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CONTROLLED NITRIC ACID DISSOLUTION
OF ALUMINUM-PLUTONIUM ALLOYS

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ABSTRACT

Small concentrations of $Ni(NO_3)_2$ inhibit dissolution of Al-Pu alloys in HNO_3 - $Hg(NO_3)_2$ solutions. Utilizing this property, a satisfactory flowsheet for controlled dissolution of Plutonium Recycle Test Reactor Al-Pu alloys in Hanford Purex plant dissolvers was devised and demonstrated.

CONTROLLED NITRIC ACID DISSOLUTION OF ALUMINUM-PLUTONIUM ALLOYS

INTRODUCTION

Various Plutonium Recycle Test Reactor (PRTR) aluminum-plutonium fuel pieces were left unirradiated when the reactor was shut down. The bulk of this material consists of unirradiated Al-1.8 wt% Pu-2 wt% Ni alloy in the form of Zircaloy-clad, 88-inch long 19-rod clusters. [Some irradiated 1.8 wt% Pu alloy fuel clusters are also available.] Single 0.5-inch diameter by 88-inch long Al-Pu alloy rods containing up to 6.5 wt% Pu make up the remainder of the unirradiated fuel load.

Reprocessing of both the unirradiated and irradiated alloys in the Hanford Purex plant to recover plutonium values is currently scheduled. Flowsheets for Purex plant dissolution of Al-Pu fuel cores which maximize the total weight of alloy charged per batch are desirable to (1) reduce the consumption of costly decladding chemicals, (2) reduce the number of total charges required, and (3) produce a dissolver solution having a relatively high aluminum concentration.

Instantaneous dissolution rates of Al-Pu alloys in boiling 3 to 4M HNO_3 -0.002M $\text{Hg}(\text{NO}_3)_2$ solutions are of the order of 70 to 100 $\text{mg min}^{-1} \text{cm}^{-2}$.^[1] At these high dissolution rates reaction heat is evolved at rates of about 1.1 to 1.6×10^5 $\text{Btu hr}^{-1} \text{ft}^{-2}$.^[2] For a desirable charge of 240 kg of aluminum (equivalent to about 17 of the 19-rod clusters) in a Purex plant dissolver the initial dissolution rate must be reduced to about 25 $\text{mg min}^{-1} \text{cm}^{-2}$ so that the total boil-up rate will not exceed the condensing capacity of the dissolver tower.

Previously Schulz and colleagues^[3,4] showed that small concentrations of nickel(II) effectively inhibit dissolution

of various commercially available aluminum alloys (*e.g.*, C-64, X-1008, and 1100 alloys) in $\text{HNO}_3\text{-Hg}(\text{NO}_3)_2$ solutions. Although not completely understood, the inhibiting mechanism apparently arises from competition between $\text{Ni}(\text{II})$ and $\text{Hg}(\text{II})$ ions for electrons supplied by the aluminum metal atoms. Control of aluminum dissolution rates is achieved by proper choice of the dissolvent $\text{Ni}(\text{II})\text{:Hg}(\text{II})$ ratio.

A conceptual flowsheet for controlled dissolution of Al-Pu alloys in $\text{HNO}_3\text{-Hg}(\text{NO}_3)_2\text{-Ni}(\text{NO}_3)_2$ solution has been prepared.^[5] Laboratory studies reported here were performed to show that small concentrations of $\text{Ni}(\text{NO}_3)_2$ do indeed suppress dissolution of Al-Pu alloys in acid $\text{Hg}(\text{NO}_3)_2$ media and to test and demonstrate the conceptual flowsheet.

