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Decontamination of HEPA Filters: April-June 1977

Don F. Luthy and Edward L. Lewis

September 22, 1977

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Abstract

Efforts this past quarter were directed toward the determination of dissolution parameters in various reagents of PuO_2, PuO_2-UO_2 solid solution, and AmO_2-PuO_2. 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 were 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.

Experimental

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 1). 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 Samples were withdrawn periodically and the percent solid solution dissolved was determined.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 1, 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 1 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 plutonium dioxide*

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*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.

*The plutonium dioxide 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-241, 0.2% plutonium-242, plus small amounts of other actinides and calcined at 950°C.

Table 1 - PuO_2-UO_2 Solid Solution Dissolution

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

[a] Abbreviation for ceric ammonium nitrate.

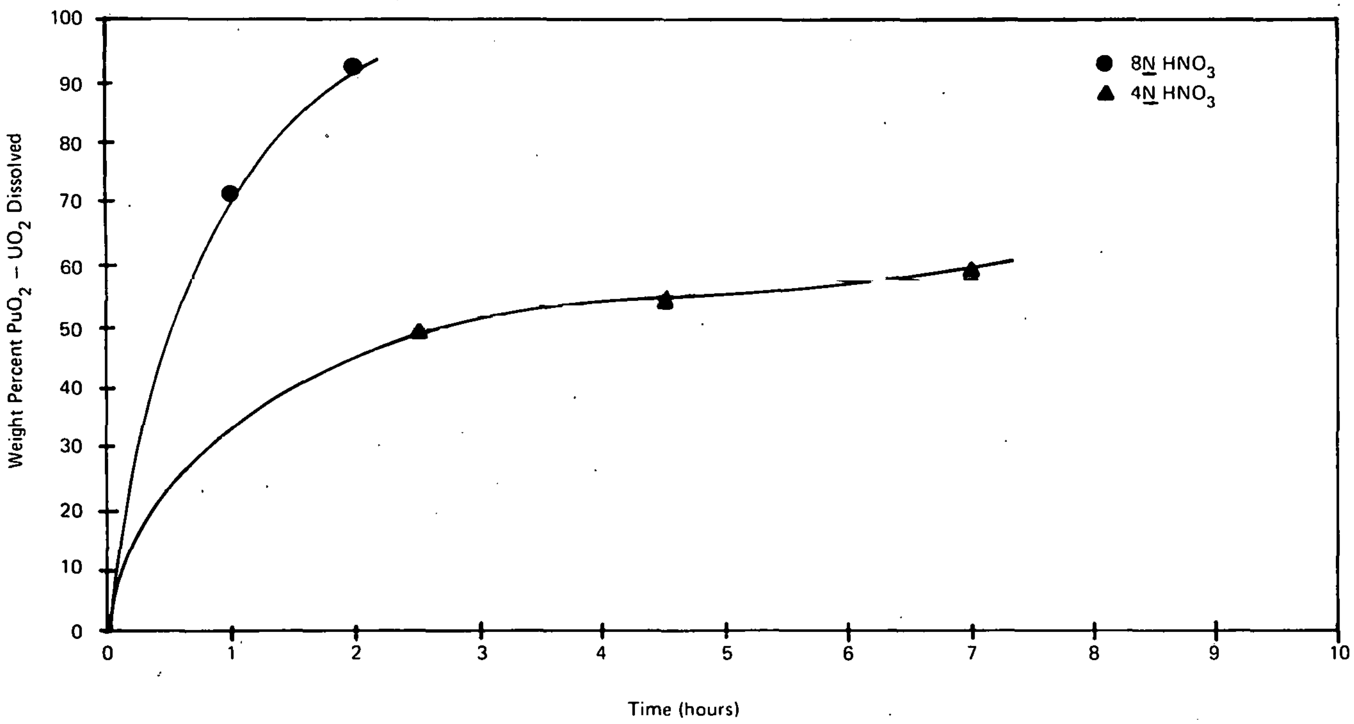

FIGURE 1 - Effect of HNO_3 Concentration on Dissolution Rate of PuO_2

contaminated filter media. Small samples were prepared by thoroughly mixing 0.1 g plutonium dioxide and 1.5 g of filter media. Approximately 13 g of salt (Na_2CO_3 or NA_2CO_3-KNO_3) were placed in a platinum crucible and 1.5 g of contaminated filter media were 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 a least 1 hr and subsequently sampled for plutonium-238 concentration. Table 2 tabulates the results achieved in these fusion experiments. As can be seen, the maximum percent dissolution obtained was 71% using a salt mixture of Na_2CO_3-30 wt % KNO_3.

