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Dissolution of HFIR Control Plates

J. C. Posey

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DISSOLUTION OF HFIR CONTROL PLATES

J. C. Posey

Radioisotope Department
Radioisotope Development and Applications

NUCLEAR WASTE PROGRAMS
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CONTENTS

ABSTRACT 1

INTRODUCTION 1

EXPERIMENTAL WORK 2

PROCEDURE 3

RESULTS AND DISCUSSION 4

SUMMARY OF CONCLUSIONS 11

REFERENCES 12

DISSOLUTION OF HFIR CONTROL PLATES

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ABSTRACT

A process was developed for the dissolution of High Flux Isotope Reactor (HFIR) control plates. These plates consist of aluminum metal, intensely radioactive europium oxide, and a small amount of tantalum metal. The radioactive solution will be diluted, mixed with grout, and disposed of by shale fracture. The plates are dissolved in nitric acid using a mercury catalyst. Conditions were determined that would produce a reaction rate compatible with existing equipment.

INTRODUCTION

A number of spent High Flux Isotope Reactor (HFIR) control plates are currently stored in the HFIR pool. The major radionuclides present are europium-152, europium-154, and europium-155. The present plans are to dissolve these plates using existing equipment at the Fission Product Development Laboratory (FPDL), Building 3517. The resulting solution will be diluted to less than 2 curies/gallon, mixed with grout, and disposed of by shale fracture.

The control plate assemblies are in the form of hollow cylinders. Each assembly consists of four quadrant sections. One section will be dissolved at a time. At present there are 22 quadrant sections awaiting disposal. The active core of the plates is Eu_2O_3 dispersed in aluminum. There is also a section of the plate which contains tantalum dispersed in aluminum. The cladding of the plates is aluminum. Each plate section contains 3,590 grams of aluminum, 1,922 grams of Eu_2O_3, and 1,297 grams of tantalum. The sections are 13.6 inches by 0.25 inches by about 30 inches. This assumes that the inactive aluminum ends have been cut off to allow the sections to fit into an available shipping cask for transport from the

HFIR to the FPDL. The section will be contained in an aluminum can inside the cask. The weight of the can is estimated to be 3,890 grams.

The process is to be carried out in tank P45 at the Fission Product Development Laboratory. This 470-gallon tank is constructed of stainless steel and is equipped with a reflux condenser and a jacket that can be used for steam heating or water cooling.

The purpose for the work described in this report was to select a dissolution process and to determine the conditions for its safe and effective use in the FPDL tank.

EXPERIMENTAL WORK

Most of the work was directed toward the dissolution of aluminum which is the principle component in the plates. The europium oxide was expected to dissolve readily in acid and the tantalum, which is the smallest component, was not expected to dissolve under any feasible process conditions.

Two processes for the dissolution of aluminum were investigated. They were: 1) the dissolution of aluminum in sodium hydroxide solution, and 2) the dissolution of aluminum in nitric acid using a mercury catalyst. The first process dissolves the aluminum but not the europium oxide which must be dissolved in a separate acid dissolution step. In the second process, both the aluminum and europium are dissolved in the same step. One advantage of the sodium hydroxide-aluminum reaction, which has been used extensively for the removal of aluminum irradiation cans from radioactive samples in this laboratory, is that hydrogen gas generated by the reaction can be reduced to a low level by the addition of sodium nitrate.

The mercury-catalyzed reaction of aluminum and nitric acid is described by Blanco[1] and by Benedict and Pigford.[2] Mercury in solution is reduced by the aluminum and forms a film on the aluminum surface. This prevents the formation of a protective oxide film and causes the aluminum to react readily with the acid. The gaseous products are H_2, N_2, N_2O, NO, and NO_2. The relative quantities depend on the conditions of the reaction. Since these gases are of some concern relative to permissible discharge concentrations into the atmosphere, quantities and compositions were considered in this study. Of these gases, NO and NO_2 are toxic, and their

concentrations are limited to 5 ppm in discharges into the atmosphere. These gases are not likely to be a problem because NO_2 reacts with water to form nitric acid and NO. The NO produced reacts with atmospheric oxygen to form more NO_2. While enroute to discharge through the isotope production area stack, the off-gas passes through a reflux condenser and three scrubbers. At the time of discharge at the stack the off-gas from the tank will have been diluted by 139,000 cfm of air.

The N_2O is generally considered to be non-toxic. Neither N_2 nor H_2 is toxic. The H_2 is a minor component in the mixture.