SUMMARY AND CONCLUSIONS

Aluminum-plutonium alloys dissolve at reduced rates in $\text{HNO}_3\text{-Hg}(\text{NO}_3)_2$ solutions which contain small concentrations of $\text{Ni}(\text{NO}_3)_2$. In such solutions the alloy dissolution rate decreases linearly as the $\text{Ni}(\text{II})\text{:Hg}(\text{II})$ concentration ratio increases. Thus, in boiling $3.86M$ $\text{HNO}_3\text{-}0.005M$ $\text{Hg}(\text{NO}_3)_2$ solution dissolution rates of Al-1.8 and 5 wt% Pu alloys are about 95, 30, and 17 $\text{mg cm}^{-2} \text{ min}^{-1}$ at $\text{Ni}(\text{II})\text{:Hg}(\text{II})$ ratios of 0, 10, and 15, respectively.

One-inch long pieces of unirradiated Al-1.8 and 5 wt% Pu alloys were totally dissolved in boiling $3.8M$ $\text{HNO}_3\text{-}0.005M$ $\text{Hg}(\text{NO}_3)_2\text{-}0.004M$ $\text{Al}(\text{NO}_3)_3\text{-}0.0$ to $0.075M$ $\text{Ni}(\text{NO}_3)_2$ dissolvents. At $\text{Ni}(\text{II})\text{:Hg}(\text{II})$ ratios of 0, 10, and 15, total dissolution times for the 1.8 wt% Pu alloy were 0.63, 4, and 5 hours, respectively; and for the 5 wt% Pu alloy 2.45, 9, and greater than 10 hours, respectively. These experiments satisfactorily demonstrated a conceptual flowsheet for controlled dissolution of Al-Pu alloys in the Purex plant dissolvers.

STUDY FLOWSHEETS

Study chemical flowsheets for decladding and dissolving PRTR Al-Pu alloys in Purex plant dissolvers have been prepared by Watrous.^[5] These flowsheets, pertinent details of which are shown in Figures 1 and 2, feature use of an $\text{HNO}_3\text{-Hg}(\text{NO}_3)_2$ dissolvent containing $0.05M$ $\text{Ni}(\text{NO}_3)_2$ to permit controlled dissolution of as many as 16.6 PRTR Pu-Al alloy fuel assemblies in one charge.

EXPERIMENTAL

MATERIALS

Several approximately one foot long pieces of unirradiated Zy-2-clad Al-1.8 and 5 wt% Pu alloys were obtained from the Pacific Northwest Laboratory, Battelle Memorial Institute. These alloys were fabricated from either type 8001 or type 1345 aluminum alloys and contained 2 wt% Ni in addition to the plutonium. One-half and one inch long pieces were cut (hack-sawed) from these rods as needed for dissolution studies.

Reagent grade chemicals were used to prepare $3.86M$ $\text{HNO}_3\text{-}0.005M$ $\text{Hg}(\text{NO}_3)_2\text{-}0.004M$ $\text{Al}(\text{NO}_3)_3\text{-}0.0$ to $0.075M$ $\text{Ni}(\text{NO}_3)_2$ dissolvents and $4.5M$ $\text{NH}_4\text{F}\text{-}0.41M$ NH_4NO_3 decladdent.

A simulated "Zirflex Rinse Heel" solution of the composition $0.015M$ $(\text{NH}_4)_2\text{ZrF}_6\text{-}0.02M$ $\text{NH}_4\text{NO}_3\text{-}0.24M$ NH_4F was prepared by dissolution of Zircaloy-2 in an $\text{NH}_4\text{F}\text{-}\text{NH}_4\text{NO}_3$ solution. As shown in Figure 2 about 25 gallons of this rinse heel will be carried over to the dissolution step.

PROCEDURE

Removal of Zy-2 Cladding. Zircaloy-2 cladding was removed from the one-half and one inch long alloy pieces by treatment for two hours in boiling $4.5M$ $\text{NH}_4\text{F}\text{-}0.41M$ NH_4NO_3 solution. The

FIGURE 1

STUDY FLOWSHEET FOR ZIRFLEX PROCESS
DECLADDING OF PRTR Al-Pu ALLOY FUEL

FIGURE 2
STUDY FLOWSHEET FOR DISSOLUTION
OF PRTR Al-Pu ALLOY FUEL

volume of decladant in each case was chosen to produce an $0.2M$ $(NH_4)_2ZrF_6$ solution.