Figure 2 shows the effect of potassium nitrate composition on plutonium dioxide solubility. The effect is linear between zero and 16% KNO_3 and then flattens off at higher potassium nitrate concentrations. The acid normality was increased to $8\underline{N}$ and the heating time increased to 7 hr (Table 2) with little increase (2%) in percent plutonium dioxide dissolved. This confirmed what had been suspected; that is, the plutonium dioxide had not been converted to a compound which was readily soluble in nitric acid. Also because of time limitations, only three Na_2CO_3-KNO_3 fusions were performed and the maximum weight percent potassium nitrate used was 30%. Time permitting, more fusions will be completed next quarter using larger potassium nitrate weight percentages. It should be noted that the greater the percent 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% KNO_3 is considered unsatisfactory for our purposes. The percent 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 plutonium dioxide.* 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 $4\underline{N}$ HNO_3-$0.1\underline{M}$ ceric ammonium nitrate and $12\underline{N}$ HNO_3-$0.05\underline{N}$ HF-$0.01\underline{N}$ 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 3 contains the results obtained in these experiments. The average percent plutonium dioxide dissolved was 92.5% using $4\underline{N}$ HNO_3-$0.1\underline{M}$ $(NH_4)_2Ce(NO_3)_6$ and 93.3% using $12\underline{N}$ HNO_3-$0.05\underline{N}$ HF-$0.01\underline{N}$ H_2SO_4. These compare well with the dissolution percentages found for simulated filter media samples

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*The same type oxide as used in the Salt Fusion Studies.

