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AQUEOUS DECLADDING AND DISSOLUTION OF PLUTONIUM RECYCLE TEST REACTOR FUELS, PART 1: PLUTONIUM-ALUMINUM ALLOY FUELS

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INTRODUCTION

The Plutonium Recycle Test Reactor (PRTR),(1-3), located at Richland, Washington, is currently operated by the Pacific Northwest Laboratory (a division of Battelle Memorial Institute). Three different types of Zircaloy-clad fuels--Pu-Al alloy, UO_2, and mixed oxide (PuO_2-UO_2)--have been used in the reactor since start-up. Part 1 of this report describes laboratory studies of the aqueous decladding and dissolution of the Pu-Al alloy fuels; studies with mixed oxide fuel are reported in Part 2.* Pertinent Hanford Redox plant dissolution experience with the Pu-Al and mixed oxide fuels is also reviewed.

SUMMARY AND CONCLUSIONS

Certain factors such as activation behavior,** instantaneous dissolution rates, and off-gas composition were determined during dissolution of various PRTR Pu-Al alloys in HNO_3-$Hg(NO_3)_2$ solutions. Pu-Al alloys irradiated to 28 to 48% burnup of their initial Pu^{239} content, as well as unirradiated Pu-Al alloys, were studied (in 0.002 to 0.02M $Hg(NO_3)_2$ solution) at HNO_3 concentrations as high as 4M. Irradiated material activated only in dilute (∿1M) HNO_3 solutions.

A key property of irradiated PRTR Pu-Al alloys was that, after activation in dilute HNO_3 was achieved, concentrated HNO_3 could be added to the dissolvent to adjust its acidity to 4 to 6M without passivating the alloy. (Dissolution to 4 to 6M HNO_3 is desirable to reduce the amount of hydrogen in the off-gas and to achieve fast dissolution rates). Advantage of this property was taken in defining an activation-dissolution procedure for use in the Hanford Redox plant. This scheme has now been used in the Redox plant to dissolve successfully 70 PRTR Pu-Al fuel assemblies in three separate campaigns.

DESCRIPTION OF PRTR Pu-Al ALLOY FUELS

The PRTR plutonium spike (Pu-Al alloy) fuel assembly is a 19-rod cluster, 3.25 in. in diameter and 98 in. long.(5,6) Each rod is individually clad in Zircaloy-2 (0.035 in. wall thickness); the diameter of one clad rod is nominally 0.57 in. The active core length is 88 in. The core consists of 1.8 wt% plutonium and 2.0 wt% nickel alloyed with either Type 1345 or Type 8001 aluminum alloy base metal. Each fuel element contains approximately 260 g of plutonium before irradiation. The Pu-Al alloy core weighs approximately 32.5 lb, and the Zircaloy cladding and end fittings are approximately 29 lb.

Type 6061 aluminum alloy canisters are used to contain irradiated PRTR elements during shipment to the Hanford Redox plant. These canisters are designed to permit direct loading of canister and contained fuel elements into the Redox plant multipurpose dissolver. The four-barrel canister used for shipping four fuel elements weigh approximately 90 lb. The barrel section has a diameter of 9.25 in. and is 98 in. long; the

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* *Similar studies with PRTR UO_2 fuels have already been reported.*(4)

** *Activation of Pu-Al alloys is defined and discussed below.*

overall length of the barrel section and bail is 113 in.

DISSOLUTION CHEMISTRY AND LITERATURE REVIEW

The passivity of aluminum metal in HNO_3 solutions is well known, as is the action of small concentrations of $Hg(NO_3)_2$ in overcoming the passivating oxide film and promoting rapid attack of aluminum metal and its alloys by HNO_3. The mechanism by which Hg(II) ion catalyzes HNO_3 dissolution of aluminum appears to be an amalgamation process where Hg(II) is reduced to Hg(0) on the aluminum surface.(7) This amalgamation process is termed activation in this report; the same term was used by Fletcher, et al.(8)

Characteristic properties of activated aluminum metal or alloys in HNO_3-$Hg(NO_3)_2$ solutions include:

- Dissolution rates are very high (10 to 120 mg/cm^2 min) as opposed to those of unactivated material (0.5 to 1.0 mg/cm^2 min).
- The metal surface loses its shiny metallic luster and becomes dark and pitted.
- The rate of gas evolution, because of the increased dissolution rate, is sharply increased over that noted for unactivated metal.
- When removed from the HNO_3-$Hg(NO_3)_2$ solution, a white to gray powder (presumably hydrated aluminum oxide) forms on the metal surface.

Hg(II)-catalyzed HNO_3 dissolution techniques have been used at Idaho Falls to dissolve irradiated U-Al alloys.(9) They have been proposed and tested also for codissolving aluminum-clad, uranium-metal, fuel elements.(10-11)

Many of these early studies (discussed in detail in Reference 12) were performed with aluminum alloy Type 1100 (previously designated Type 2S) or U-Al and Pu-Al alloys fabricated with alloy Type 1100 as the base metal. This particular alloy activates readily at HNO_3 concentrations as high as 9<u>M</u>. More recently, activation and dissolution of many other aluminum alloys, including irradiated Pu-Al alloys, have been studied as part of this work, as well as at various other USAEC sites. Several important observations regarding activation have emerged from these studies and are cited below. (A comprehensive theory of activation of aluminum alloys which accounts for these experimental facts is lacking.)

- Silicon, nickel, and copper as elements in aluminum alloys strongly inhibit activation in $Hg(NO_3)_2$ solutions. For example, in the present work we observed that unirradiated Pu-Al-Ni and Pu-Al-Ni-Si alloys activated only at HNO_3 concentrations of 4<u>M</u> or below, irrespective of $Hg(NO_3)_2$ concentration. Similar behavior was noted for aluminum alloy Type X-8001 containing 1 wt% nickel. (Activation behavior of alloy Type X-8001 is of interest because some aluminum cans for Hanford reactor uranium metal fuel elements have been fabricated from this alloy.) The passivating effects of silicon and nickel were observed also by Fletcher, et al(8) who further noted a strong passivating effect due to copper present in aluminum alloys.

