = kC^{1/n} \tag{1}$$

or

$$\log (x/m) = \log k + (1/n) \log C \tag{2}$$

The plot of log (x/m) as a function of log C should be a straight line with slope 1/n and log k the point of intercept. The straight lines in Figure 2 are such a plot. It should be noted that for any given concentration, the x/m ratio is smaller for the 8N HNO_3-0.1N HF system. This means that a larger decontamination factor could be achieved using the HNO_3-HF leaching agent (assuming that the same percentage of PuO_2 is dissolved by the reagent in the dissolution step).

Tests were also performed to determine the solubility of the filter media in various dissolution reagents. It was determined that approximately 30 wt% of the filter media is soluble in 8N HNO_3 and approximately 50 wt% of the filter media dissolves in 8N HNO_3-0.1N HF. Also, in another adsorption test it was found that the use of 4N HNO_3-0.05M ceric ammonium nitrate (see point A, Figure 2) would result in a decontamination factor between that obtained with 8N HNO_3-0.1N HF and that with 8N HNO_3 (assuming each leaching agent was equally effective in dissolving PuO_2).

PuO_2 Dissolution Studies

Contaminated HEPA filter media were prepared by mixing PuO_2* powder with shredded filter media. The plutonium-238 concentration of the mixture was 11 mg/cm³ of prepared media. Small samples of this prepared mixture (about 3 g) were added to glass beakers containing 250 ml of leaching solution. All tests were performed at boiling temperatures. Samples were withdrawn periodically and the plutonium-238 concentration of the solution was determined. The contents of the beakers were stirred every 2 hr. The solution volume and concentration were kept constant by adding acid of proper concentration in order to replace evaporated acid.

Table I lists results from dissolution tests for PuO_2 in various acid mixtures. The HNO_3-H_2SO_4 mixtures were relatively ineffective dissolution agents as illustrated in Figure 3. A fivefold increase in H_2SO_4 concentration increased the dissolution rate by only 3%. The maximum weight percent of plutonium-238 dioxide dissolved was only 18% after an 18-hr reaction time. Figure 4 illustrates the effect of initial cerium(IV) concentration on the dissolution rate. The 4N HNO_3 -0.1M $(NH_4)_2Ce(NO_3)_6$ leaching agent was by far the most effective of the three HNO_3-cerium(IV) solutions, with 88% of the plutonium-238 dioxide dissolved in 3 hr.

The reaction mechanism for dissolving PuO_2 in HNO_3-cerium(IV) solutions is shown in Equations 3 and 4.

$$2Ce^{+4} + 2e^- \rightleftarrows 2Ce^{+3} \quad (3)$$

$$Pu^{+4} \rightleftarrows Pu^{+6} + 2e^- \quad (4)$$

Because stoichiometric quantities of cerium(IV) are required for complete dissolution of the PuO_2, large amounts of cerium(IV) are required to dissolve large quantities of PuO_2. Therefore, it would seem advantageous to use small amounts of cerium(IV) and then add oxidizing compounds to oxidize the cerium(III) to cerium(IV). An example of this would be the addition of $KMnO_4$ to the depleted solution. This would cause the $Mn^{+7} + 3e^- \rightleftarrows Mn^{+4}$ reaction which would oxidize the depleted cerium as follows:

$$3Ce^{+3} \rightleftarrows 3Ce^{+4} + 3e^- \quad (5)$$

$$Mn^{+7} + 3e^- \rightleftarrows Mn^{+4} \quad (6)$$

where one mole of manganese oxidizes three moles of cerium. This was done in acid tests 25 and 25A (see Table I). Approximately 1 g of $KMnO_4$ was added to a depleted 4N HNO_3-0.005M$(NH_4)_2Ce(NO_3)_6$ solution and the solution heated an additional 15 hr. In this period of time, the concentration of PuO_2 dissolved increased significantly from 12 wt% in the depleted solution to 26 wt% in the regenerated solution.

---

*The PuO_2 was fine powder having a composition of 80 wt% plutonium-238, 16 wt% plutonium-239, 2.5 wt% plutonium-240, 0.8 wt% plutonium-241, 0.2 wt% plutonium-242, plus small amounts of other actinides. It was calcined for 2 hr at 950°C.

Table I - DISSOLUTION OF PLUTONIUM DIOXIDE IN VARIOUS ACID MIXTURES

Acid Test Number	Reagent Composition[a]	Time Heated (hr)	PuO_2 Dissolved (wt %)
19-1	4N HNO_3-0.05M CAN	5 3/4	42.9
19-2	4N HNO_3-0.05M CAN	12 1/4	41.4
19-3	4N HNO_3-0.05M CAN	18 3/4	38.5
20-1	8N HNO_3-0.1N H_2SO_4	5 3/4	14.4
20-2	8N HNO_3-0.1N H_2SO_4	12	12.7
20-3	8N HNO_3-0.1N H_2SO_4	18	15.9
21-1	12N HNO_3-0.1N HF-0.1N H_2SO_4	4 3/4	115.2
21-2	12N HNO_3-0.1N HF-0.1N H_2SO_4	10 1/2	107.1
22-1	12N HNO_3-0.1N HF	1 3/4	87.0
22-2	12N HNO_3-0.1N HF	6 3/4	94.1
22-3	12N HNO_3-0.1N HF	11 1/2	107.9
25-1	4N HNO_3-0.005M CAN	2 1/4	11.1
25-2	4N HNO_3-0.005M CAN	7 3/4	13.4
25-3	4N HNO_3-0.005M CAN	13 1/4	11.9
25-A-1	4N HNO_3-0.005M CAN- $KMnO_4$	3	13.4
25-A-2	4N HNO_3-0.005M CAN- $KMnO_4$	8 1/2	18.9
25-A-3	4N HNO_3-0.005M CAN- $KMnO_4$	14 3/4	26.3
26-1	12N HNO_3-0.01N HF	1 3/4	31.6
26-2	12N HNO_3-0.01N HF	7 1/4	41.0
26-3	12N HNO_3-0.01N HF	12 3/4	40.9
27-1	12N HNO_3-0.01N HF-0.1N H_2SO_4	1 1/4	30.1
27-2	12N HNO_3-0.01N HF-0.1N H_2SO_4	6 3/4	33.1
27-3	12N HNO_3-0.01N HF-0.1N H_2SO_4	12 1/4	36.3
28-1	12N HNO_3-0.1N HF-0.01N H_2SO_4	1	96.3
28-2	12N HNO_3-0.1N HF-0.01N H_2SO_4	6 1/2	100.9
28-3	12N HNO_3-0.1N HF-0.01N H_2SO_4	12	101.8
29-1	8N HNO_3-0.5N H_2SO_4	5 1/2	15.8
29-2	8N HNO_3-0.5N H_2SO_4	10 3/4	17.4
29-3	8N HNO_3-0.5N H_2SO_4	15 1/4	17.4
30-1	12N HNO_3-0.05N HF 0.01N H_2SO_4	3	95.9
30-2	12N HNO_3-0.05N HF 0.01N H_2SO_4	8 1/4	88.0
30-3	12N HNO_3-0.05N HF 0.01N H_2SO_4	14 1/2	97.7
31-1	4N HNO_3-0.1M CAN	3	87.7
31-2	4N HNO_3-0.1M CAN	8 1/4	88.0
31-3	4N HNO_3-0.1M CAN	14 1/4	80.6
32-1	8N HNO_3-$K_2S_2O_8$	3	0.86
32-2	8N HNO_3-$K_2S_2O_8$	7 1/2	0.82
32-3	8N HNO_3-$K_2S_2O_8$	13 1/2	1.89

[a] CAN is abbreviation for ceric ammonium nitrate

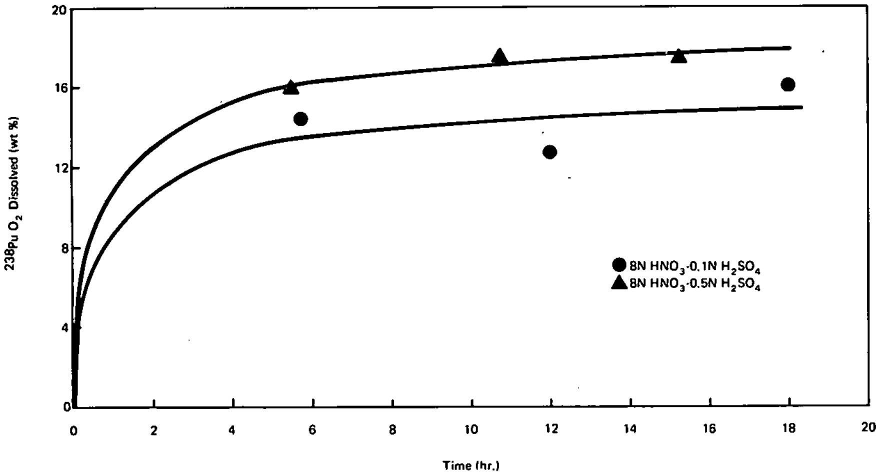

Figure 3 - Effect of H_2SO_4 concentration on dissolution rate.

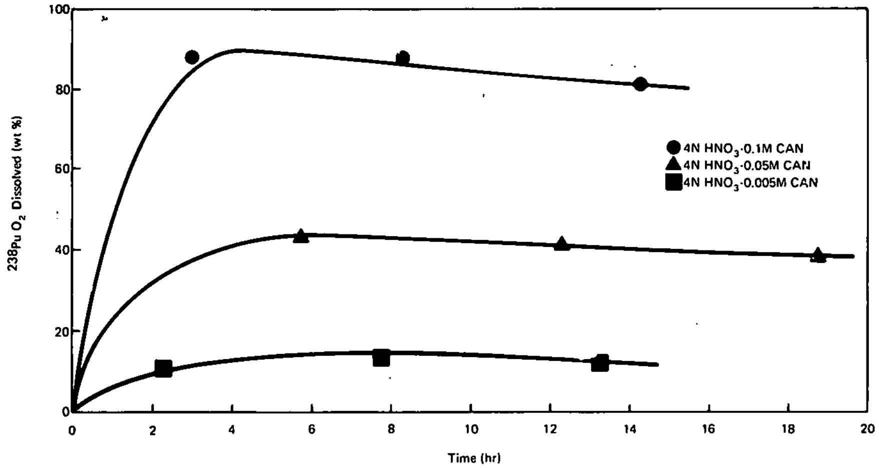

Figure 4 - Effect of ceric ammonium nitrate (CAN) concentration on dissolution rate.

This method does, however, add manganese and potassium to the dissolved salts of the waste stream.