Table 2 - 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

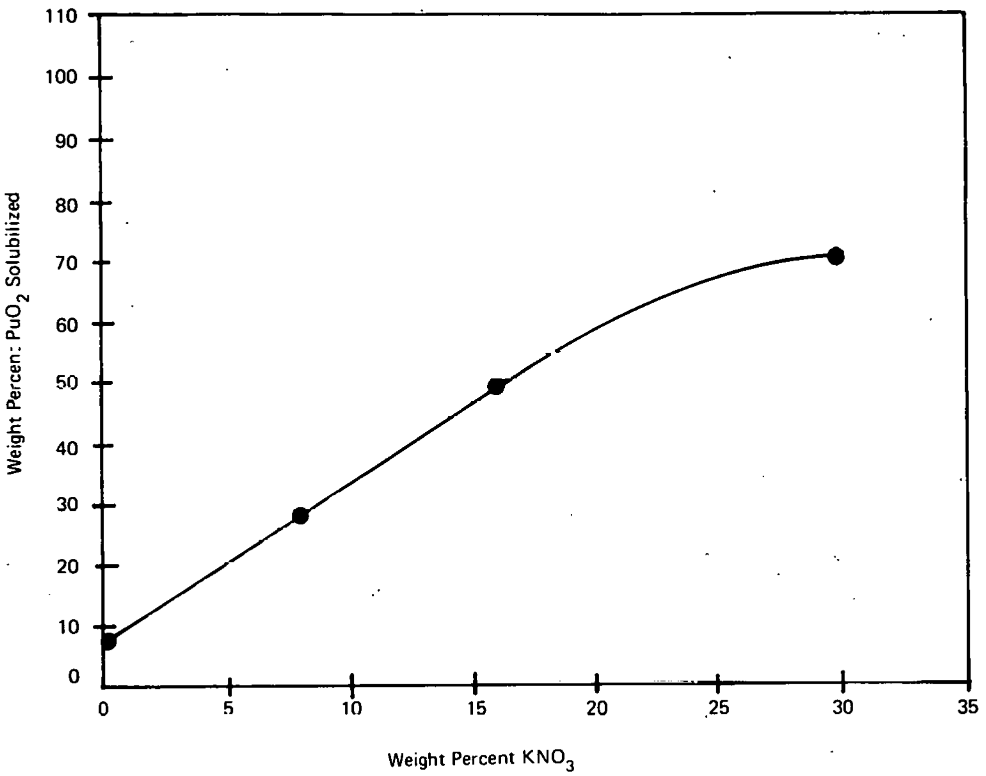

FIGURE 2 - Effect of Salt Composition on Percent PuO_2 Solubilized

last quarter (85.4% and 93.9% respectively) [1]. Figure 3 is a graph of the dissolution rate for plutonium dioxide in 12N HNO_3-0.05N HF-0.01N H_2SO_4. As can be seen, the dissolution reaction is rapid with approximately 90% of the plutonium dioxide dissolved in 4 hr.

Larger samples (40 g) of an 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 4 and Figure 4). As can be seen in Figure 4, an acid volume/plutonium dioxide weight ratio of 0.67 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 we have a decontamination factor of 154 for the smaller 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.

A possible explanation for the fact that a larger volume acid/weight plutonium dioxide produces a higher dissolution is thought to be the following. The HF in the leaching solution is reacting with both plutonium dioxide 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 plutonium dioxide 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 plutonium dioxide. 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, a 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 volume and concentration were kept constant by adding acid of proper concentration in order to replace evaporated acid. Figure 5 shows the effect of Ce^{+4} concentration on plutonium dioxide dissolution rate. The 4N HNO_3-0.1M $(NH_4)_2Ce(NO_3)_6$ curve is drawn from

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*The same type oxide used in previous sections.

Table 3 - 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	$4\underline{N}$ HNO_3-$0.1\underline{M}$ CAN	3-1/2	103.2	1.84
3265-3B	$4\underline{N}$ HNO_3-$0.1\underline{M}$ CAN	5	103.3	1.84
3265-3C	$4\underline{N}$ HNO_3-$0.1\underline{M}$ CAN	11-3/4	81.9	1.84
3265-3D	$4\underline{N}$ HNO_3-$0.1\underline{M}$ CAN	14-3/4	81.5	1.84
3265-4A	$12\underline{N}$ HNO_3-$0.05\underline{N}$ HF-$0.01\underline{N}$ H_2SO_4	3-1/2	96.9	1.83
3265-4B	$12\underline{N}$ HNO_3-$0.05\underline{N}$ HF-$0.01\underline{N}$ H_2SO_4	5	89.1	1.83
3265-4C	$12\underline{N}$ HNO_3-$0.05\underline{N}$ HF-$0.01\underline{N}$ H_2SO_4	12-1/2	93.9	1.83

[a] Abbreviation for ceric ammonium nitrate - $(NH_4)_2Ce(NO_3)_6$.