- Irradiation has a profound passivating effect on the activation behavior of Pu-Al and U-Al alloys, but apparently does not effect the activation of aluminum alloys not containing a fissile element. This passivating effect on U-Al alloys has been noted at Idaho Falls(13) and at Savannah River,(14) while the effect on Pu-Al alloys was noted in the present work at various other USAEC sites.(15-16) Special procedures were developed in this work (see page 6) to activate PRTR Pu-Al alloy irradiated to 28 to 48% burnup of the Pu^{239} content. Also special procedures were developed at Savannah River(15) to activate an Al—7 wt% Pu alloy irradiated to 60% burnup of the Pu^{239} content. However, when Al—7 wt% Pu alloy was irradiated to over 99% burnup of the Pu^{239}, all attempts(17) to achieve activation in HNO_3 solutions failed, and a procedure for dissolution in NaOH-$NaNO_3$ media was developed.
- Small concentrations of fluoride ion in HNO_3-$Hg(NO_3)_2$ solutions promote activation of aluminum alloys. This effect was first noted at the Savannah River Laboratory(15) and was incorporated in their procedure for dissolving Pu-Al alloys irradiated to 60% burnup of the Pu^{239}. In the present work, unirradiated PRTR Pu-Al alloys and Type X-8001 alloy could be made to activate in 5-6$\underline{M}$ HNO_3-$Hg(NO_3)_2$ solutions by adding small concentrations of NH_4F to the test solution. The beneficial effect of fluoride ion does not, however, compensate fully for the deleterious effect of irradiation on activation behavior. Thus, in the work at Savannah River cited above, the Pu-Al alloy irradiated to over 99% burnup of the Pu^{239} could not be activated even when the HNO_3-$Hg(NO_3)_2$ solutions contained large concentrations of fluoride. Also in the present work, fluoride ion was ineffective in promoting activation of irradiated Pu-Al alloy (see page 6).

Finally, in Redox plant processing of PRTR fuels, Type 6061 aluminum alloy canisters were dissolved in NaOH-$NaNO_3$ solutions, and Zircaloy cladding in NH_4F-NH_4NO_3 solutions. Technology for these steps is well known.(18)

EXPERIMENTAL

Materials

For use in measuring instantaneous dissolution rates, right circular cylinders, 0.5 in. in diameter and 0.25 to 0.50 in. long, were cut from various unirradiated PRTR Pu-Al alloy rods. The nominal composition of the alloys is shown in Table I. Alloys 1 and 2 were the standard PRTR Pu-Al spike fuel. Type X-8001 aluminum alloy base metal was used to prepare alloy 1, and special high purity Type 1345 aluminum alloy base metal was used to prepare alloy 2. Alloy 3, prepared only in experimental amounts, had essentially the same composition as alloys 1 and 2 except for the presence of a small amount of titanium. The high silicon content alloy (alloy 4) was originally chosen as the standard PRTR fuel. This decision was altered when dissolver solutions prepared from this type fuel

TABLE I

COMPOSITION OF PRTR Pu-Al ALLOY FUELS

Alloy Number[(a)]	Nominal Composition, wt%					
	Pu	Ni	Si	Fe	Ti	Al
1	1.8	2.0	0.30(Max)	0.40(Max)	0.0	Remainder
2	1.8	2.0	0.03	0.07	0.0	Remainder
3	1.8	2.0	0.17(Max)	0.10(Max)	0.15	Remainder
4	1.8	1.3	1.0	0.35	0.0	Remainder

(a) For identification purposes only

were found to have unsatisfactory properties in solvent extraction operations (see page 11),

Five-inch long pieces were cut from irradiated PRTR fuel elements 5075 (49.5 MWd) and 5042 (80.1 MWd). Element 5042 was irradiated to about projected goal exposure (∿48% Pu^{239} burnup) while element 5075 was irradiated to about 60% of the projected goal exposure. The 5 in. segments were cut from the center section of a rod on the outer ring of the 19-rod cluster. Except at the ends, Zircaloy cladding was intact. Similar 5 in. long pieces were also cut from unirradiated PRTR Pu-Al alloy (alloy 1, Table I) rods for total dissolution experiments. Activation behavior of Type X-8001 aluminum alloy was studied with cylinders, 0.25 to 0.5 in. long and cut from an extruded 0.5 in. diam rod.

Procedures and Equipment

Instantaneous Dissolution Rates

All instantaneous dissolution rates listed in this report were measured in boiling solutions. Dissolution rates of various aluminum alloys were determined by the following procedure: The alloy sample, contained in a 304 L stainless steel mesh basket, was immersed in 250 ml of boiling 1.0$\underline{M}$ HNO_3-0.002M $Hg(NO_3)_2$ solution for 1 min. The specimen was removed, washed with water, and while still wet, its diameter and height were measured. The sample, contained in the stainless steel basket, was then immersed in 250 ml of boiling test solution of the desired composition for a measured time. After this second immersion, the sample was washed with water and, while still wet, its diameter and height again measured. Penetration rates (mils/hr) for both radial and end attack were calculated from dimension changes. Penetration rates were then converted to dissolution rate in units of mg/cm^2-min. In some cases dissolution rates were also determined by weighing alloy specimens before and after the second immersion. The first immersion in boiling 1.0$\underline{M}$ HNO_3-0.002$\underline{M}$ $Hg(NO_3)_2$ solution in the procedure just described was made to activate the alloy surface.

Total Dissolution Experiments

A dissolver vessel constructed of Ni-O-Nel was used to declad and, subsequently, to activate and dissolve 5 in. long rods of PRTR Pu-Al alloy. The alloy piece was contained in a mesh Ni-O-Nel basket which could be removed quickly for inspection of the alloy surface. Dimensions of the basket and dissolver were such that the alloy piece was maintained in a vertical position when immersed in solution. The vessel was heated electrically and was fitted with an updraft condenser, a thermocouple, and a sample port.

Details of the decladding and dissolution procedures are given on page 7 of this report.

Off-Gas Composition

Composition of the gas evolved when PRTR alloys were dissolved in HNO_3-$Hg(NO_3)_2$ solutions was measured as a function of solution acidity. Metal cylinders, like those used in measuring instantaneous rates, were activated by exposure to boiling 1.0M HNO_3-0.002M $Hg(NO_3)_2$ for 1 min. Activated specimens were immediately plunged into a boiling HNO_3-0.002M $Hg(NO_3)_2$ solution of the desired composition. A large volume was used to maintain essentially constant acidity. Gas that evolved during the first 2 min of reaction was allowed to sweep air from the reaction vessel and from the line leading to a gas burette. About 90 ml of off-gas was collected by displacement of mercury in the burette during a measured time and then cooled until no further volume change occurred. Temperature and barometric pressure were noted, and composition of the gas was determined mass spectrometrically.

