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**Decontamination of HEPA Filters:
January-March 1977**

Don F. Luthy and Edward L. Lewis

July 22, 1977

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Abstract

Various leaching agents were tested to determine their capability for dissolving PuO_2 , UO_2 , and U_3O_8 . The amount of radionuclides retained by the filter media was investigated. Adsorption isotherms for two leaching systems were obtained. A four-stage dissolution process was developed.

Introduction

Efforts this past quarter were directed toward determining the dissolution parameters of PuO_2 , UO_2 , and U_3O_8 * in various leach reagents. The reagents used were various concentrations of HNO_3 , $\text{HNO}_3\text{-HF}$, $\text{HNO}_3\text{-HF-H}_2\text{SO}_4$, $\text{HNO}_3\text{-(NH}_4)_2\text{Ce(NO}_3)_6$, and $\text{HNO}_3\text{-H}_2\text{SO}_4$. Two types of plutonium dissolution tests were conducted with 8N HNO_3 . In the one, PuO_2 was placed in 8N HNO_3 at boiling temperature. In the other, HEPA filter media contaminated with PuO_2 were added to boiling 8N HNO_3 . The dissolution ratios of PuO_2 as measured by the alpha activity of the acid media were determined for each test and are shown in Figure 1. As can be seen, 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. This is of great importance since the amount of adsorbed plutonium would be the limiting factor as to what decontamination factor could be achieved. Adsorption isotherms were determined for the Pu-HNO_3 and $\text{Pu-HNO}_3\text{-HF}$ systems.

*The uranium oxides were depleted uranium-238, whereas the plutonium dioxide 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.

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 filter media (expressed in milligrams plutonium-238 per milliliter of solution). The Freundlich equation [1] relates x/m and C as follows:

$$x/m = kC^{1/n} \quad (1)$$

or

$$\log (x/m) = \log k + (1/n) \log C \quad (2)$$

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 $\text{HNO}_3\text{-0.1N HF}$ system. This means that a larger decontamination factor could be achieved using the $\text{HNO}_3\text{-HF}$ leaching agent (assuming that the same percentage of plutonium dioxide is

FIGURE 1 - Effect of filter media on dissolution rates of PuO_2 in boiling 8N HNO_3 .

FIGURE 2 - Adsorption of ^{238}Pu on filter media at ambient temperature ($\sim 20^\circ\text{C}$) in different acids.

dissolved by either 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 HNO₃ and approximately 50 wt % of the filter media dissolves in 8N HNO₃-0.1N HF. Also, in another adsorption test it was found that the use of 4N HNO₃-0.05M ceric ammonium nitrate (see point A, Figure 2) would achieve a decontamination factor somewhere between 8N HNO₃-0.1N HF and 8N HNO₃ (assuming each leaching agent was equally effective in dissolving plutonium dioxide).

PuO₂ Dissolution Studies

Contaminated HEPA filter media were prepared by mixing plutonium dioxide powder with shredded filter media. The plutonium-238 concentration of the mixture was 11 mg/ml 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 1 lists results from dissolution tests for plutonium dioxide in various acid mixtures. The HNO₃-H₂SO₄ mixtures were relatively ineffective dissolution agents as illustrated in Figure 3. A

fivefold increase in H₂SO₄ concentration increased the dissolution rate by only 3%. The maximum weight percent 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 HNO₃-0.1M (NH₄)₂Ce(NO₃)₆ leaching agent was by far the most effective of the three HNO₃-cerium(IV) solutions with 88% of the plutonium-238 dioxide dissolved in 3 hr. Figure 5 is a companion graph showing the effect of initial cerium(IV) concentration on the dissolution rate for a 6-hr reaction time. Since the plot is approximately a straight line, the weight percent plutonium dioxide dissolved is directly proportional to the initial cerium(IV) concentration in the leaching solution.

The dissolution reaction mechanism for dissolving plutonium dioxide in HNO₃-cerium(IV) solutions is shown in Equations 3 and 4.