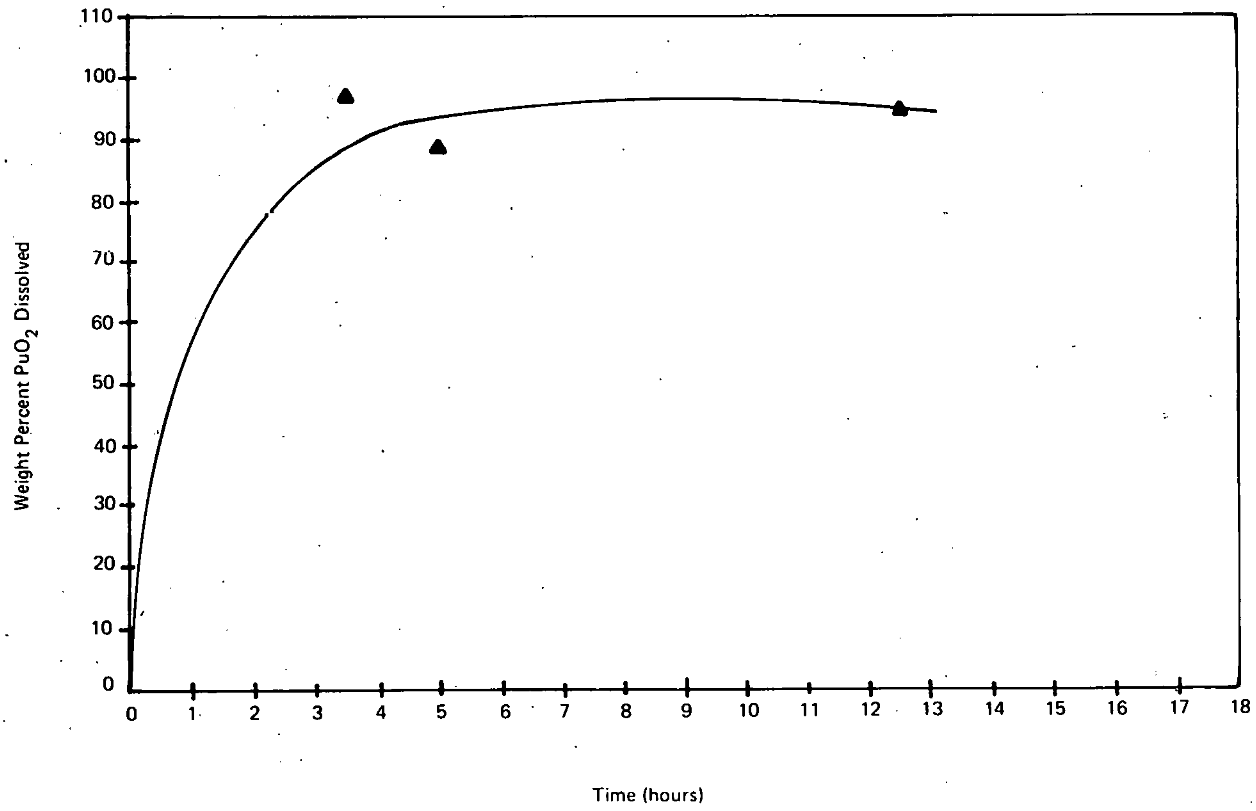

FIGURE 3 - Dissolution Rate of PuO_2 in $12\underline{N}$ HNO_3-$0.05\underline{N}$ HF-$0.01\underline{N}$ H_2SO_4

Table 4 - $12\underline{N}\ HNO_3-0.05\underline{N}\ HF-0.01\underline{N}\ H_2SO_4$