Disengaging Time Studies

Redox process(12) acid feed solutions were prepared from Pu-Al dissolver solutions. These feed solutions were contacted with methyl isobutyl ketone (hexone), and phase disengaging times were measured with an apparatus of the type described by Mendel and Moore.(19) The measurement procedure was that described by Mendel and Moore. In some cases a deemulsification agent, Mistron 25* (magnesium silicate), was added to the aqueous phase before contact with hexone. A stock suspension of 2 g of Mistron 25 in 200 ml water was prepared; definite volumes of this suspension were added as desired. In all cases neutral hexone was used.

Analyses

Plutonium in dissolver solutions obtained from unirradiated fuels was determined by direct alpha counting of aliquots. Sequential tri-isoctylamine extractions(20) were used to determine plutonium in decladding solutions and also in dissolver solutions obtained from irradiated fuels.

RESULTS AND DISCUSSION

Dissolution of Pu-Al Alloys in HNO_3-$Hg(NO_3)_2$ Solutions

Conditions for Activation

Type X-8001 aluminum alloy and unirradiated PRTR Pu-Al alloys activated readily and reproducibly (a) in boiling 0.02M $Hg(NO_3)_2$ solutions, (b) in boiling HNO_3-0.002 to 0.01M $Hg(NO_3)_2$ solutions (provided the HNO_3 concentration was 4M or lower), and (c) in boiling 5 and 6M HNO_3-0.005M $Hg(NO_3)_2$ solutions also containing 0.03 to 0.1M NH_4F. In the latter case, addition of $Hg(NO_3)_2$ to the boiling solution, rather than having it present while the solution was heated to boiling, appeared to aid activation.

PRTR Pu-Al alloys irradiated to either 28 or 48% burnup of their Pu^{239} content did not activate in the following solutions:

- Boiling 6.0M HNO_3-0.03M NH_4F-0.005 or 0.01M $Hg(NO_3)_2$
- Boiling 3.25M HNO_3-0.005M $Hg(NO_3)_2$

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* *Sierra Talc and Clay Company*

- Boiling $3.25\underline{M}\ HNO_3-0.05\underline{M}\ Hg(NO_3)_2-0.032\underline{M}\ NH_4F$
- Boiling $0.02\underline{M}\ Hg(NO_3)_2$.

Substitution of a stainless steel type 304-L basket for a Ni-O-Nel basket (see page 4) had no effect on activation. Addition of $Hg(NO_3)_2$ to the boiling solution in (a) also had no effect.

Irradiated PRTR Pu-Al alloy <u>did</u> activate in boiling $1.0\underline{M}\ HNO_3-0.015\underline{M}\ Hg(NO_3)_2-0.0$ to $0.01\underline{M}\ NH_4F$ solutions. Significantly, once activation occurred, the HNO_3 concentration could be increased to 4 to $6\underline{M}$ without passivating the active surface.

In further studies, unactivated, irradiated Pu-Al alloy and activated, unirradiated Pu-Al alloy rods were brought into contact while immersed in boiling $6.0\underline{M}\ HNO_3-0.03\underline{M}\ NH_4F-0.005\underline{M}\ Hg(NO_3)_2$ solution. (Fletcher, et al used this technique to overcome the passivating effect of silicon in certain Al-Si alloys and termed it "contact activation"). Activation of the irradiated rod occurred only where the two metal surfaces came in contact and did not propagate over the entire alloy rod surface. Furthermore, activation persisted only while the metal-to-metal contact was maintained. Failure of the activation reaction to propagate and to persist, once initiated, was characteristic of irradiated alloy but was not noted with unirradiated alloy.

Instantaneous Dissolution Rates

Instantaneous dissolution rates of activated PRTR Pu-Al alloys in boiling 0.5 to $4.0\underline{M}\ HNO_3-0.002\underline{M}\ Hg(NO_3)_2$ solutions are shown in Table II. Although some scatter is obvious, rates determined by weight changes are generally in agreement with those determined by measuring changes in dimensions of test cylinders. The experimental error in these measurements was sufficiently high to mask any effects of small differences in alloy composition on dissolution rate. Thus, the average dissolution rates listed in Table II were calculated on the assumption that all four alloys tested dissolved at the same rate in a particular $HNO_3-Hg(NO_3)_2$ solution.

Over the range of HNO_3 concentrations studied, the dissolution rate appeared to vary in a linear manner with HNO_3 concentration (Figure 1).

Off-Gas Composition

Mercury-catalyzed HNO_3 dissolution of aluminum can proceed according to one of several reactions depending on HNO_3 concentration:(12)

$$2Al + 6HNO_3 \rightarrow 2Al(NO_3)_3 + 3H_2 \quad (1)$$
$$10Al + 36\ HNO_3 \rightarrow 10Al(NO_3)_3 + 3N_2 + 18H_2O \quad (2)$$
$$8Al + 30HNO_3 \rightarrow 8Al(NO_3)_3 + 3N_2O + 15H_2O \quad (3)$$
$$Al + 4HNO_3 \rightarrow Al(NO_3)_3 + NO + 2H_2 \quad (4)$$
$$Al + 6HNO_3 \rightarrow Al(NO_3)_3 + 3NO_2 + 3H_2O \quad (5)$$

Only Reactions 1-4 occurred when PRTR Pu-Al alloys were dissolved in boiling 1 to $6\underline{M}\ HNO_3-0.002\underline{M}\ Hg(NO_3)_2$ solutions (Table III). The amount of hydrogen in the off-gas from both alloys increased steadily as the HNO_3 concentration decreased from 6 to $1\underline{M}$. Correspondingly, the amount of NO evolved from both alloys decreased steadily for this same change in acidity. The percentages of N_2 and N_2O in the off-gas varied little with HNO_3 concentration, however.