Another experiment was conducted using 8N HNO_3 and $K_2S_2O_8$ (potassium persulphate) as an oxidizing agent (see Table I, acid test 32). After 13½ hr of reaction time at boiling temperature, only 1.89% of the PuO_2 had dissolved. Figure 1 shows that approximately 7.5% of the PuO_2 dissolved in 13½ hr with no additional oxidizing agent present. Thus the $K_2S_2O_8$ actually decreased the dissolution rate of the PuO_2.

Figures 5 and 6 show the effect of the HF concentration on the dissolution rate of PuO_2. For the HNO_3-HF system, a tenfold increase in the HF concentration increases the concentration of dissolved PuO_2 from about 40 wt% to approximately 100 wt% for 9 hr of reaction time (Figure 5). A twofold increase in the HF concentration for the HNO_3-HF-H_2SO_4 system increases the concentration of dissolved PuO_2 from 94 wt% to 100 wt% for 9 hr of reaction time (Figure 6). As can be seen in Table I, any dissolution test in which the HF concentration was 0.05N, or greater, was successful in obtaining a 90 to 100% dissolution of the PuO_2. The effect of sintering temperature on dissolution rate for various reagents can be seen in Figures 7 and 8.

UO_2 and U_3O_8 Dissolution Studies

Contaminated filter media samples were prepared by mixing 0.2 g of either UO_2 or U_3O_8* with 2.8 g of shredded filter media. These samples were combined in a glass round-bottom flask containing 250 ml of the desired leaching solution. The flasks were attached to reflux condensers, and the contents were heated and refluxed at boiling temperatures. Samples were withdrawn periodically, and the uranium concentration of the solution was determined.

Table 2 lists results of dissolution tests for uranium oxide in various acid mixtures; in every test the uranium oxides dissolved rapidly. The percentage of uranium oxide dissolved was always greater than 90%; 8N HNO_3 performed as well as any of the acid mixtures, dissolving essentially 100% of the UO_2 or U_3O_8 after 6 hr of heating. As a comparison, the percentage of PuO_2 dissolved after 6 hr was $\sim$4% (see Figure 1).

PuO_2-75 wt% UO_2 Solid Solution Studies

The solid solution was composed of plutonium** and uranium-238 oxides which had been fired at 1600°C in a reducing atmosphere. Six dissolution tests were performed (see Table III). The powdered PuO_2-UO_2 solid solution was mixed thoroughly with shredded filter media using a ratio of 1 g of solid solution to 12 g of filter media. A small sample of the mixture (approximately 3 g) was added to a glass beaker containing 250 ml of leaching solution. Samples were withdrawn periodically

---

*The U_3O_8 had been fired at 950°C for 2 hr.

**Assay of the plutonium was 85.0 wt% plutonium-239, 12.0% plutonium-240, 1.7% plutonium-241, 0.75% plutonium-238, plus small amounts of other actinides.

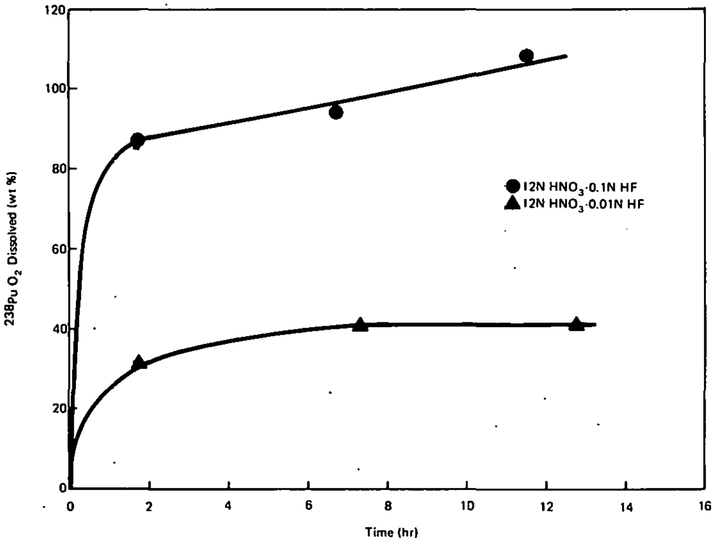

Figure 5 - Effect of HF concentration on dissolution rate of PuO_2.

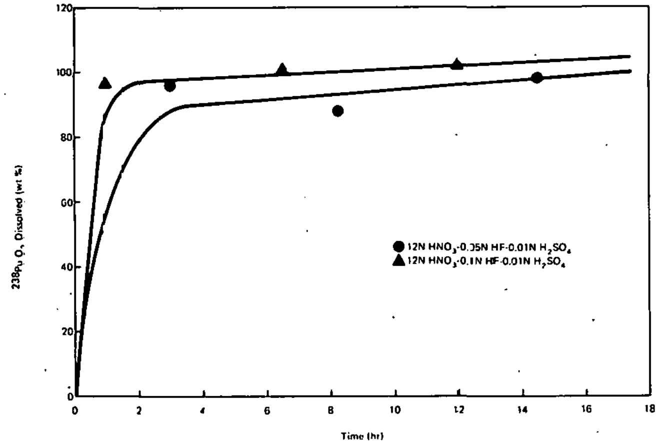

Figure 6 - Effects of HF and H_2SO_4 concentrations on dissolution rates.

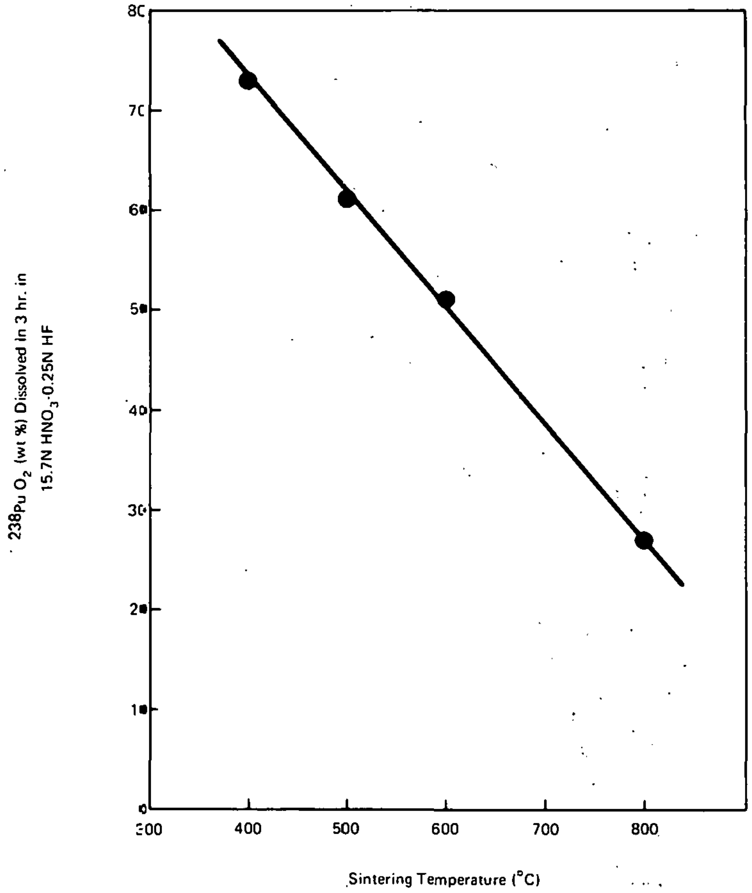

Figure 7 - Effect of sintering temperature on dissolution rate (2).

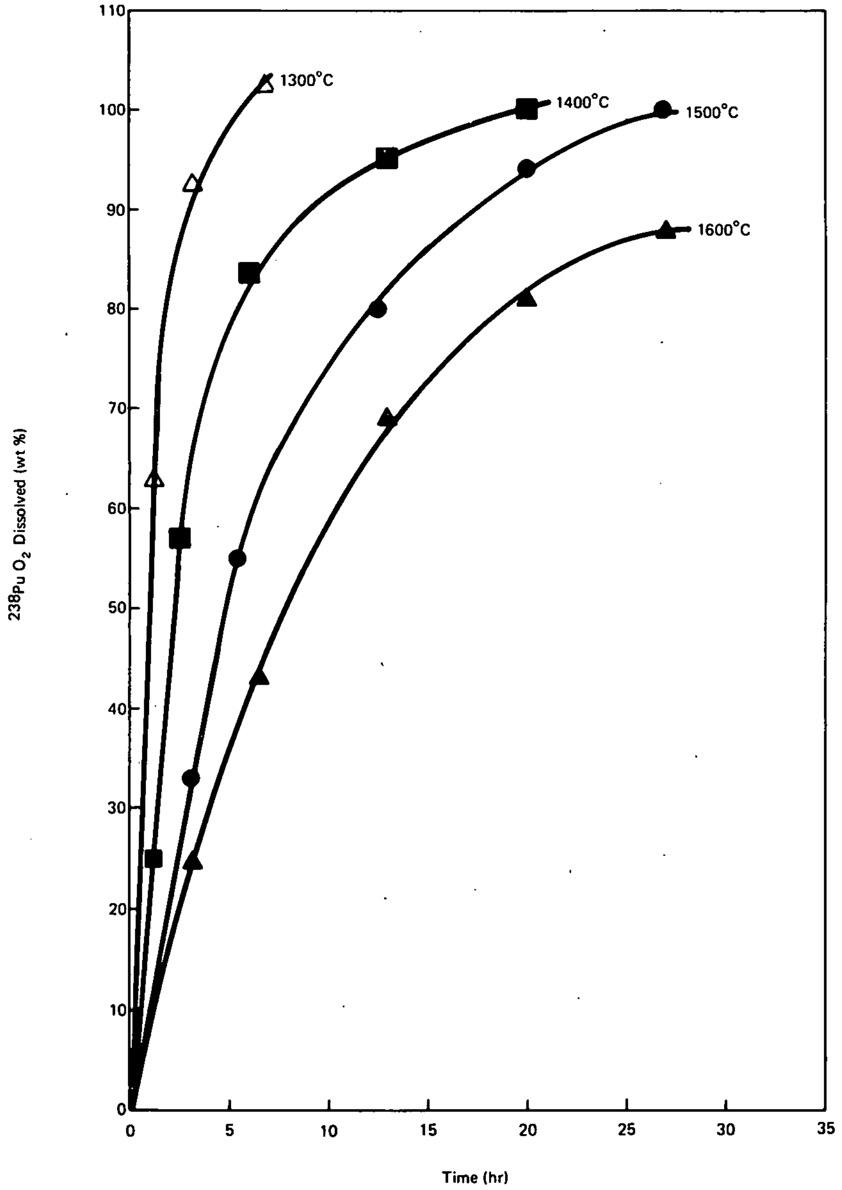

Figure 8 - Effect of sintering temperature on plutonium dioxide dissolution in $4\underline{N}\ HNO_3-0.15\underline{M}$ cerium(IV) (3).