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

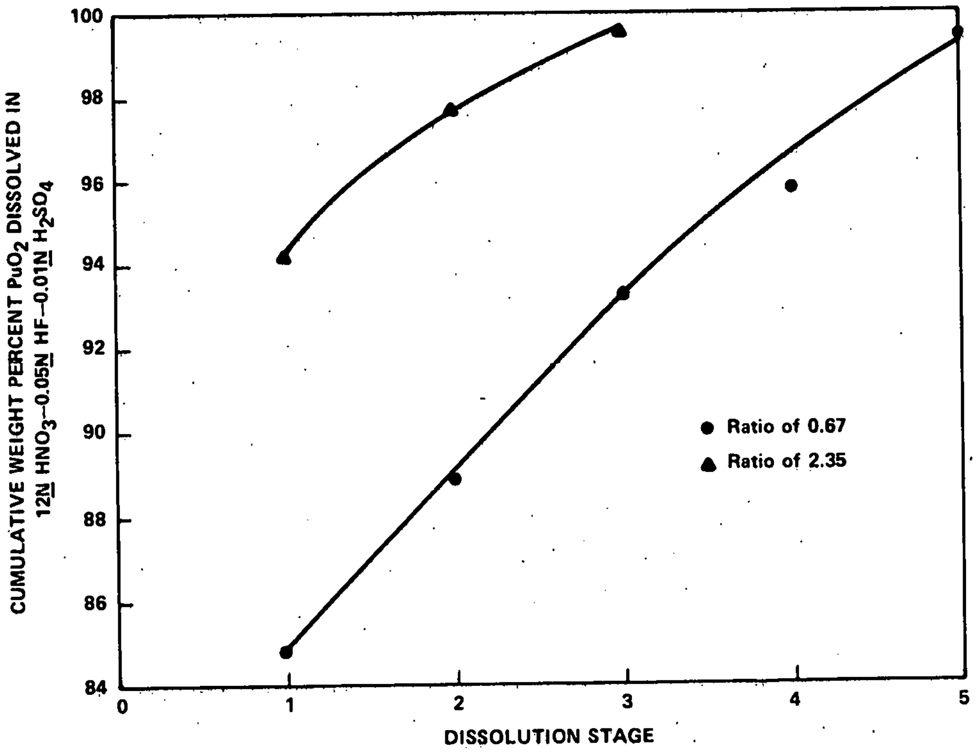

FIGURE 4 - Effect of Acid Volume/PuO_2 Weight Ratio on Dissolution Percentage.