Evolution of hydrogen during fuel decladding or dissolution represents a fire and explosion hazard. Dilution of evolved hydrogen to below the lower explosion limit in air (about 4%)(21) is mandatory in Redox plant operation. It is significant, therefore, that,

TABLE II

INSTANTANEOUS DISSOLUTION RATES OF PRTR Pu-Al ALLOYS IN HNO_3-$Hg(NO_3)_2$ SOLUTIONS

All solutions were 0.002M $Hg(NO_3)_2$

Alloy Number[a]	HNO_3 M	Immersion Time, min	Dissolution Rate, mg/cm^2 min		
			From Changes in Dimensions	From Weight Changes	Average Rate[b]
1	0.5	2	18.4	25.8	20.2
2	0.5	5	21.4	19.8	
3	0.5	6	21.8	-	
4	0.5	6	14.0	-	
1	1.0	2	25.2	27.7	23.1
2	1.0	5	27.3	22.0	
3	1.0	6	16.5	-	
4	1.0	6	19.6	-	
1	2.0	2	32.6	49.8	39.4
2	2.0	4	43.8	41.8	
3	2.0	4	27.2	-	
4	2.0	4	41.1	-	
1	3.0	2	60.8	63.8	58.3
2	3.0	4	55.7	50.5	
3	3.0	4	55.3	-	
4	3.0	4	63.7	-	
1	4.0	2	54.1	75.5	68.0
2	4.0	4	57.2	56.3	
3	4.0	2	75.4	-	
4	4.0	2	89.7	-	

(a) Numbers correspond to those used in Table I

(b) For all four alloy compositions

over the range 1 to 3M HNO_3, less hydrogen is evolved from the Pu-Al-Ni alloy than from the Pu-Al-Ni-Si alloy.

Decladding and Dissolution of Irradiated Alloy

The 5 in. long rods were declad by treatment for 5 to 6 hr with boiling 4.0M NH_4F-0.50M NH_4NO_3 solution. Terminal decladding wastes were 0.19M $(NH_4)_2ZrF_6$. With unirradiated alloy the loss of plutonium to the decladding waste was 2.1%. For alloy irradiated to 49.5 and 80.1 MWd/assembly, plutonium losses to the decladding solution were 1.0 and 0.43%, respectively. These losses were somewhat higher than noted in subsequent Redox plant decladdings. (Redox plant decladdings appear later in Table V)

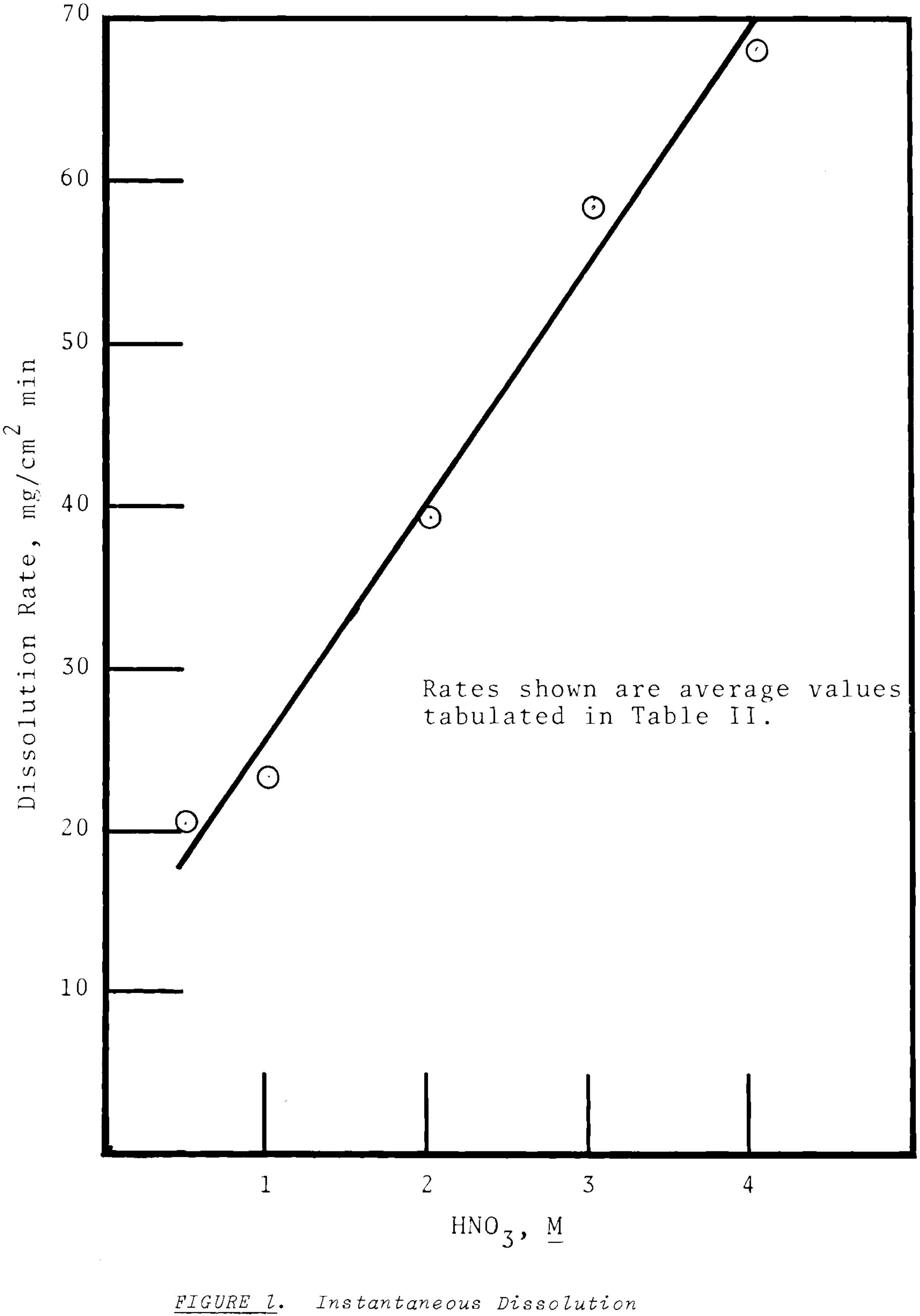

FIGURE 1. Instantaneous Dissolution Rates of PRTR Pu-Al Alloys in HNO_3-$Hg(NO_3)_2$ Solutions.