Table II - DISSOLUTION OF URANIUM OXIDES IN VARIOUS ACID MIXTURES

Acid Test Number	Reagent Composition	Time Heated (hr)	UO_2 or U_3O_8 Dissolved (wt %)
UO_2-1-1	$12N\ HNO_3-0.01N\ HF-0.1N\ H_2SO_4$	1/2	92.8
UO_2-1-2	$12N\ HNO_3-0.01N\ HF-0.1N\ H_2SO_4$	6 1/2	94.1
UO_2-2-1	$12N\ HNO_3-0.1N\ HF-0.01N\ H_2SO_4$	1	91.0
UO_2-2-2	$12N\ HNO_3-0.1N\ HF-0.01N\ H_2SO_4$	7	99.6
UO_2-3-1	$12N\ HNO_3-0.1N\ H_2SO_4$	4 3/4	99.3
UO_2-4-1	$8N\ HNO_3$	5 3/4	102.8
U_3O_8-5-1	$8N\ HNO_3$	1	107.0
U_3O_8-6-1	$12N\ HNO_3-0.1N\ H_2SO_4$	1	103.0

and the percentage of solid solution dissolved was determined. The solution volume and concentration were kept constant by adding acid of proper concentration in order to replace evaporated acid.

As can be seen in Table III, four reagents were successful in dissolving greater than 93% of the PuO_2-UO_2 in 2 hr. These were $12\underline{N}\ HNO_3-0.1\underline{N}\ HF$, $12\underline{N}\ HNO_3-0.05\underline{N}\ HF-0.01\underline{N}\ H_2SO_4$, $4\underline{N}\ HNO_3-0.1\underline{M}\ (NH_4)_2Ce(NO_3)_6$, and $8\underline{N}\ HNO_3$. Both the $4\underline{N}\ HNO_3$ and the $4\underline{N}\ HNO_3-0.1\underline{N}\ H_2SO_4$ were unsuccessful in attaining a 90% dissolution even when leaching times of 7 hr were used. Figure 9 shows the effect of HNO_3 concentration on the dissolution rate. Doubling the acid normality (from $4\underline{N}$ to $8\underline{N}$) doubled the percent dissolved (after 2 hr of heating) from 46% to 93%. Therefore, it can be concluded that $8\underline{N}\ HNO_3$, $12\underline{N}\ HNO_3-0.1\underline{N}\ HF$, $12\underline{N}\ HNO_3-0.05\underline{N}\ HF-0.01\underline{N}\ H_2SO_4$, and $4\underline{N}\ HNO_3-0.1\underline{M}\ (NH_4)_2Ce(NO_3)_6$ would be acceptable leaching reagents for PuO_2-UO_2 solid solution whereas $4\underline{N}\ HNO_3$ and $4\underline{N}\ HNO_3-0.1\underline{N}\ H_2SO_4$ are unacceptable.

Salt Fusion Studies

Sodium carbonate and $Na_2CO_3-KNO_3$ fusions were completed using PuO_2* contaminated filter media. Small samples were prepared by thoroughly mixing 0.1 g PuO_2 and 1.5 g of filter media. Approximately 13 g of salt (Na_2CO_3 or $Na_2CO_3-KNO_3$) was placed in a platinum crucible and 1.6 g of contaminated filter media was then added. This was mixed thoroughly and then heated slowly to 950°C. The crucible and contents were maintained at 950°C for 1 hr and then allowed to cool slowly to ambient temperature. The cooled melt was then removed from the crucible and dissolved in $4\underline{N}\ HNO_3$. The acid was maintained at boiling temperature for at least 1 hr and subsequently sampled for plutonium-238 concentration. Table IV tabulates the results achieved in these

---

*The PuO_2 was a fine powder, having a composition of 80 wt% plutonium-238, 16% plutonium-239, 2.5% plutonium-240, 0.8% plutonium-241, 0.2% plutonium-242, plus small amounts of other actinides, calcined at 950°C.

Table III - PuO_2-UO_2 Solid Solution Dissclution

Acid Test Number	Reagent Composition	Time Heated (hr)	PuO_2-UO_2 Dissolved (wt %)
Pu-U-1	12N HNO_3-0.1N HF	2	100.0
Pu-U-2	12N HNO_3-0.05N HF-0.01N H_2SO_4	2	97.6
Pu-U-3	4N HNO_3-0.1M CAN[*]	2	94.8
Pu-U-4A	8N HNO_3	1	71.8
Pu-U-4B	8N HNO_3	2	93.2
Pu-U-5A	4N HNO_3	2-1/2	49.6
Pu-U-5B	4N HNO_3	4-1/2	54.2
Pu-U-5C	4N HNO_3	7	60.0
Pu-U-6	4N HNO_3-0.1N H_2SO_4	3-3/4	80.2

[*]Abbreviation for ceric ammonium nitrate.

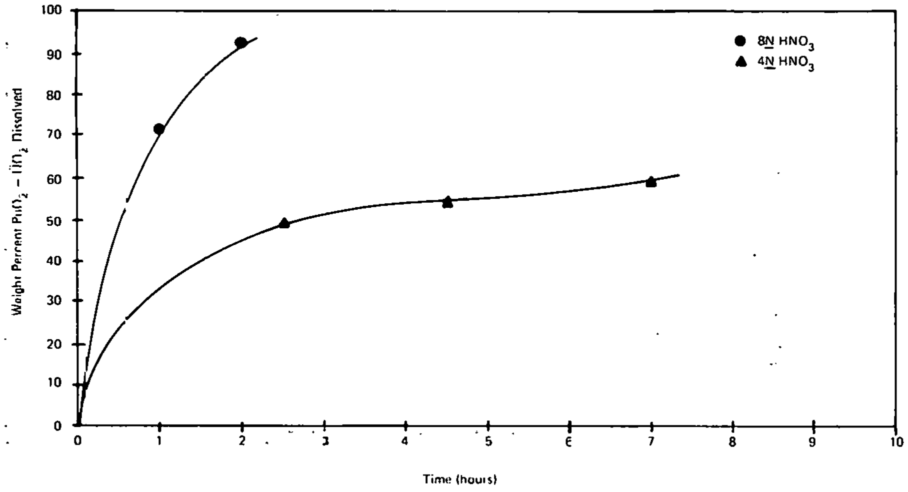

Figure 9 - Effect of HNO_3 concentration on dissolution rate of PuO_2.

Table IV - Na_2CO_3-KNO_3 Fusion of PuO_2

Fusion Test Number	Salt Composition (wt %)	Time Heated (hr)	Operating Temperature (°C)	PuO_2 Solubilized (wt %)
Pu-38	100% Na_2CO_3	1	950	8.83
Pu-39	Na_2CO_3-8% KNO_3	1	950	27.8
Pu-40	Na_2CO_3-16% KNO_3	1	950	48.7
Pu-41	Na_2CO_3-30% KNO_3	1	950	71.0

fusion experiments. As can be seen, the maximum percent of dissolution obtained was 71% using a salt mixture of Na_2CO_3-30 wt% KNO_3.

Figure 10 shows the effect of potassium nitrate composition on PuO_2 solubility. The effect is linear between zero and 16% KNO_3 and nonlinear at higher potassium nitrate concentrations. Also because of time limitations, only three Na_2CO_3-KNO_3 fusions were performed and the maximum concentration of potassium nitrate used was 30 wt%. It should be noted that the greater the concentration (wt%) of potassium nitrate, the more vigorous the reaction.

The temperature must be raised slowly in order to prevent the contents of the crucible from spilling over. The 71% recovery obtained using Na_2CO_3-30 wt% KNO_3 is considered unsatisfactory for our purposes. The dissolution must be greater than 90% in order to achieve large decontamination factors. Perhaps by using greater than 30% KNO_3 this result can be achieved.

Dissolution of Actual HEPA Glovebox Filter Media

Small test samples of approximately 3 g each were removed from an actual glovebox filter contaminated with PuO_2*. Each sample contained approximately 55 mg of plutonium-238. These samples were placed in a glass beaker containing 100 ml of leaching reagent. The leaching agents used were 4N HNO_3-0.1M ceric ammonium nitrate and 12N HNO_3-0.05N HF-0.01N H_2SO_4. The tests were performed at boiling temperatures. The contents of the beakers were stirred every hour, and samples were withdrawn periodically for plutonium analysis. The solution volume and acid concentration were kept constant by adding acid of proper concentration in order to replace evaporated acid. Table V contains the results obtained in these experiments. The average PuO_2 dissolution was 92.5 wt% using 4N HNO_3-0.1M $(NH_4)_2Ce(NO_3)_6$ and 93.3 wt% using 12N HNO_3-0.05N HF-0.01N H_2SO_4. These compare well with the average dissolution percentages found for simulated filter media samples listed in Table I (85.4% and 93.9% respectively). Figure 11 is a graph of the dissolution rate for PuO_2 in

---

*The PuO_2 was a fine powder, having a composition of 80 wt% plutonium-238, 16% plutonium-239, 2.5% plutonium-240, 0.8% plutonium-241, 0.2% plutonium-242, plus small amounts of other actinides, calcined at 950°C.

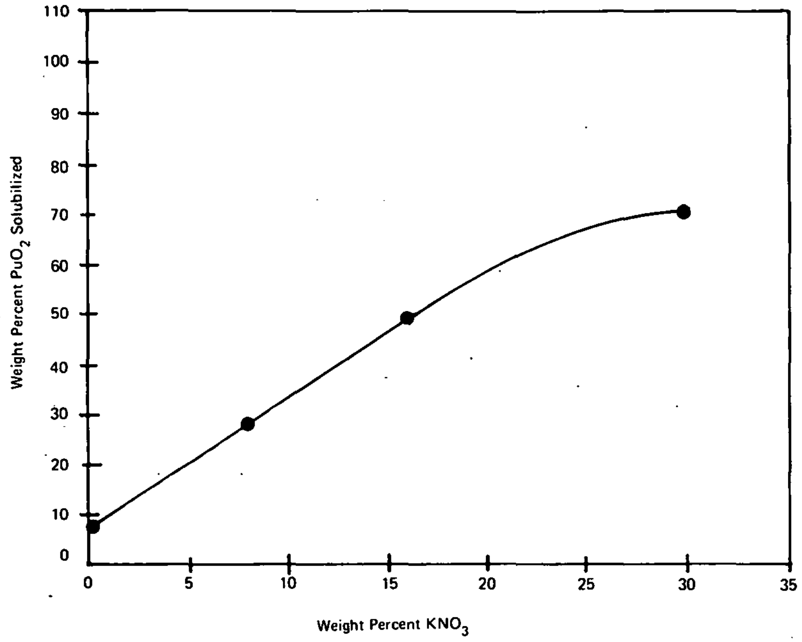

Figure 10 - Effect of salt composition on percent PuO_2 solubilized.