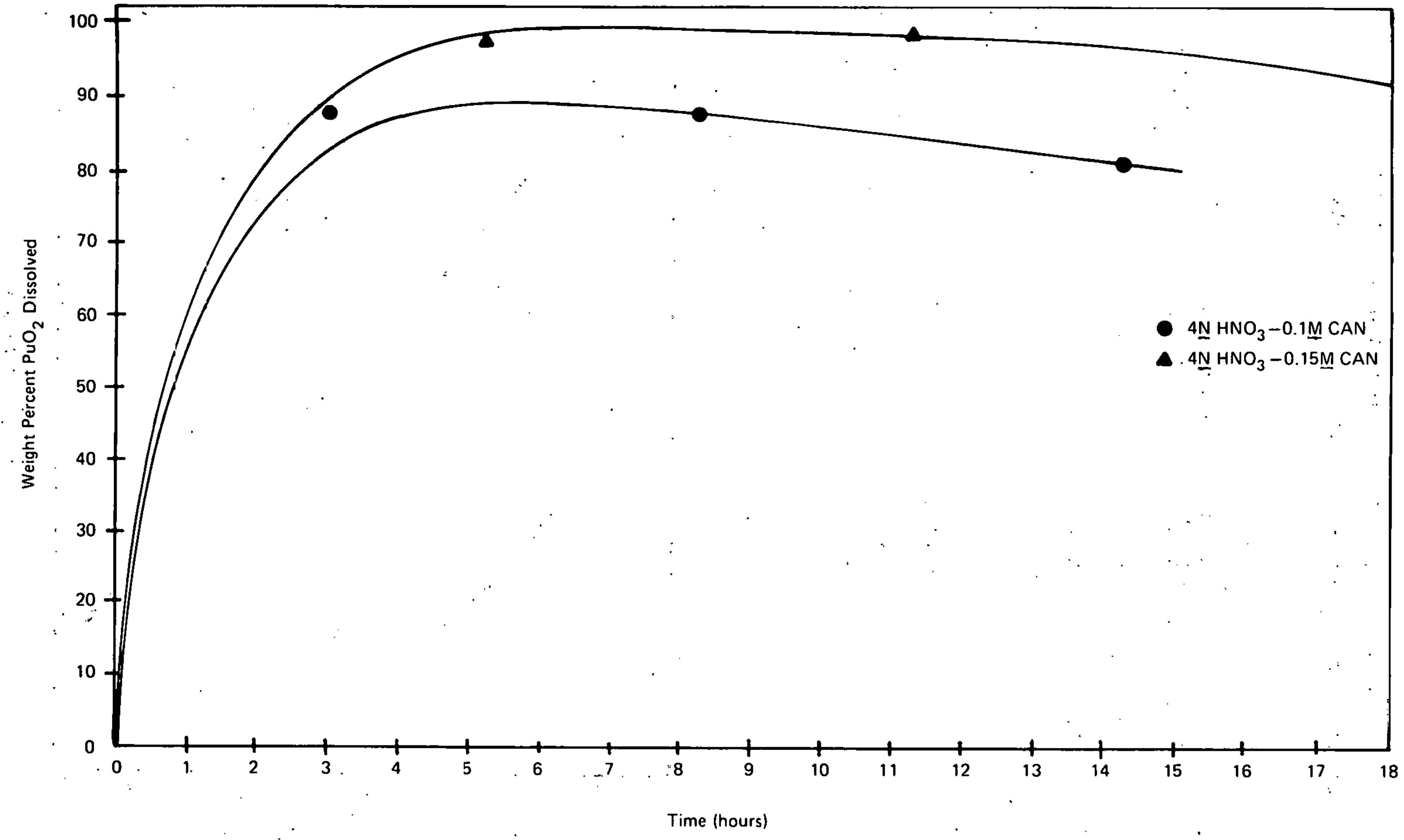

FIGURE 5 - Effect of Ceric Ammonium Nitrate Concentration on PuO_2 Dissolution Rate

data contained in Reference 2. It should be noted that a 50% increase in the Ce^{+4} concentration results in a 10% increase in weight percent plutonium dissolved. Figure 6 is a proposed flowsheet using $4\underline{N}$ HNO_3 combined with various concentrations of $(NH_4)_2Ce(NO_3)_6$ as leaching reagents. The concentrations of ceric ammonium nitrate are based on calculations using experimental data. These calculations indicate that 0.01 mole Ce^{+4} is required for each curie of actinide in order to achieve a dissolution of 90% or greater. This process will provide an overall decontamination factor of 10,000 for the four stages. One disadvantage of this process is the large amounts of high-cost Ce^{+4} required (approximately 20 times the stoichiometric amount). A subsequent separation of the Ce^{+3} ions and actinide ions would also have to be achieved thus adding more complication and expense to the overall process.

Americium - Plutonium* Dissolution Studies

Leaching studies were performed using a procedure identical to the PuO_2-UO_2 solid-solution experiments. Contaminated filter media were 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 $4\underline{N}$ HNO_3-$0.1\underline{M}$ $(NH_4)_2Ce(NO_3)_6$, $12\underline{N}$ HNO_3-$0.05\underline{N}$ HF-$0.01\underline{N}$ H_2SO_4, $12\underline{N}$ HNO_3-$0.1\underline{N}$ HF-$0.1\underline{N}$ H_2SO_4, and $8\underline{N}$ HNO_3. These experiments have not been concluded at this time and as a result will be included in the next quarterly report.

Summary

Both Na_2CO_3 and Na_2CO_3-KNO_3 were not satisfactory as fusion agents for plutonium dioxide. The greatest percentage plutonium dioxide 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. Further fusion tests using higher potassium nitrate percentages are to be done next quarter.