TABLE III

COMPOSITION OF OFF-GAS FROM DISSOLUTION OF Pu-Al ALLOYS IN HNO_3-$Hg(NO_3)_2$ SOLUTIONS

HNO_3 M	Alloy Area, cm^2	Collection Time, min	Gas Vol, ml$^{(b)}$	Off-Gas Composition, (Vol %)			
				H_2	NO	N_2O	N_2
A. Pu-Al-Ni-Si Alloy (Alloy 4, Table I)							
1.0	4.93	1.13	85.3	45.9	24.0	14.2	15.5
1.5	4.43	1.27	84.4	41.4	27.8	13.4	16.9
2.0	4.70	0.60	86.2	28.9	43.3	15.3	12.1
2.5	5.03	0.60	82.6	25.1	49.7	14.2	10.7
3.2	4.99	0.57	81.7	11.9	56.1	17.7	14.1
4.0	4.93	0.63	82.6	2.72		14.4	
5.0	4.91	0.90	85.3	2.47	60.4	17.2	19.0
6.0	5.04	0.83	84.4	1.61	61.0	17.0	19.5
B. Pu-Al-Ni Alloy (Alloy 1, Table I)							
1.0	5.67	1.40	83.9	15.9	37.5	19.2	27.0
2.0	5.09	0.80	87.5	12.6	47.0	16.4	23.2
3.0	3.92	1.18	79.6	3.0	60.4	20.7	17.5
4.0	3.46	0.97	85.2	1.79	66.8	17.2	13.6
5.0	4.15	0.73	86.1	2.56	63.2	17.2	16.6
6.0	4.84	0.70	85.2	3.67	52.4		12.4

(a) *All solutions were also 0.002M* $Hg(NO_3)_2$

(b) *At STP*

After removal of the decladding waste, the dissolver was thoroughly flushed with water and HNO_3. The declad rods were then recharged and activated and dissolved as follows:

Activation: 242 ml of 1.0M HNO_3-0.015M $Hg(NO_3)_2$ or 1.0M HNO_3-0.015M $Hg(NO_3)_2$-0.01M NH_4F solution were charged to immerse the rod to a depth of about 3 in. This solution was heated; in all cases activation occurred when the temperature reached about 85 °C as indicated by the sudden increased evolution of heat and gas and, in some cases, by visual observation of the alloy surface.

Dissolution: Within 1 to 2 min after activation occurred, 195 ml of 12.2M HNO_3 were added. This quantity of acid was calculated to make the dissolvent approximately 6M HNO_3. Dissolution at boiling temperature was allowed to proceed about 3 hr. Nitric acid concentration of the dissolver solution as a function of time is plotted in Figure 2.

When removed from solution after 3 hr, all the rods had passivated as evidenced by their smooth shiny appearance. Data plotted in Figure 2 show that, in all cases, dissolution was rapid for the first hour, but thereafter, the rods dissolved as if passivated. As indicated in Figure 2, irradiated alloy passivated at higher HNO_3 concentrations (and lower $Al(NO_3)_3$ concentrations) than unirradiated fuel.

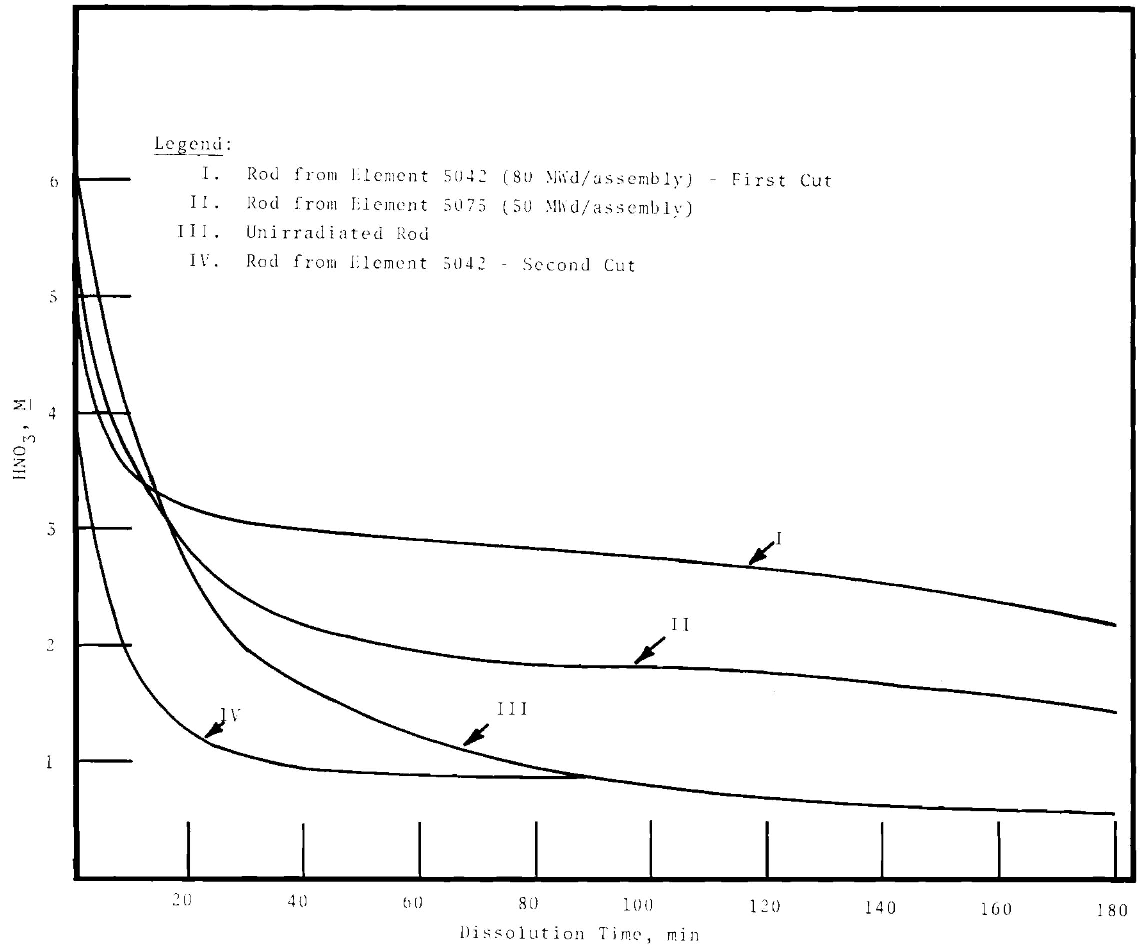

FIGURE 2. HNO_3-$Hg(NO_3)_2$ Dissolution of Irradiated Pu-Al Alloy Rods.

Approximately one-half the rod from element 5042 (80 MWd/assembly) remained undissolved after the procedure described above. To dissolve this material, it was activated in 915 ml of 1.0$\underline{M}$ HNO_3-0.015$\underline{M}$ $Hg(NO_3)_2$. When activated, 335 ml of 12.2$\underline{M}$ HNO_3 were added to produce a 4$\underline{M}$ HNO_3 solution. The rod dissolved completely without passivating in 60 min to produce a 0.89$\underline{M}$ HNO_3-0.85$\underline{M}$ $Al(NO_3)_3$ solution.