12N HNO_3-0.05N HF-0.01N H_2SO_4. It shows that the dissolution reaction is rapid, with approximately 90% of the PuO_2 dissolved in 4 hr.

Larger samples (40 g) of actual HEPA filter were treated with 12N HNO_3-0.05N HF-0.01N H_2SO_4. These experiments were conducted similarly to those previously described (using 3-g samples) except that different ratios of acid volume (liters) to plutonium-238 weight (grams) were used. Also the filter media were processed through several successive, identical stages in an attempt to obtain the greatest overall decontamination factor (see Table VI and Figure 12). As can be seen in Figure 6, a value of 0.67 for the ratio of acid volume:PuO_2 weight yields a 99.35% dissolution in five stages. On the other hand, a volume:weight ratio of 2.35 produces a 99.53% dissolution in three stages. Thus the decontamination factor is 154 for the lower volume: weight ratio and 213 for the higher ratio. These final dissolution percentages and decontamination factors were determined by calorimetry and gamma counting of the final filter media residues. All other dissolution percentages and decontamination factors were determined by alpha counting of solution samples.

The fact that a higher volume of acid:weight of PuO_2 ratio produces a higher dissolution is explained as follows: The HF in the

Table V - Dissolution of Small Samples of Actual HEPA Filters

Acid Test Number	Reagent Composition	Time Heated (hr)	PuO_2 Dissolved (wt %)	Acid/Pu-238 Ratio (liters/grams)
3265-3A	4N HNO_3-0.1M CAN	3-1/2	103.2	1.84
3265-3B	4N HNO_3-0.1M CAN	5	103.3	1.84
3265-3C	4N HNO_3-0.1M CAN	11-3/4	81.9	1.84
3265-3D	4N HNO_3-0.1M CAN	14-3/4	81.5	1.84
3265-4A	12N HNO_3-0.05N HF-0.01N H_2SO_4	3-1/2	96.9	1.83
3265-4B	12N HNO_3-0.05N HF-0.01N H_2SO_4	5	89.1	1.83
3265-4C	12N HNO_3-0.05N HF-0.01N H_2SO_4	12-1/2	93.9	1.83

*Abbreviation for ceric ammonium nitrate - $(NH_4)_2Ce(NO_3)_6$.

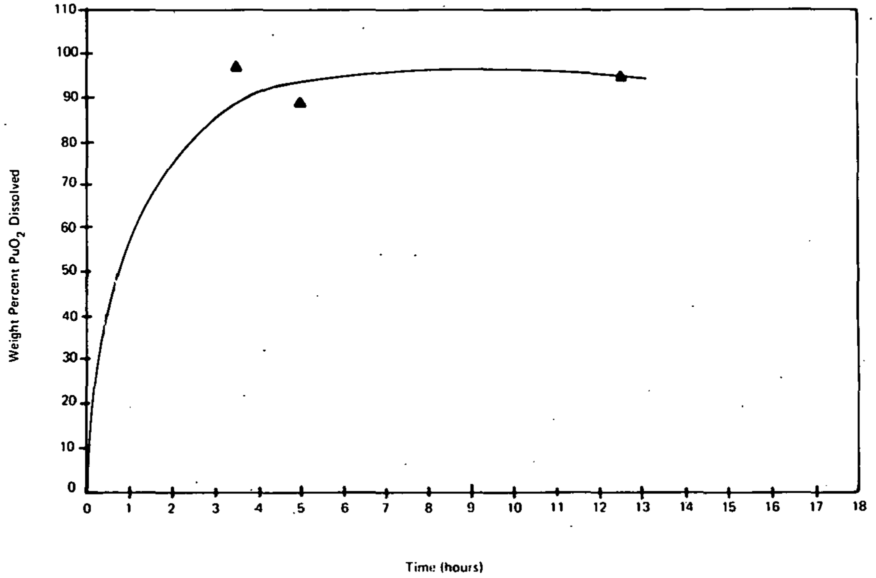

Figure 11 - Dissolution rate of PuO_2 in 12N HNO_3-0.05N HF-0.01N H_2SO_4.

Table VI - $12N\ HNO_3$-$0.05N\ HF$-$0.01N\ H_2SO_4$
Dissolution of Large Samples of Actual HEPA Filters

Acid Test Number	Stage	Cumulative PuO_2 Dissolved (wt %)	Acid/Pu-238 Ratio (liters/g)	Time Heated (hr)
3265-7-1	1	84.9	0.67	3-1/2
3265-7-2	2	88.9	0.67	5-1/4
3265-7-3	3	93.3	0.67	5-3/4
3265-7-4	4	95.8	0.67	7-1/4
3265-7-5	5	99.35	0.67	6-1/2
3265-9-1	1	94.2	2.35	10-1/2
3265-9-2	2	97.6	2.35	10-3/4
3265-9-3	3	99.53	2.35	7

leaching solution is reacting with both PuO_2 particles and glass present in the filter media. When a small amount of leachant is added to a relatively large amount of contaminated filter media, the fluoride ion concentration of the solution is quickly depleted as SiF_4 gas is produced. The remaining HF is not sufficient to dissolve 90% of the PuO_2 present, as desired. Conversely, if a large amount of leachant is added to the same amount of contaminated filter media, there is sufficient HF present to react with the glass and dissolve 90% (or greater) of the PuO_2. What is needed, therefore, is a larger amount of HF in the first stage of the process. This could be accomplished using a larger volume of $12N\ HNO_3$-$0.05N\ HF$-$0.01N\ H_2SO_4$ or a higher concentration of HF in the acid mixture. For the subsequent stages, an HF concentration of 0.05N should be sufficient since most of the glass has reacted.

Dissolution of PuO_2* in $4N\ HNO_3$-$0.15M\ (NH_4)_2Ce(NO_3)_6$

A contaminated filter media sample was prepared by mixing 0.16 g of plutonium dioxide with 3 g of shredded filter media. This sample was placed into a glass beaker containing 250 ml of $4N\ HNO_3$-$0.15M$ ceric ammonium nitrate. The beaker and contents were heated to boiling. Samples were withdrawn periodically and analyzed for plutonium concentration. The solution volme and concentration were kept constant by adding acid of proper concentration in order to replace evaporated acid. Figure 13 shows the effect of Ce^{+4} concentration on plutonium dioxide dissolution rate. The $4N\ HNO_3$-$0.10M\ (NH_4)_2Ce(NO_3)_6$ curve is drawn from data contained in Figure 4. It should be noted that a 50% increase in the Ce^{+4} concentration results in a 10% increase in weight percent plutonium dissolved.

---

*The PuO_2 was a fine powder, having a composition of 80 wt% plutonium-238, 16% plutonium-239, 2.5% plutonium-240, 0.8% plutonium-241, 0.2% plutonium-242, plus small amounts of other actinides, calcined at 950°C.

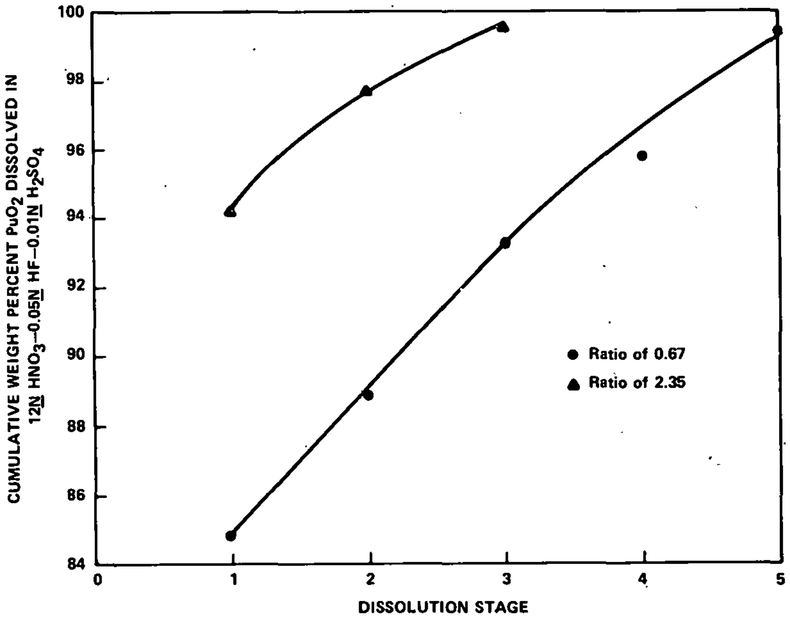

Figure 12 - Effect of acid volume:PuO_2 weight ratio on dissolution percentage.

Americium-241 and Plutonium-239* Mixed Oxide Dissolution Studies

Contaminated filter media was prepared by mixing AmO_2-PuO_2 powder with shredded filter media. Small samples of this mixture were then treated with various leaching agents, including $4N\ HNO_3$-$0.1M\ (NH_4)_2Ce(NO_3)_6$, $12N\ HNO_3$-$0.05N\ HF$-$0.01N\ H_2SO_4$, and $8N\ HNO_3$. A sample of filter media was placed in a beaker, 250 ml of the leaching agent was added, and the temperature was increased to the boiling point of the solution. Samples were withdrawn periodically and filtered through a 4-5 μm glass filter. The americium-241 and plutonium-239 concentrations were determined by alpha spectrometry. The solution volume and concentration were kept constant by adding acid of the proper concentration to replace evaporated acid. As can be seen in Table VII, the $4N\ HNO_3$-$0.1M\ (NH_4)_2Ce(NO_3)_6$ was an effective leaching agent, dissolving

---

* This material was approximately three parts plutonium-239 oxide mixed with one part americium-241 oxide by weight. It had been fired for 2 hr at 1000°C.