Because stoichiometric quantities of cerium(IV) are required for complete dissolution of the plutonium dioxide, large amounts of cerium(IV) are required to dissolve large quantities of plutonium dioxide. Therefore, it would seem advantageous to use small amounts of cerium(IV) and then add oxidizing compounds to re-oxidize the cerium(III) to cerium(IV). An example of this would be the addition of KMnO₄ to the depleted solution. This would cause the $\text{Mn}^{+7} + 3\text{e}^{-} \rightleftharpoons \text{Mn}^{+4}$ reaction which would reoxidize the depleted cerium, i.e.,

Table 1 - DISSOLUTION OF PLUTONIUM DIOXIDE IN VARIOUS ACID MIXTURES

Acid Test Number	Reagent Composition ^b	Time Heated (hr)	PuO ₂ Dissolved ^a (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 ₂ SO ₄	5 3/4	14.4
20-2	8N HNO ₃ -0.1N H ₂ SO ₄	12	12.7
20-3	8N HNO ₃ -0.1N H ₂ SO ₄	18	15.9
21-1	12N HNO ₃ -0.1N HF-0.1N H ₂ SO ₄	4 3/4	115.2
21-2	12N HNO ₃ -0.1N HF-0.1N H ₂ SO 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 ₂ SO ₄	1 1/4	30.1
27-2	12N HNO ₃ -0.01N HF-0.1N H ₂ SO ₄	6 3/4	33.1
27-3	12N HNO ₃ -0.01N HF-0.1N H ₂ SO ₄	12 1/4	36.3
28-1	12N HNO ₃ -0.1N HF-0.01N H ₂ SO ₄	1	96.3
28-2	12N HNO ₃ -0.1N HF-0.01N H ₂ SO ₄	6 1/2	100.9
28-3	12N HNO ₃ -0.1N HF-0.01N H ₂ SO ₄	12	101.8
29-1	8N HNO ₃ -0.5N H ₂ SO ₄	5 1/2	15.8
29-2	8N HNO ₃ -0.5N H ₂ SO ₄	10 3/4	17.4
29-3	8N HNO ₃ -0.5N H ₂ SO ₄	15 1/4	17.4
30-1	12N HNO ₃ -0.05N HF 0.01N H ₂ SO ₄	3	95.9
30-2	12N HNO ₃ -0.05N HF 0.01N H ₂ SO ₄	8 1/4	88.0
30-3	12N HNO ₃ -0.05N HF 0.01N H ₂ SO 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 ₂ S ₂ O ₈	3	0.86
32-2	8N HNO ₃ -K ₂ S ₂ O ₈	7 1/2	0.82
32-3	8N HNO ₃ -K ₂ S ₂ O ₈	13 1/2	1.89

^aExpressed as % plutonium-238 metal.
^bCAN is abbreviation for ceric ammonium nitrate

where one mole of manganese oxidizes three moles of cerium. This was done in acid tests 25 and 25A (see Table 1).

Approximately 1 g of KMnO₄ was added to a depleted 4N HNO₃-0.005M (NH₄)₂Ce(NO₃)₆ solution and the solution heated an additional 15 hr. In this period of time, the weight percent plutonium dioxide

dissolved increased significantly from 12% in the depleted solution to 26% in the regenerated solution. This method does, however, add manganese and potassium to the dissolved salts of the waste stream.

Another experiment was conducted using 8N HNO₃ and K₂S₂O₈ (potassium persulphate) as an oxidizing agent (see Table 1, acid test 32). After 13½ hr of reaction time

FIGURE 3 - Effect of H_2SO_4 concentration on dissolution rate.

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

FIGURE 5 - Effect of Ce^{+4} on the dissolution of PuO_2 in 4N HNO_3 .

at boiling temperature, only 1.89% of the plutonium dioxide had dissolved. From Figure 1, one can see that approximately 7.5% of the plutonium dioxide dissolved in 8 hr with no additional oxidizing agent present. Thus the $\text{K}_2\text{S}_2\text{O}_8$ actually decreased the dissolution rate of the plutonium dioxide.

Figures 6 and 7 show the effect of the HF concentration on the dissolution rate

of plutonium dioxide. For the HNO_3 -HF system, a tenfold increase in the HF concentration increases the weight percent plutonium dioxide dissolved from about 40% to approximately 100% for 9 hr of reaction time (Figure 6). A twofold increase in the HF concentration for the HNO_3 -HF- H_2SO_4 system increases the weight percent plutonium dioxide dissolved from 94% to 100% for 9 hr of reaction time (Figure 7). As can be seen in Table 1, any dissolution

FIGURE 6 - Effect of HF concentration on dissolution rate of PuO₂.

FIGURE 7 - Effects of HF and H₂SO₄ concentrations on dissolution rate.

test in which HF concentration was 0.05N, or greater, was successful in obtaining a 90 to 100% dissolution of the plutonium dioxide.