Total Dissolution Experiments. Declad, one-inch long alloy pieces were dissolved in a glass dissolver fitted with an up-draft condenser and heated on a hot plate. A stainless steel mesh basket was used to contain the alloy piece during dissolution. The dissolver solution was sampled periodically by means of a Teflon* stopcock mounted about two inches from the bottom of the dissolver pot.

Corresponding to conditions shown in Figure 2, 45 ml of nitric acid dissolvent and 0.37 ml of Zirflex Rinse Heel were used per gram of Al-Pu alloy. Total dissolutions of both 1.8 and 5 wt% Pu alloys were performed at Ni(II):Hg(II) ratios of 0, 10, and 15. In each case immediate activation[†] occurred when declad alloy pieces were immersed at room temperature in dissolvent mixtures, and all pieces remained activated throughout the dissolution cycle. Dissolution time was counted from the time of immersion; boiling temperature was achieved about 10 minutes after alloy immersion.

Instantaneous Dissolution Rates. To determine instantaneous dissolution rates, one-half inch long declad Al-Pu alloy pieces of known weight and dimensions were immersed for one to two minutes in 500 ml of boiling HNO_3 - $Hg(NO_3)_2$ - $Al(NO_3)_3$ solution. Alloy pieces were removed from solution, rinsed with water and acetone, dried, and weighed. Dissolution rates were calculated from the weight loss, immersion time, and initial geometric area.

* E. I. du Pont de Nemours and Company.

† "Activation" is defined and described in Reference 1.

ANALYSES

Standard alpha counting and energy analysis procedures were used to determine plutonium concentrations of dissolver solutions.

RESULTS

INSTANTANEOUS DISSOLUTION RATES

Data plotted in Figure 3 clearly show that small concentrations of Ni(II) suppress the rate at which Al-Pu alloys dissolve in $\text{HNO}_3\text{-Hg}(\text{NO}_3)_2$ solutions. For the conditions used, dissolution rates of both the 1.8 and 5 wt% alloys varied equally and linearly with dissolvent Ni(II):Hg(II) ratio. The dissolution rate of both alloys at an Ni(II):Hg(II) ratio of 10 was about $30 \text{ mg cm}^{-2} \text{ min}^{-1}$, only slightly higher than specified in the conceptual flowsheet.

TOTAL DISSOLUTION EXPERIMENTS

The effect of small concentrations of $\text{Ni}(\text{NO}_3)_2$ in suppressing dissolution rates of Al-Pu alloys in $\text{HNO}_3\text{-Hg}(\text{NO}_3)_2$ solutions was very evident in total dissolution experiments (Figures 4 and 5). Thus, at Ni(II):Hg(II) ratios of 0, 10, and 15, total dissolution of the 1.8 wt% Pu alloy required 0.62, 4, and 5 hours, respectively. At these same Ni(II):Hg(II) ratios total dissolution of the 5 wt% Pu alloy required 2.45, 9, and greater than 10 hours, respectively.

Results in Figures 4 and 5 also show that the 5 wt% alloy definitely dissolves more slowly than the 1.8 wt% Pu alloy even though initial dissolution rates (Figure 3) are approximately equal.

FIGURE 3
VARIATION OF Al-Pu ALLOY DISSOLUTION
RATE WITH Ni(II):Hg(II) RATIO

FIGURE 4
TOTAL DISSOLUTION OF Al-1.8 wt% Pu ALLOY

FIGURE 5
TOTAL DISSOLUTION OF Al-5 wt% Pu ALLOY

NITRIC ACID CONSUMPTION

Approximately 1.3 moles of nitric acid were required for total dissolution of 9.29 grams of the 1.8 wt% Pu alloy in 3.86M HNO₃-0.005M Hg(NO₃)₂ solution. This value corresponds to consumption of 3.9 moles of HNO₃ per mole of aluminum dissolved and compares favorably with a value of 3.75 moles HNO₃/mole Al required for dissolution according to the reaction:^[6]

ACKNOWLEDGMENT

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