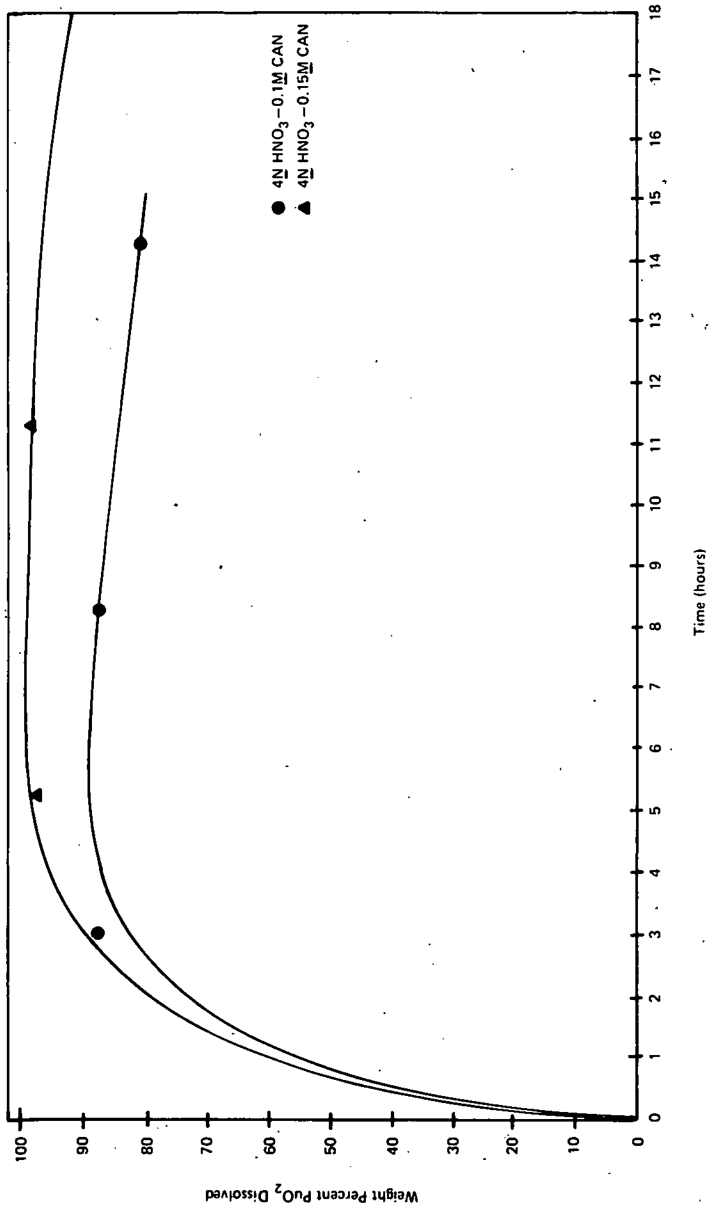

Figure 13 - Effect of ceric ammonium nitrate concentration on PuO_2 dissolution rate.

Table VII - AmO_2-PuO_2 DISSOLUTION TESTS

Acid Test Number	Reagent Composition	Time Heated (hr)	PuO_2 Dissolved (wt%)	AmO_2 Dissolved (wt%)
Am-Pu-1A	4N HNO_3-0.1M CAN*	5 3/4	72.9	63.2
Am-Pu-1B	4N HNO_3-0.1M CAN*	11 3/4	93.7	111.8
Am-Pu-2A	12N HNO_3-0.05N HF-0.01N H_2SO_4	5 3/4	68.9	72.4
Am-Pu-2B	"	11 1/4	80.2	90.4
Am-Pu-4A	8N HNO_3	7 1/4	37.2	88.9
Am-Pu-4B	"	13 1/2	36.3	96.7

*CAN is an acronym for ceric ammonium nitrate.

greater than 90% of both AmO_2 and PuO_2 in 11-3/4 hr. On the other hand, the 8N HNO_3 was not a satisfactory leaching agent since only 36% of the PuO_2 dissolved in 13½ hr, although 97% of the AmO_2 dissolved during this time (see Figure 14). The mixture of HNO_3-HF-H_2SO_4 was effective in dissolving the AmO_2 (90% in 11-1/4 hr) but not as effective in dissolving the PuO_2 (80% in 11-1/4 hr). Of the three reagents tested, the 4N HNO_3-0.1M $(NH_4)_2Ce(NO_3)_6$ is the recommended leaching agent for mixtures of AmO_2-PuO_2.

Uranium-233 Oxide Dissolution Studies

These studies were conducted using U_3O_8 mixed with filter media. The oxide had been fired at 950°C for 2 hr. A small sample of the prepared filter media (approximately 3.2 g) was placed into a beaker containing 250 ml of boiling reagent. The reagents used were 8N HNO_3, 4N HNO_3-0.1M $(NH_4)_2Ce(NO_3)_6$, and 12N HNO_3-0.05N HF-0.01N H_2SO_4. Samples were withdrawn periodically for alpha analysis. All samples were filtered through 4-5 µm glass filters. The solution volume and concentration were kept constant by adding acid of the proper concentration to replace evaporated acid. As can be seen from Table VIII, in all three cases the dissolution was very rapid and exceeded 90%. For example, the dissolution rate in 8N HNO_3 is depicted in Figure 15. All three reagents would be acceptable dissolution reagents for uranium-233 oxide.

Sodium Carbonate Fusion of PuO_2*

These studies were conducted in order to determine the effect of temperature on fusion efficiency. Small samples were prepared by mixing 64 mg of PuO_2 with 2.25 g of Na_2CO_3. The PuO_2-Na_2CO_3 mixture was then placed into a platinum crucible and contents were then heated to the desired operating temperature (1200°C and 1300°C) and maintained

---

*The PuO_2 was a fine powder having a composition of 80 wt% plutonium-238, 16 wt% plutonium-239, 2.5 wt% plutonium-240, 0.8 wt% plutonium-241, 0.2 wt% plutonium-242, plus small amounts of other actinides. It was calcined for 2 hr at 950°C.

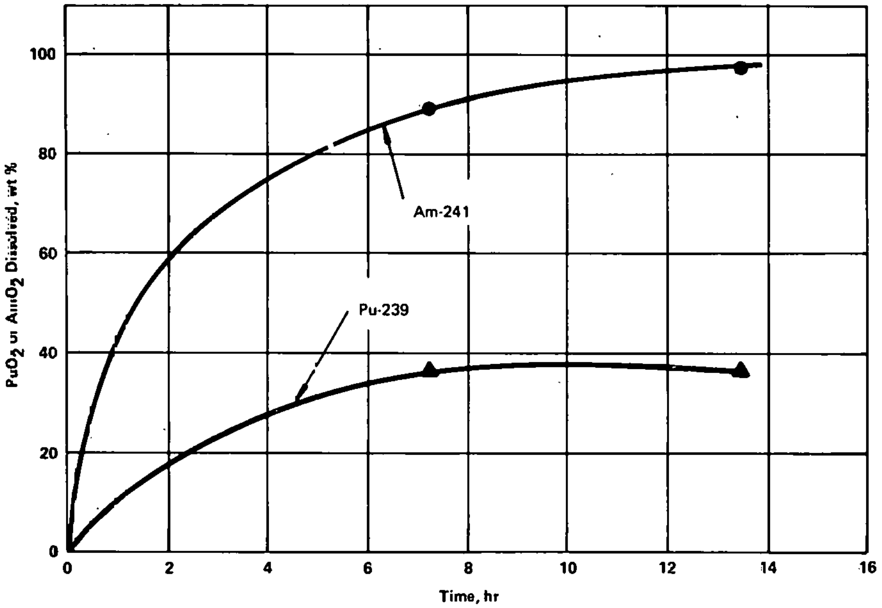

Figure 14 - Dissolution rate of Am^{241}-Pu^{239} oxides in 8N HNO_3.

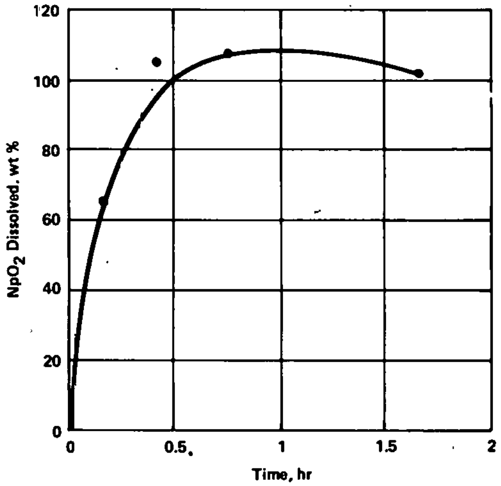

Figure 15 - Dissolution rate of U_3O_8 in 8N HNO_3.

Table VIII - U-233 OXIDE DISSOLUTION TESTS

Acid Test Number	Reagent Composition	Time Heated (min)	U-233 Oxide Dissolved (wt%)
U-3-1	8N HNO_3	5	97.4
U-3-2	"	20	106.1
U-3-3	"	65	93.8
U-3-4	"	255	95.9
U-4-1	4N HNO_3-0.1M CAN*	5	89.7
U-4-2	"	15	104.8
U-4-3	"	60	95.2
U-4-4	"	360	95.7
U-5-1	12N HNO_3-0.05N HF- 0.01N H_2SO_4	5	100.9
U-5-2	"	15	106.2
U-5-3	"	50	100.1
U-5-4	"	240	102.5

*CAN is an acronym for ceric ammonium nitrate.

there for 1 hr. The crucible and melt were cooled to room temperature, and the melt was removed from the crucible and dissolved in 4N HNO_3. As can be seen in Table IX, there is not a significant difference (4.6%) in the two dissolution percentages and it is probable that the difference is due to experimental error. Therefore, it can be concluded that within the temperature range under investigation, the fusion efficiency is approximately 58% (average value).

Neptunium-237 Oxide Dissolution Studies

The NpO_2 was fired for 2 hr at 950°C. Samples of contaminated filter media were prepared by mixing 0.2 g of NpO_2 with 3 g of filter media. The procedure was identical to that used in the uranium-233 oxide dissolution studies. The following three leaching reagents were tested: 8N HNO_3, 4N HNO_3-0.1M $(NH_4)_2Ce(NO_3)_6$, and 12N HNO_3-0.05N HF-0.01N H_2SO_4. Table X lists the results from these experiments. As can be seen, the 8N HNO_3 was unsuccessful in dissolving the NpO_2 rapidly with only 32% solubilized in 8 hr. On the other hand, each of the other two reagents dissolved the NpO_2 rapidly with greater than 90% dissolved after 1/2 hr of boiling (see Figure 16 for dissolution percentage as a function of time). Therefore, both the 4N HNO_3-0.1M $(NH_4)_2Ce(NO_3)_6$ and the 12N HNO_3-0.05N HF-0.01N H_2SO_4 acid mixtures would be recommended for dissolution of NpO_2 from filter media.

Table IX - Na_2CO_3 FUSIONS OF PuO_2

Fusion Test Number	Time Heated (hr)	Operating Temperature (°C)	PuO_2 Solubilized (wt%)	Dissolution Reagent
Pu-44	1	1300°C	56.4	4N HNO_3
Pu-45	1	1200°C	61.0	4N HNO_3

Table X - Np-237 OXIDE DISSOLUTION TESTS

Acid Test Number	Reagent Composition	Time Heated (min)	NpO_2 Dissolved (wt%)
Np-3-1	8N HNO_3	10	1.3
Np-3-2	"	25	1.9
Np-3-3	"	45	4.1
Np-3-4	"	75	6.1
Np-3-5	"	480	32.3
Np-4-1	4N HNO_3-0.1M CAN*	10	93.7
Np-4-2	"	25	97.2
Np-4-3	"	40	88.9
Np-4-4	"	60	89.1
Np-5-1	12N HNO_3-0.05N HF-0.01N H_2SO_4	10	64.7
Np-5-2	"	25	105.2
Np-5-3	"	45	107.4
Np-5-4	"	100	102.3

*CAN is an acronym for ceric ammonium nitrate.