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. As can be seen, in every test the uranium oxides dissolved rapidly with the percent dissolved being greater than 90%. Eight normal HNO_3 performed as well as any of

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

the acid mixtures with essentially 100% of the uranium dioxide or U_3O_8 dissolved after 6 hr of heating. As a comparison, the percent plutonium dioxide dissolved after 6 hr was ~4% (see Figure 1).

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 plutonium dioxide.**

**The effect of sintering temperature on dissolution rate for various reagents can be seen in Figures 8 and 9.

Table 2 - DISSOLUTION OF URANIUM OXIDES IN VARIOUS ACID MIXTURES

Acid Test Number	Reagent Composition	Time Heated (hr)	UO_2 or U_3O_8 Dissolved ^a (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

^aExpressed as weight percent uranium metal.

FIGURE 8 - Effect of sintering temperature on dissolution rate.

The HNO₃-H₂SO₄ mixtures were relatively ineffective as leaching agents (see Figure 3). The best dissolution agents found were mixtures of HNO₃-HF and HNO₃-HF-H₂SO₄, in which the HF concentration was 0.05N or greater. These solutions dissolved greater than 90% of the plutonium dioxide in 15 hr (see Figures 6 and 7). Several tests were performed with HNO₃-(NH₄)₂Ce(NO₃)₆ solutions (see Figures 4 and 5). It was found that 4N HNO₃-0.1M (NH₄)₂Ce(NO₃)₆ was the best of these mixtures with 88% of the plutonium dioxide dissolved in 3 hr. Also, the

percent plutonium dioxide dissolved was found to be directly proportional to the initial cerium(IV) concentration in the leaching solution. Addition of KMnO₄ to 4N HNO₃-cerium(III) dissolution mixtures was successful in oxidizing the cerium(III) to cerium(IV) and thus allowing more of the plutonium dioxide to dissolve.

Several dissolution tests were completed with uranium dioxide and U₃O₈ contaminated filter media. All leaching agents tested dissolved the uranium oxide rapidly (see Table 2). Eight normal HNO₃ performed as

FIGURE 9 - Effect of sintering temperature on plutonium dioxide dissolution in 4N HNO_3 - 0.15M cerium(IV).

well as any of the leaching solutions with ~100% of the uranium dioxide or U_3O_8 dissolved in 6 hr.

Figure 10 is a proposed flowsheet showing a four-stage dissolution process, assuming 90% actinide removal in each stage. The dissolution agent used is 12N HNO_3 -0.05N HF -0.01N H_2SO_4 which proved to be successful in the recent plutonium dioxide studies. Another possible dissolution agent is 4N HNO_3 -0.1M $(NH_4)_2Ce(NO_3)_6$, but this would require a five-stage process in order to obtain a decontamination factor of 10^4 . On the other hand, if higher concentrations of cerium(IV) were used, a four-stage process is possible.

Next quarter, Na_2CO_3 - KNO_3 fusion tests will be performed. Tests will be conducted using plutonium dioxide, and if a high percentage of dissolution is achieved, additional tests will be performed using other actinides. Decontamination solutions, such as EDTA, will also be investigated. The work next quarter, however, will be directed primarily toward evaluating 12N HNO_3 -0.05N HF -0.01N H_2SO_4 and 4N HNO_3 -0.1M $(NH_4)_2Ce(NO_3)_6$ reagents for tests on oxides of americium-241, neptunium-237, uranium-233, and curium-244.

The milestone chart status is shown in Figure 11. Milestones A and B have been completed except for fusion tests using plutonium. Part C will involve determining leach parameters (possibly fusion parameters also) for other actinides as americium-241, uranium-233, curium-244, and neptunium-237. Material balances will be done, flowsheets will be prepared, and decontamination factors will be determined. At this time, indications are that the decontamination process will be a four-stage operation with each stage

removing approximately 90% of the actinides (see Figure 10). In Part D, waste streams from the most feasible processes will be studied, and comparisons will be made among them. Materials balances will also be prepared on the waste streams.

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*WEF 2 - Nonorganic contaminated, tritiated water feed stream

FIGURE 10 - Proposed flow sheet for HEPA filter process basis: one 10,000-g HEPA filter.

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MILESTONES
PHASE I

- A. Determine Parameters of HNO₃ Leach Tests with Plutonium
- B. Determine Parameters of Alternate Reagent Leach Tests with Plutonium
- C. Determine Leach Parameters for Other Actinides
- D. Determine and Compare Waste Streams from Selected Processes

FIGURE 11 - Milestone chart status.

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