The PuO_2-75% UO_2 solid solution dissolved readily in $8\underline{N}$ 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-$0.1\underline{M}$ $(NH_4)_2Ce(NO_3)_6$. These would be acceptable leaching agents since greater than 93% of the plutonium dioxide dissolved in 2 hr at boiling temperatures. Hueda [3] has reported that PuO_2-UO_2 can be dissolved in nitric acid alone (up to 35% PuO_2). Baehr and Dippel [4] report that UO_2-15% PuO_2 fired at 1600°C will dissolve easily in $14\underline{M}$ HNO_3. These sources substantiate recent findings at Mound Laboratory.

Small and large samples of <u>actual</u> HEPA glovebox filters (contaminated with plutonium dioxide) were treated with various leaching solutions. For small samples, $12\underline{N}$ HNO_3-$0.05\underline{N}$ HF-0.01N H_2SO_4 proved superior to $4\underline{N}$ HNO_3-$0.1\underline{M}$ $(NH_4)_2Ce(NO_3)_6$ with greater than 89% of the plutonium dioxide dissolved. For larger samples, it was found that an increase in the ratio of acid volume to plutonium dioxide weight increased the dissolution percentage. Figure 4 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

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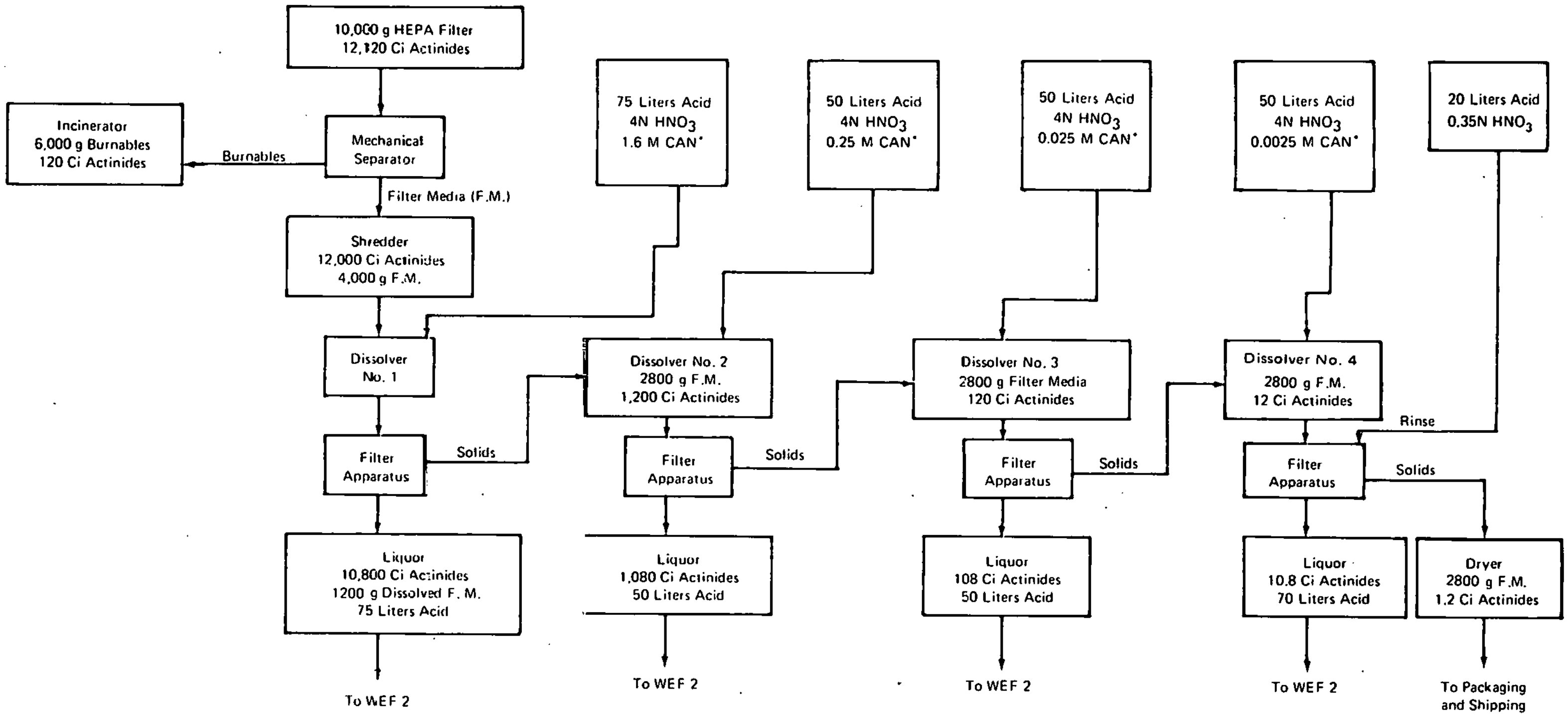
*This was mainly americium-241 oxide and plutonium-239 oxide which had been fired at 1000°C.