Disengaging Behavior of Pu-Al Alloy Dissolver Solutions

PRTR Pu-Al alloy cylinders were completely dissolved (60 to 90 min) in boiling 3.21$\underline{M}$ HNO_3-0.002$\underline{M}$ $Hg(NO_3)_2$ solutions. Dissolver solutions of the composition 0.72$\underline{M}$ $Al(NO_3)_3$-0.5$\underline{M}$ HNO_3-0.002$\underline{M}$ $Hg(NO_3)_2$ were produced. To these solutions were added $UO_2(NO_3)_2$, $Na_2Cr_2O_7$, and HNO_3 (or NaOH) to obtain Redox process acid feeds of the composition 1.25$\underline{M}$ $UO_2(NO_3)_2$-1.0$\underline{M}$ $Al(NO_3)_3$-0.1$\underline{M}$ $Na_2Cr_2O_7$-0.003$\underline{M}$ $Hg(NO_3)_2$-0.1 to 0.5$\underline{M}$ HNO_3. Solutions of this latter composition were also prepared from reagent grade chemicals. In Table IV are listed disengaging times noted when these solutions were contacted with hexone.

Two significant observations were:

- Disengaging behavior of feed solutions prepared from the Pu-Al-Ni

TABLE IV

PRTR Pu-Al ALLOY DISSOLVER SOLUTIONS - DISENGAGING BEHAVIOR

Procedure: Redox process feeds prepared from Pu-Al alloy dissolver solutions contacted with hexone in standard dispersion-disengaging apparatus.

Feed Prepared from Pu-Al Alloy Number[a]	Feed Composition[b]		Disengaging Time
	HNO_3 M	Mistron 25 ppm	Sec
1	0.1	0	200
1	0.5	0	249
2	0.5	0	217
4	0.1	0	>600[c]
4	0.5	0	>600[c]
4	0.1	64	135
4	0.5	64	100
Reagents	0.5	0	233

(a) Numbers correspond to those used in Table I.

(b) Feed solutions were also 1.25M $UO_2(NO_3)_2$-1.0M $Al(NO_3)_3$-.003M $Hg(NO_3)_2$ and 0.1M $Na_2Cr_2O_7$.

(c) Stable emulsions formed and persisted for more than 10 min.

alloys (alloy 1 and 2) was identical to that of feed solutions prepared from reagent grade chemicals.

- Stable emulsions, resembling chicken wire in appearance, formed in the organic phase when feed solutions prepared from the silicon alloy (alloy 4) were contacted with hexone. Addition of small amounts of the deemulsification agent, Mistron 25, to these feeds prevented emulsion formation.

The propensity of silicon-containing feed solutions to form emulsions when contacted with organic extractants has been noted in other solvent extraction studies.(22-23) Our results demonstrated satisfactory Redox process feeds probably could be prepared routinely from Pu-Al-Ni-Si alloy dissolver solution by addition of a deemulsification agent. (In the Hanford Recuplex process,(12,24) Mistron 25 is added routinely to feed prepared from plutonium reduction slag and crucible material, and phase disengaging properties are greatly improved thereby.) In the PRTR program, however, an alternative was to eliminate the silicon from the alloy; this was the action taken.

CHEMICAL FLOWSHEETS

Typical chemical flowsheets used(25) in the Hanford Redox plant to dissolve aluminum canisters, to remove Zircaloy cladding, and to activate and dissolve Pu-Al core material are shown in Figures 3, 4, and 5, respectively.

Core dissolution conditions (Figure 5) were essentially those used successfully in laboratory studies. In plant usage they permitted maximal charge size, while assuring positive activation, rapid dissolution, and minimal evolution of hydrogen. To achieve