Curium-244* Oxide Dissolution Studies

Contaminated filter media were prepared by mixing 13 mg of CmO_2 with 3 g of filter media. The experimental procedures were identical to those used for the uranium-233 dissolution studies. The two leaching reagents tested were 12N HNO_3-0.05N HF and 4N HNO_3-0.1M $(NH_4)_2Ce(NO_3)_6$. The results of these tests, listed in Table XI, show that both reagents dissolved the CmO_2 very rapidly (essentially 100% dissolution in 10 min). Figure 17 shows the dissolution rate for 4N HNO_3-0.1M $(NH_4)_2Ce(NO_3)_6$. Both reagents are recommended for dissolution of CmO_2 from contaminated filter media.

---

*This was a powder which was approximately 94% curium-244 and 4% curium-246, the remainder being curium-245, -247, and -248.

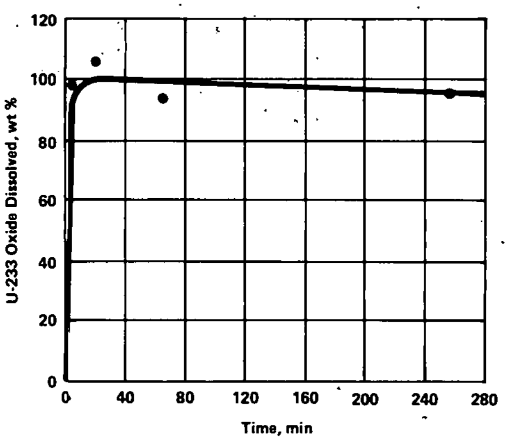

Figure 16 - Dissolution rate of Np-237 oxide in 12N HNO_3-0.05N HF-0.01N H_2SO_4.

Table XI - Cm-244 OXIDE DISSOLUTION TESTS

Acid Test Number	Reagent Composition	Time Heated (min)	CmO_2 Dissolved (wt%)
Cm-2A	12N HNO_3-0.05N HF	10	103.3
Cm-2B	"	25	100.8
Cm-2C	"	60	105.0
Cm-2D	"	120	99.1
Cm-2E	"	180	104.5
Cm-2F	"	540	93.3
Cm-2G	"	540	99.0
Cm-3A	4N HNO_3-0.1M CAN*	10	112.1
Cm-3B	"	25	110.0
Cm-3C	"	60	109.0
Cm-3D	"	120	107.6
Cm-3E	"	330	110.5

*CAN is an acronym for ceric ammonium nitrate.

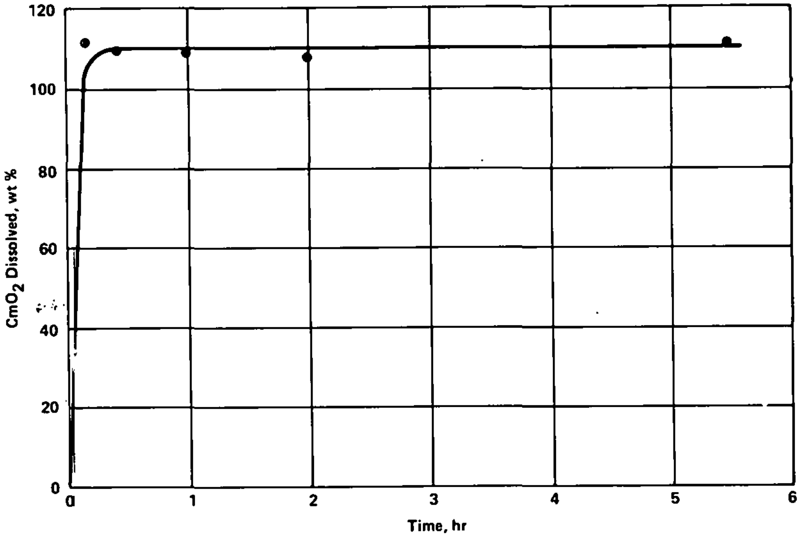

Figure 17 - Dissolution rate of CmO$_2$ in $4\underline{N}$ HNO$_3$-0.1$\underline{M}$ (NH$_4$)$_2$Ce(NO$_3$)$_6$.

Thorium-232 Oxide Dissolution Tests

Contaminated filter media were prepared by mixing 0.24 g of ThO$_2$ with 3 g of filter media. The experimental procedure was identical to that used in the uranium-233 oxide studies. The ThO$_2$ was a fine powder which had been fired at 500°C. The purpose of the experiment was to determine whether ThO$_2$ would dissolve in $4\underline{N}$ HNO$_3$-0.1$\underline{M}$ (NH$_4$)$_2$Ce(NO$_3$)$_6$ similarly to other actinide oxides previously tested (PuO$_2$, CmO$_2$, AmO$_2$, U$_3$O$_8$, and NpO$_2$). As shown by the data in Table XII and Figure 18, the dissolution rate was slow at first (0-7 hr), rapid from 7 to 9 hr, and slow again from 9 to 20 hr. The reason for this is not known at this time, but it is thought that it took 7 hr to attack the surface of the ThO$_2$ and open the pores so that rapid dissolution could begin. It therefore appears that $4\underline{N}$ HNO$_3$-0.1$\underline{M}$ (NH$_4$)$_2$Ce(NO$_3$)$_6$ would be an acceptable leaching agent for ThO$_2$ from filter media, although dissolution time is longer than for other actinides.

A point of interest is that in a similar experiment using just ThO$_2$ (no filter media), the dissolution percentage obtained was only 25% after 20 hr of boiling. The reason for the difference in dissolution percentages (25% versus 100%) is that the filter media contains 0.14 wt% F^{-1}. This small amount of fluoride ion has been found to be sufficient to catalyze the dissolution reaction.

Dissolution of PuO$_2$ from Actual Glovebox Filters

These tests were conducted using samples of filter media removed from actual spent glovebox filters. The PuO$_2$ on the filters was the same type as that used in the fusion experiments.

Table XII - ThO$_2$ DISSOLUTION DATA

Acid Test Number	Reagent Composition	Time Heated (min)	ThO$_2$ Dissolved (wt%)
Th-1	4N HNO$_3$-0.1M CAN*	5	0.6
Th-2	"	10	0.4
Th-3	"	20	1.4
Th-4	"	35	2.4
Th-5	"	60	5.1
Th-6	"	180	4.7
Th-7	"	300	12.5
Th-8	"	440	31.7
Th-9	"	440	29.3
Th-10	"	470	42.1
Th-11	"	545	82.3
Th-12	"	905	100.5
Th-13	"	1205	104.3

*CAN is an acronym for ceric ammonium nitrate.

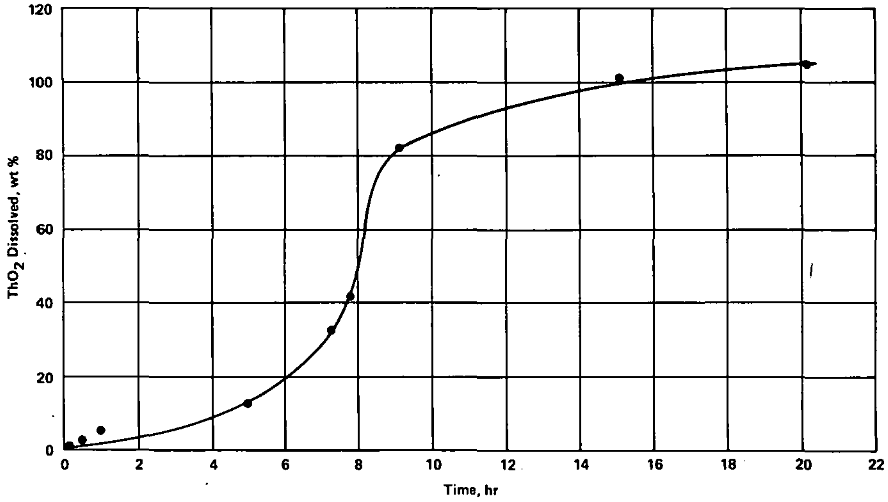

Figure 18 - Wt % ThO$_2$ dissolved in $4\underline{N}$ HNO$_3$-0.1M (NH$_4$)$_2$Ce(NO$_3$)$_6$.

Experiment A

A 9.5 g sample of filter media containing 0.18 g of PuO_2 was dissolved in a six-stage dissolution procedure. The leaching reagent in the first five stages was 170 ml of 4N HNO_3- 0.23M $(NH_4)_2Ce(NO_3)_6$, and the sixth stage contained 12N HNO_3-0.1N HF. The 12N HNO_3-0.1N HF was used because the 4N HNO_3-0.23M $(NH_4)_2Ce(NO_3)_6$ had proved ineffective in the fifth stage of dissolution. The volume of 12N HNO_3-0.1N HF used was 250 ml and all studies were done at boiling temperature. The solution was sampled periodically for plutonium concentration, and all samples were filtered through 4-5 µm glass filters. When the dissolution rate for a particular stage had become very slow (as indicated by α analysis of solution), the filter media were separated from the leaching solution by filtration and placed in the next stage of dissolution.

Results for this experiment are given in Table XIII. Figures 19 through 21 show the dissolution rate for each stage, and Figure 22 shows the cumulative PuO_2 dissolution percentage for the six-stage process. It should be noted that final dissolution percentage was 99.88% (a contamination factor of 833). This was determined by gamma ray spectrometry of the residual filter media and agrees well with the final value as determined by alpha counting of the solution samples (99.80%). It should also be noted that the 12N HNO_3-0.1N HF solution used in the sixth stage was more than twice as effective as the 4N HNO_3-0.1M $(NH_4)_2Ce(NO_3)_6$ used in the fifth stage (0.079% dissolved versus 0.031%). The reason for this is not understood at this time. More studies will be done to investigate this phenomenon.

Experiment B

A 25.6 g sample of filter media containing 0.31 g of PuO_2 was dissolved in a four-stage dissolution process. The leaching reagent used in the test was 460 ml of 4N HNO_3-0.3M $(NH_4)_2Ce(NO_3)_6$. The experimental procedure was identical to that used in Experiment A of this section. The results for this experiment are given in Table XIV; Figure 23 shows the cumulative PuO_2 dissolution percentage for the four stage process. The dissolution percentages in Table XIV were determined by alpha counting, but the cumulative percentages used in Figure 23 were based on a final gamma spectrometry value of 98.24%. This latter value compares well with the value of 97.62% obtained by alpha counting. The gamma value is, however, considered more accurate than the total obtained by simple addition of the individual alpha count values. The decontamination factor obtained using this gamma value is 88.5. The decontamination factor obtained after four stages in Experiment A of this section was 417.