*CAN is abbreviation for Ceric Ammonium Nitrate

June 22, 1977

FIGURE 6 - Proposed Flowsheet for HEPA Filter
Process Basis: One 10,000 Gram HEPA Filter

the latter process obtained a higher percent 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 plutonium dioxide. Therefore, 4$\underline{N}$ HNO_3 in combination with $(NH_4)_2Ce(NO_3)_6$ is a recommeded leaching reagent. Figure 6 is a proposed flowsheet using various concentration of ceric ammonium nitrate in combination with 4$\underline{N}$ HNO_3. The Ce^{+4} concentrations were calculated using as a basis 0.01 mole Ce^{+4} per curie of actinide. This ratio of 0.01 was found to be effective in dissolving greater than 90% of the initial plutonium dioxide in filter media samples.

The milestone chart status is shown in Figure 7. Milestones A and B have been completed; C remains incompleted at this time. Leach parameters (and possibly fusion parameters) still remain to be determined for americium-241, uranium-233, curium-244, neptunium-237, and mixtures of these. The main reasons for not completing part C as scheduled were the fusion studies not planned, but requested by the sponsor, and a shorter working period to meet the July 1 due date on this Quarterly Report. Material balances will be done, flowsheets will be prepared, and decontamination factors will be calculated. In part D, waste streams from the two most feasible processes will be studied and compared. Waste stream material balances will also be prepared.

PHASE I

A. Determine Parameters of HNO_3 Leach Tests with Pu

B. Determine Parameters of Alternate Reagent Leach Tests With Pu

C. Determine Leach Parameters for Other Actinides

D. Determine and Compare Waste Streams from Selected Processes

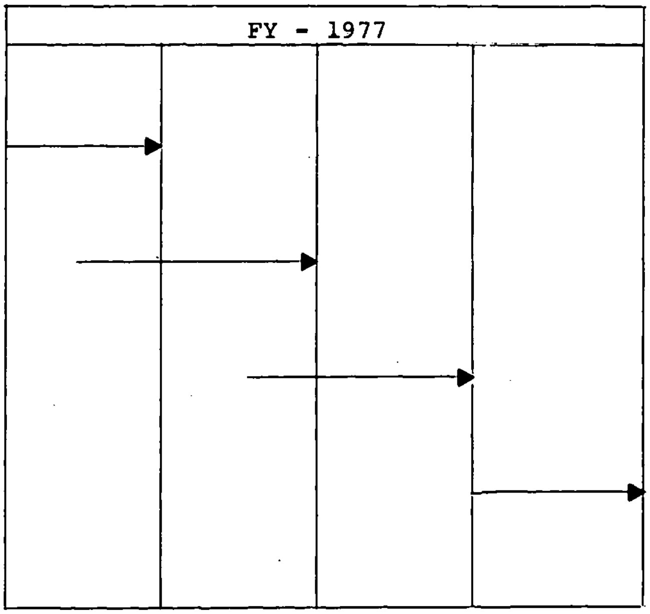


FIGURE 7 - Milestone Chart Status

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