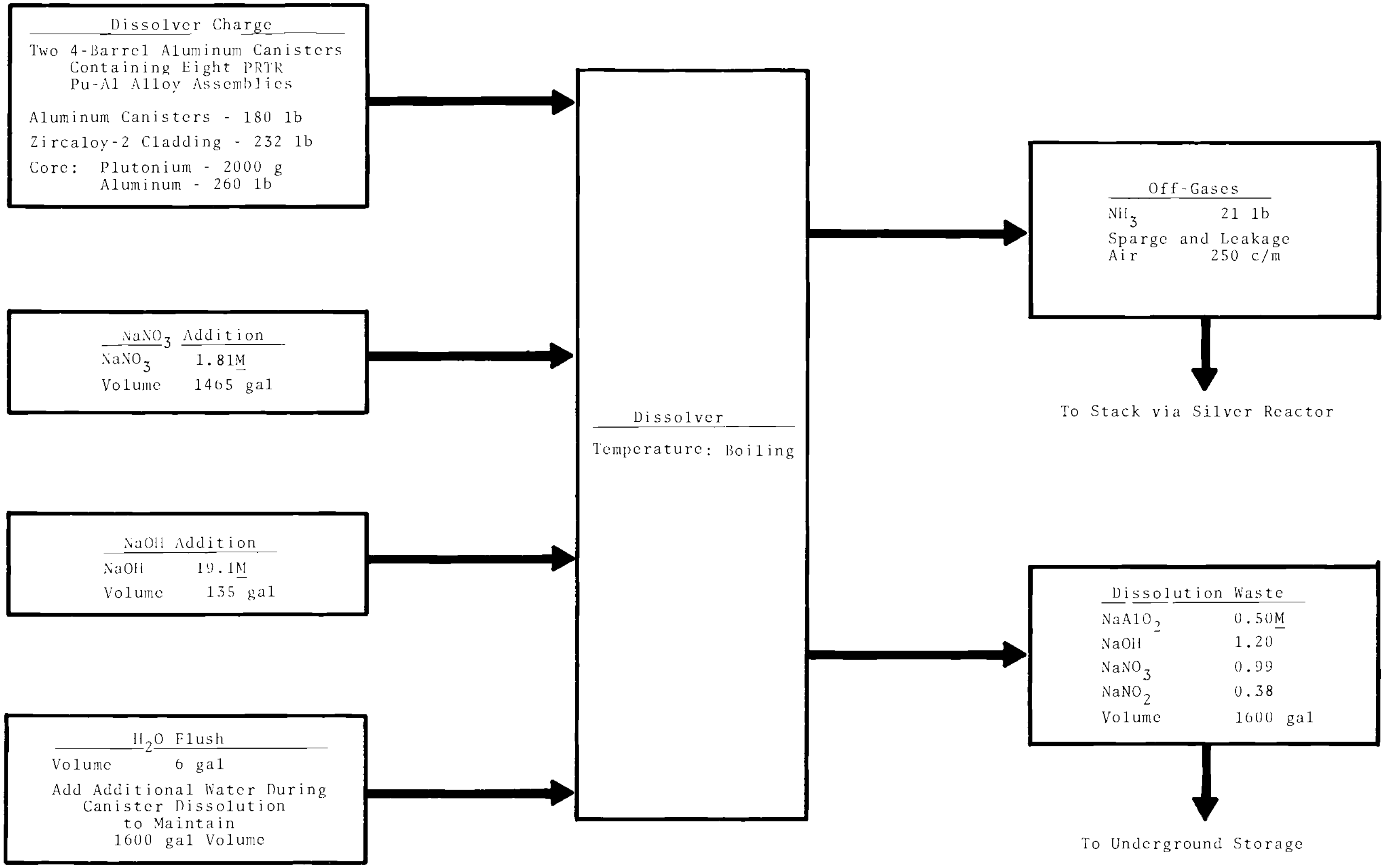

FIGURE 3. Flowsheet for Dissolution of PRTR Aluminum Canisters.

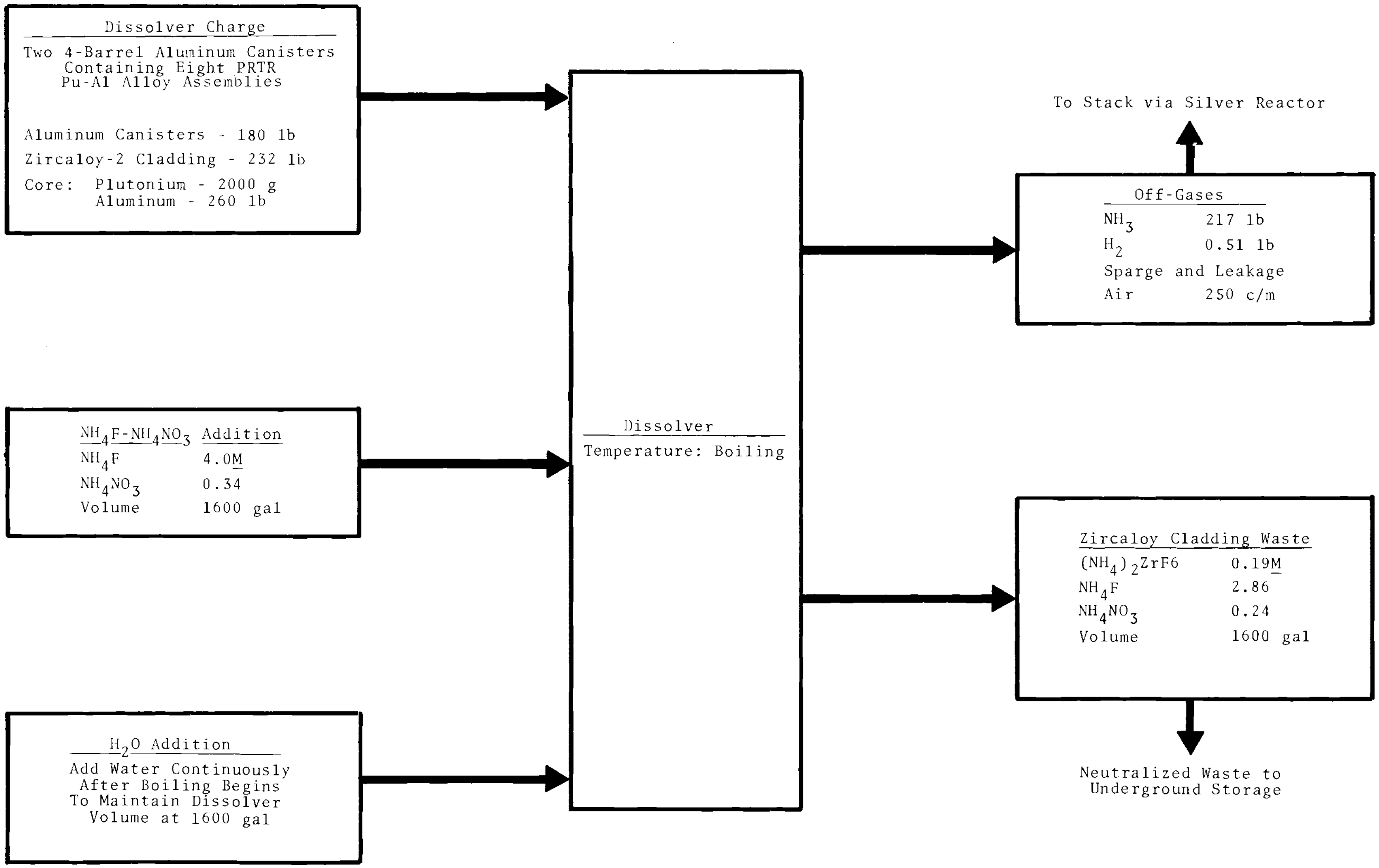

FIGURE 4. Flowsheet for Dissolution of Zircaloy Cladding.