A logical question would be: Why was the decontamination factor less when more ceric ammonium nitrate per mole of PuO_2 was used? It is known that the 25.6 g sample filter media contained a greater percentage of pack-to-frame sealant* than the 9.5-g sample. It is also

---

*This is the material that is used to seal the asbestos-glass filter pack to the wooden frame. It is a fire retardant polyurethane foam and a rubber base adhesive.

TableXIII- PuO_2 DISSOLUTION DATA (9.5-g sample)

Acid Test Number	Reagent Composition	Time Heated (min)	PuO_2 Dissolved (wt%)	Process Stage
256-1 A	4N HNO_3-0.23M CAN*	10	82.0	1
256-2 A	"	20	79.5	1
256-3 A	"	40	87.3	1
256-4 A	"	60	80.9	1
256-5 A	"	120	85.8	1
256-6 A	"	210	90.6	1
256-1 B	"	10	0.41	2
256-2 B	"	20	1.17	2
256-3 B	"	45	2.50	2
256-4 B	"	65	2.97	2
256-5 B	"	120	4.75	2
256-6 B	"	360	7.30	2
256-7 B	"	510	7.47	2
256-1 C	"	30	0.29	3
256-2 C	"	75	0.55	3
256-3 C	"	135	0.87	3
256-4 C	"	315	1.06	3
256-5 C	"	435	1.09	3
256-6 C	"	675	1.31	3
256-7 C	"	675	1.39	3
256-1 D	"	20	0.029	4
256-2 D	"	45	0.063	4
256-3 D	"	60	0.079	4
256-4 D	"	135	0.139	4
256-5 D	"	330	0.213	4
256-6 D	"	645	0.222	4
256-7 D	"	645	0.228	4
256-1 E	"	15	0.011	5
256-2 E	"	30	0.012	5
256-3 E	"	60	0.015	5
256-4 E	"	135	0.023	5
256-5 E	"	195	0.025	5
256-6 E	"	465	0.029	5
256-7 E	"	600	0.031	5
256-8 E	"	780	0.032	5
256-9 E	"	780	0.025	5
256-1 F	12N HNO_3-0.1N HF	30	0.016	6
256-2 F	"	60	0.030	6
256-3 F	"	240	0.047	6
256-4 F	"	585	0.079	6
256-5 F	"	945	0.075	6

*CAN is an acronym for $(NH_4)_2Ce(NO_3)_6$.

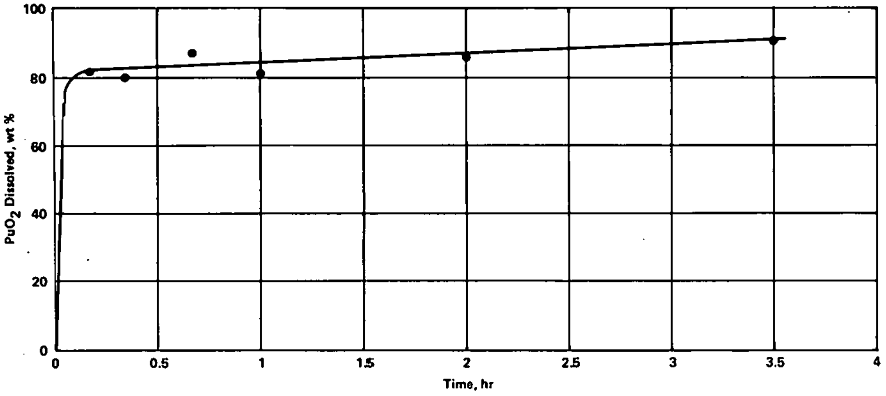

Figure 19 - Dissolution rate of PuO_2 from filter media (1st stage).

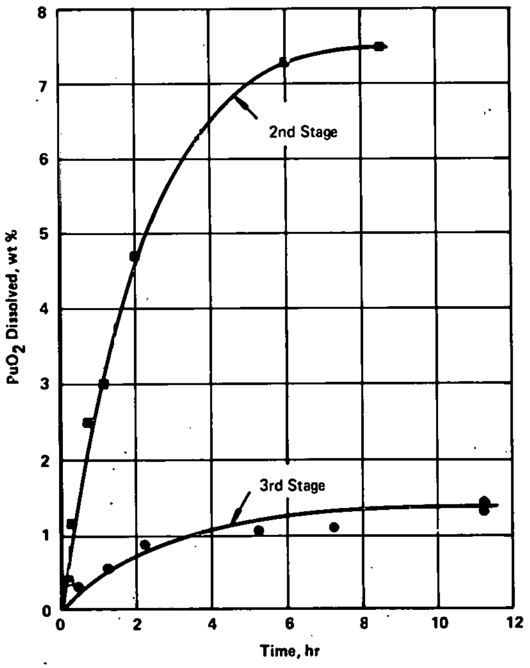

Figure 20 - Dissolution of PuO_2 from filter media (2nd and 3rd stage).

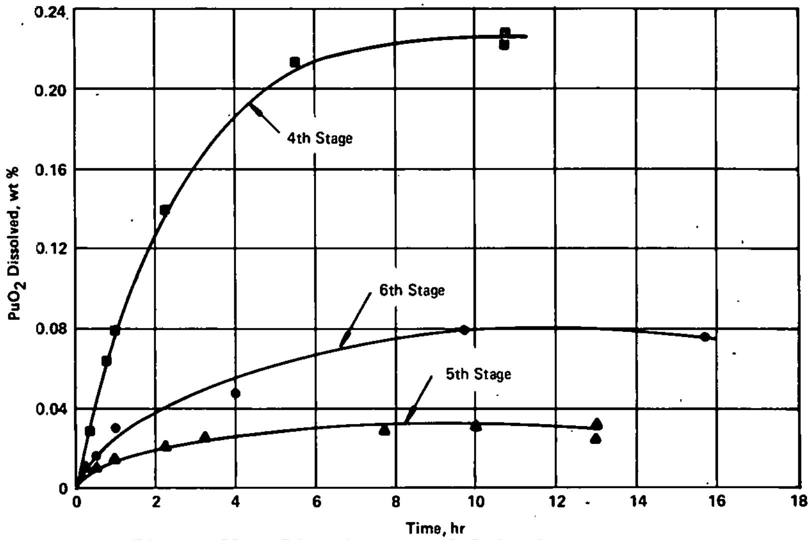

Figure 21 - Dissolution of PuO_2 from filter media (4th, 5th, and 6th stage).

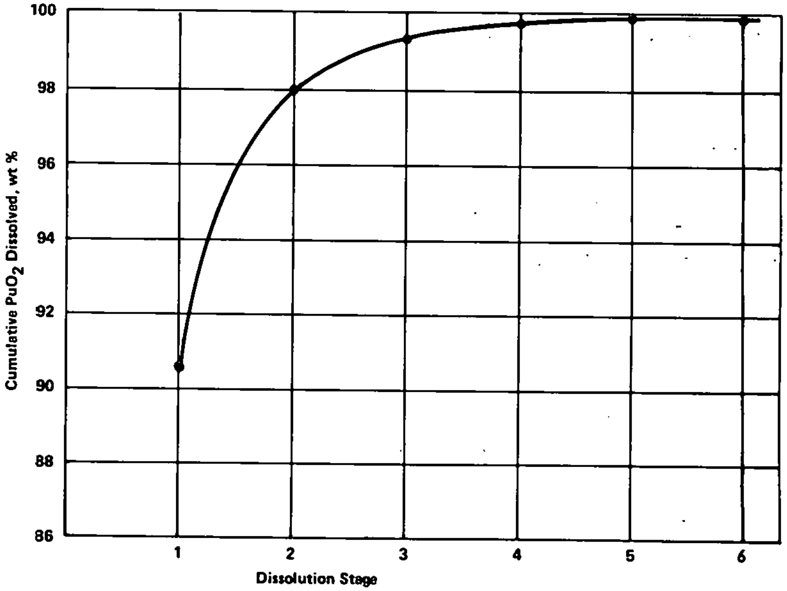

Figure 22 - Cumulative wt % PuO_2 dissolved during six-stage process.

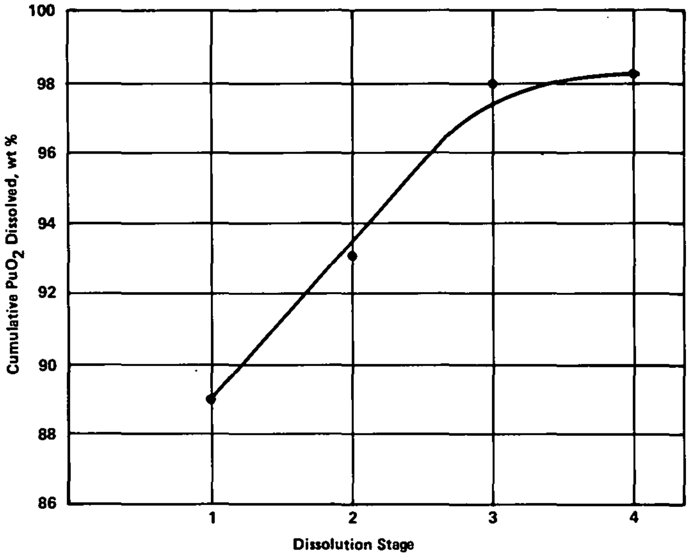

Figure 23 - Cumulative wt % PuO_2 dissolved during four-stage process.

Table XIV- PuO_2 DISSOLUTION DATA (25.6-g sample)

Acid Test Number	Reagent Composition	Stage	Time Heated (hr)	PuO_2 Dissolved (wt%)	Cumulative PuO_2 Dissolved (wt%)
12-1	4N HNO_3-0.3M CAN[a]	1	6 1/2	88.40	88.40
12-2	"	2	15	4.04	92.44
12-3	"	3	7 1/4	4.91	97.35
12-4	"	4	7	0.27	97.62[b]

[a] CAN is an acronym for ceric ammonium nitrate.

[b] Gamma ray analysis of remaining filter media indicated that 98.24% of the PuO_2 had been dissolved.

known (from the color change of the leaching solution) that the Ce^{+4} ions were reduced much more quickly during the dissolution of PuO_2 from the 25.6-g filter media sample. Therefore, it is surmised that the reason for the smaller decontamination factor (smaller percentage dissolved) is that the Ce^{+4} ions were used mainly to oxidize the sealant thus leaving fewer Ce^{+4} ions to oxidize to Pu^{+4}. A simple solution to this problem might be to increase the amount of ceric ammonium nitrate when larger amounts of sealant are present with the filter media.

Summary

Plutonium adsorption isotherms were developed for the Pu-HNO_3 and Pu-HNO_3-HF systems which proved that the filter media did indeed adsorb plutonium. The x/m ratio for the Pu-HNO_3-HF system was less than that for the Pu-HNO_3 system at any given concentration. Thus, higher decontamination factors can be obtained with HNO_3-HF (assuming each leaching agent is equally effective in the dissolution of plutonium dioxide).

Dissolution tests were conducted on filter media contaminated with PuO_2. The HNO_3-H_2SO_4 mixtures were relatively ineffective as leaching agents (see Figure 3). The best dissolution agents found were mixtures of HNO_3-HF and HNO_3-HF-H_2SO_4 in which the HF concentration was 0.05N or greater. These solutions dissolved greater than 90% of the PuO_2 in 15 hr (see Figures 5 and 6). Several tests were performed with HNO_3-$(NH_4)_2Ce(NO_3)_6$ solutions (see Figure 4). It was found that 4N HNO_3-0.1M $(NH_4)_2Ce(NO_3)_6$ was the best of these mixtures with 88% of the PuO_2 dissolved in 3 hr. Addition of $KMnO_4$ to 4N HNO_3-cerium(III) dissolution mixtures was successful in oxidizing the cerium(III) to cerium(IV) and thus allowing more of the PuO_2 to dissolve.

Several dissolution tests were completed with UO_2 and U_3O_8 contaminated filter media. All leaching agents tested dissolved the uranium oxide rapidly (see Table II). Equally good results were obtained with 8N HNO_3 wich dissolved ∿100% of the UO_2 or U_3O_8 in 6 hr.

Neither Na_2CO_3 nor Na_2CO_3-KNO_3 was satisfactory as a fusion agent for PuO_2. The greatest percentage of PuO_2 recovered was 71% using a Na_2CO_3-30 wt % KNO_3 salt mixture. Also there are tremendous corrosion problems associated with this process. The platinum crucibles and the furnace used in these experiments were corrosively attacked by the resultant vapors.

The PuO_2-75% UO_2 solid solution dissolved readily in 8N HNO_3, 12N HNO_3-0.1N HF, 12N HNO_3-0.05N HF-0.01N H_2SO_4, and 4N HNO_3-0.1M $(NH_4)_2Ce(NO_3)_6$. These would be acceptable leaching agents since greater than 93% of the PuO_2 dissolved in 2 hr at boiling temperatures. Hueda (4) has reported that PuO_2-UO_2 can be dissolved in nitric acid alone (up to 35% PuO_2). Baehr and Dippel(5) reported that UO_2-15% PuO_2 fired at 1600°C will dissolve easily in 14M HNO_3. These sources substantiate recent findings at Mound Facility.

Small and large samples of actual HEPA glovebox filters (contaminated with PuO_2) were treated with various leaching solutions. For small samples, 12N HNO_3-0.05N HF-0.01N H_2SO_4 proved superior to 4N HNO_3-0.1M $(NH_4)_2Ce(NO_3)_6$ with greater than 89% of the PuO_2 dissolved. For larger samples, it was found that an increase in the ratio of acid volume to PuO_2 weight increased the dissolution percentage. Figure 12 compares a five-stage process (volume/weight ratio of 0.67) with a three-stage process having volume:weight ratio of 2.35. It should be noted that the latter process obtained a higher percentage of dissolution than the former.

Dissolution studies using $4\underline{N}$ HNO_3-$0.15\underline{M}$ ceric ammonium nitrate dissolved greater than 93% of the initial PuO_2. Therefore, $4\underline{N}$ HNO_3 in combination with $(NH_4)_2Ce(NO_3)_6$ is a recommended leaching reagent.

Filter media which were contaminated with americium-241 and plutonium-239 oxides were treated with three different leaching reagents to determine the effectiveness of each reagent in dissolving the actinide oxides. The three reagents used were $8\underline{N}$ HNO_3, $4\underline{N}$ HNO_3-$0.1\underline{M}$ $(NH_4)_2Ce(NO_3)_6$, and $12\underline{N}$ HNO_3-$0.05\underline{N}$ HF-$0.01\underline{N}$ H_2SO_4. It was found that the best leaching agent was the $4\underline{N}$ HNO_3-$0.1\underline{M}$ $(NH_4)_2Ce(NO_3)_6$ which dissolved greater than 90% of the AmO_2 and the PuO_2.

Another series of tests was conducted to determine the best leaching agent for uranium-233 oxide (U_3O_8). Simulated samples of contaminated filter media were prepared by mixing 0.2 g of U_3O_8 powder with 3 g of shredded filter media. The reagents used were the same three as were used for the AmO_2-PuO_2 studies. It was found that all three reagents were successful in dissolving greater than 90% of the U_3O_8 in a very short time (15 min).

Fusion studies were conducted using Na_2CO_3 and PuO_2. The purpose of these experiments was to determine the effect of temperature on fusion efficiency. It was found that there was not a significant difference (4.6%) in the PuO_2 solubilized within the temperature range under investigation (1200-1300°C).

Experiments were conducted using filter media contaminated with neptunium-237 oxide. The purpose of the tests was to determine which of the three reagents would be successful in dissolving the NpO_2. Results indicate that both the $4\underline{N}$ HNO_3-$0.1\underline{M}$ $(NH_4)_2Ce(NO_3)_6$ and the $12\underline{N}$ HNO_3-$0.05\underline{N}$ HF-$0.01\underline{N}$ H_2SO_4 were successful in dissolving greater than 90% of the NpO_2 in 0.5 hr. The $8\underline{N}$ HNO_3 on the other hand solubilized only 32% of the NpO_2 in 8 hr and therefore would not be recommended as a leaching agent for NpO_2.

In other series of experiments, filter media contaminated with curium-244 oxide were dissolved in leaching tests using both $4\underline{N}$ HNO_3-$0.1\underline{M}$ $(NH_4)_2Ce(NO_3)_6$ and $12\underline{N}$ HNO_3-$0.05\underline{N}$ HF. Both reagents dissolved essentially 100% of the CmO_2 in approximately 10 min and therefore would be recommended for dissolving CmO_2 from filter media.

Filter media contaminated with thorium-232 oxide were leached with a $4\underline{N}$ HNO_3-$0.1\underline{M}$ $(NH_4)_2Ce(NO_3)_6$ solution in an attempt to dissolve the ThO_2. The rate of dissolution was slow at the beginning (0-7 hr), rapid from 7 to 9 hr, and slow again at the end (9-20 hr). Complete dissolution was achieved in 20 hr, considerably longer than for the other actinide oxides previously tested. A point of interest is that in a similar experiment using only $4\underline{N}$ HNO_3-$0.1\underline{M}$ ceric ammonium nitrate and ThO_2 (no filter media), the amount dissolved was only 25% after 20 hr. The reason for this difference is that the F^- catalyst is present in the filter media. Therefore, it is concluded that although the dissolution time was much longer for the ThO_2, it is still an acceptable leaching reagent for ThO_2 from filter media.

Several experiments were completed using PuO_2 contaminated filter media from spent glovebox filters. These tests were made in order to determine how much $(NH_4)_2Ce(NO_3)_6$ is required for dissolution of PuO_2 from such filters. In one experiment, a 9.5-g sample of filter media was processed through a six-stage dissolution process. In the intial five stages, $4\underline{N}$ HNO_3-$0.23\underline{M}$ $(NH_4)_2Ce(NO_3)_6$ was used and in the sixth stage $12\underline{N}$ HNO_3-$0.1\underline{N}$ HF was used. The amount of $(NH_4)_2Ce(NO_3)_6$ used in each stage was 60 times the intial moles of PuO_2 present in the filter media. The overall decontamination factor obtained for the six-stage process was 833. In a second experiment, a 25.6-g sample of filter media was processed through a four-stage dissolution procedure. The leaching solution was $4\underline{N}$ HNO_3-$0.30\underline{M}$ $(NH_4)_2Ce(NO_3)_6$. The amount of ceric ammonium nitrate used in each stage was 120 times the initial moles of PuO_2 present in the filter media. The overall decontamination factor achieved in the four-stage process was 55.8.

The amount of ceric ammonium nitrate required cannot be based exclusively upon the amount of actinide present in the filter media. The reason for this is that other reactants such as pack-to-frame sealant* and other organic materials are present in the spent filter media. A high percentage of sealant was present in the 25.6-g sample and this is perhaps why less plutonium was dissolved. In other words, even though more ceric ammonium nitrate was used per mole of plutonium present, a lower percentage of the plutonium dissolved because a large percentage of the Ce^{+4} ions was depleted by reaction with the organics present. A formula for calculating the $(NH_4)_2Ce(NO_3)_6$ required per gram of filter media has not been developed. More studies must be done before the relationship can be determined.

---

*This is a fire retardant polyurethane and a rubber base adhesive.

References

1. G. L. Silver and J. W. Koenst, A Study of the Reaction of Uranium and Plutonium with Bone Char, MLM-2384 (January 17, 1977), p. 24.
2. D. E. Etter and W. R. Herald, Plutonium-238 Dioxide Dissolution Study. MLM-2153 (July 31, 1974), 8 pp.
3. H. D. Harmon, Dissolution of PuO$_2$ with Ce^{+4} and Fluoride Promoters, DP-1371, Savannah River Laboratory (1975), 31 pp.
4. A. Uriate Hueda, Dissolution of Nuclear Fuels, JEN-201-DMa/I-22, Junta de Energia Nuclear (1968), 27 pp.
5. W. Baehr and T. Dippel, The Dissolution of PuO$_2$-Containing Breeder Fuels in HNO$_3$ for Aqueous Reprocessing by Purex Method, EUR-3704, Institute for Heisse Chemie (July 1967), 21 pp.

Bibliography

C. H. H. Chong, T. W. Crockett and J. W. Doty, Jr., J. Inorg. Nucl. Chem., 31, 81 (1969).

G. L. Silver, Dissolution Processes, MLM-2372 (October 1976), 17 pp.

R. M. Black and J. L. Drummond, A Comparison of Procedures for Dissolving Ignited Plutonium Oxides for Analysis, TRG Report 1072(D), Reactor Group, United Kingdom Atomic Energy Authority, Risley, England (October 4, 1965).

D. R. Rogers and W. B. Brown, Potassium Plutonium Sulphate, MLM-1212 (1964), 13 pp.

G. F. Molen, Dissolution of Plutonium Oxide, RFP-922, Dow Chemical - Rocky Flats, (August 29, 1967), 20 pp.

J. A. Ayres, Decontamination of Nuclear Reactors and Equipment, Pacific Northwest Laboratory, Battelle Memorial Institute, Ronald Press, New York (1970), 825 pp.

E. L. Christensen and W. J. Maraman, Plutonium Processing at the Los Alamos Scientific Laboratory, LA-3542, Los Alamos Scientific Laboratory (April 1969), 85 pp.

Managment of Radioactive Waste: Waste Partitioning as an Alternative, NR-CONF-001, United States Regulatory Commission (June 1976), 523 pp.