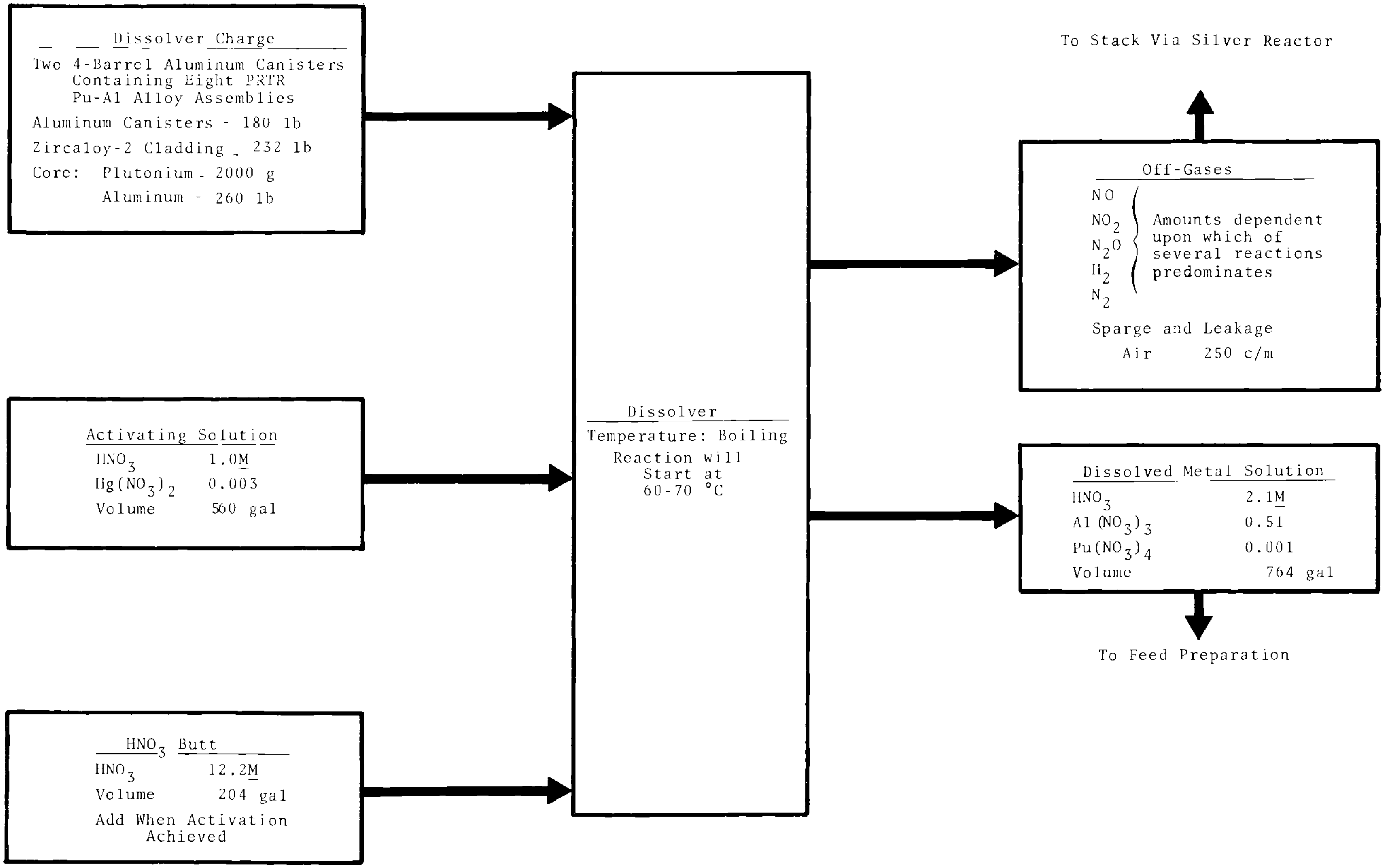

FIGURE 5. Flowsheet for Activation and Dissolution of PRTR Pu-Al Alloy Core.

these objectives, however, it was necessary to limit the amount of alloy activated in each dissolution cut. Typically, only 22 to 33 in. of the 88 in. long rods were activated and dissolved in each cut.

Limitation of the amount of alloy activated was necessary, primarily, to insure adequate air flow to dilute hydrogen in the off-gas to below the lower explosive limit. A secondary consideration was the desire not to overtax the capacity of the dissolver condenser to condense steam. In this connection, for the reaction

$$\mathrm{Al} + 3.75\mathrm{HNO_3} \rightleftarrows \mathrm{Al(NO_3)_3} + 0.225\mathrm{NO} + 0.15\mathrm{N_2O} + 0.1125\mathrm{N_2} + 1.875\mathrm{H_2O},$$

Benedict and Pigford estimate(26) $\Delta H = -190$ kcal.

RESUMÉ OF REDOX PLANT DISSOLUTION EXPERIENCE

To date, 70 irradiated, intact PRTR Pu-Al alloy assemblies have been dissolved in three separate campaigns in the Redox plant. Pertinent reprocessing data are summarized in Table V.

ACKNOWLEDGEMENT

The cooperation and courtesy of G. L. Hanson of the General Electric

TABLE V

SUMMARY: REDOX PLANT DISSOLUTION OF PRTR Pu-Al ALLOY FUEL

Date	Campaign 1 Feb.-Mar. 1963	Campaign 2 Mar.-April 1964	Campaign 3 June-July 1965
Charge:			
Number Dissolver Charges	4	7	1
Intact Assemblies Dissolved	32(a)	35(b)	3(c)
Irradiation History:			
Minimum MWd/assembly	57	0.5	0.5
Maximum MWd/assembly	80	152(d)	102(d)
Average MWd/assembly	72	102(d)	98(d)
Zirflex Process Decladding(e):			
Time at boiling temp., hr	6	6	6
Average percent Pu loss	0.23	0.14	0.14
Core Dissolution:(f)			
Equivalent $\mathrm{HNO_3}$, $\underline{M}$(g)	3.0-4.0	3.5	3.5
Time per cut, min	45 at 4.0$\underline{M}$ $\mathrm{HNO_3}$ 90 at 3.0-3.5$\underline{M}$ $\mathrm{HNO_3}$	(h)	(h)
Diluted Off-Gas $\mathrm{H_2}$:			
Maximum vol%	3.2 at 4.0$\underline{M}$ $\mathrm{HNO_3}$ 2.9 at 3.0-3.5$\underline{M}$ $\mathrm{HNO_3}$	(h)	(h)
Average vol%	1.4 at 4.0$\underline{M}$ $\mathrm{HNO_3}$ 1.0 at 3.0-3.5$\underline{M}$ $\mathrm{HNO_3}$		

(a) Eight intact assemblies/charge

(b) Four charges of eight assemblies, one charge of four assemblies, and two charges of cut, irradiated Pu-Al alloy scrap.

(c) Remainder charge was cut Pu-Al alloy scrap containing about 250 g plutonium.

(d) For intact assemblies.

(e) According to conditions shown in Figure 4.

(f) For intact assemblies, three cuts plus heel removal according to Flowsheet shown in Figure 5. Heel and scrap dissolved in 1.0$\underline{M}$ $\mathrm{HNO_3}$.

(g) Calculated concentration from addition of 12.2$\underline{M}$ $\mathrm{HNO_3}$ after activation in 1$\underline{M}$ $\mathrm{HNO_3}$.

(h) Data not available.

Company in providing an account of plant dissolving experience and in permitting reproduction of certain chemical flowsheets is gratefully acknowledged. Special thanks are due also to L. D. Turner and E. A. Coppinger, Battelle-Northwest, for their advice and assistance in obtaining alloy samples.

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