A limited investigation was made of the chemical methods necessary to prevent nitrogen oxide formation. In preliminary tests small additions of hydrazine eliminated all visible brown $(NO_2)_2$ fumes while slowing the reaction only moderately, but this method was abandoned because of the danger of explosive reaction. The influence of hydrogen peroxide also was investigated. It was hypothesized that this substance would oxidize nitrous acid and nitrogen oxides to nitric acid.

It became apparent in the course of this work that the heat produced by the reaction would cause vigorous boiling and that the reflux condenser on tank P45 at FPDL was inadequate if the reaction rate were near the maximum. Work was directed to determining reaction conditions that would not cause extremely vigorous boiling. Several experiments were conducted in which the reaction was carried out under nearly adiabatic conditions and the rates of heat generation and steam production were measured.

PROCEDURE

A series of tests were carried out in 2-liter beakers. Aluminum alloy samples (6061F, ASTM B 809-61) were cut from the end of a non-irradiated HFIR control plate and were approximately 1 inch by 1 inch by 0.25 inches in size. Mercury was added as mercuric nitrate solution. Normally, 1 liter of acid was used to dissolve each piece, but in some cases the volume was increased. Dissolver solutions were titrated with 1.00 M sodium hydroxide to determine the stoichiometry of the reaction. In addition to the aluminum, small strips of stainless steel and tantalum were added to the solution prior to the nitric acid and mercuric nitrate addition. This

provided a qualitative evaluation of the effect the dissolver solution would have on the tanks in which the reaction would be carried out.

The adiabatic tests were carried out in a 1-liter vacuum flask (Dewar). In these tests, aluminum samples weighing 3 to 5 grams were dissolved, and the heat produced was measured. The temperature rise time was determined, and the condensate produced was measured to provide a heat balance.

RESULTS AND DISCUSSION

Tests of the dissolution rate of aluminum were made using 1, 2, 4, and 6 M sodium hydroxide solutions. The reactions spontaneously started at room temperature and the reaction rate increased with increasing temperature and with increasing sodium hydroxide concentration. When the aluminum sample was heated on a hot plate in 6 M sodium hydroxide solution the aluminum was completely dissolved in 25 minutes. Seventy minutes were required when no external heat was added.

When one of the sodium hydroxide dissolver solutions that contained europium oxide was acidified to dissolve the europium, a gummy precipitate of aluminum hydroxide formed as the pH of the solution reached 7. This precipitate was difficult to redissolve in acid and its dissolution would be difficult, especially without agitation. The problem was solved in the laboratory by adding all of the acid in a single quick addition, causing the solution to boil. This provided good mixing and quick dissolution of the precipitate. However, the caustic dissolution was not investigated further because the acid dissolution process seemed more attractive.

The exploratory tests of the mercury catalyzed nitric acid-aluminum reaction showed the reaction was very slow when the acid concentration was in the 10 to 11 M range. At acid concentrations of 4 to 6 M the reaction was rapid. At concentrations of from 1 to 2 M the rate was slower but still comparatively fast. Mercury concentrations of from 0.3 to 0.5 grams/liter were used in these tests.

The tests in the 4 to 6 M range followed a consistent pattern when the reactants were heated together, starting at room temperature. At low temperatures the reaction rate was very slow. It increased at a moderate rate as the temperature increased until a critical temperature was reached. At this point the reaction rate increased very rapidly and heated the solution to the boiling point. Very vigorous boiling took place for several minutes (in several cases the beaker boiled over). This was followed by a much longer period of slower reaction that lasted until the aluminum was dissolved. The temperature at which the rapid reaction started varied from 60 to 85°C. In other tests the onset of the rapid reaction was controlled by delaying the addition of the mercury catalyst until the desired temperature was reached. It was found that the later slow part of the reaction could be speeded up by a second addition of mercury catalyst, while the addition of nitric acid late in the reaction had no apparent effect.

The influence of iron was tested at two different ratios of iron to aluminum. The higher ratio, 2.6 grams iron per gram of aluminum, would occur if the control plate were lowered into the reaction tank in a mild steel carrying can. In the first test, using 5.0 M acid and 0.5 grams/liter mercury, only 3% of the aluminum dissolved in 35 minutes. In similar tests, but with no iron present, complete dissolution took place in 47 and 53 minutes. In a second test the concentration of mercury was doubled. Complete dissolution took place in 170 minutes.

The lower iron/aluminum ratio, 0.12, would result from the use of an iron cable and clamp to lower the control plate in an aluminum can into the reaction tank. A test using this ratio was carried out using 5.7 M nitric acid and 0.5 gram/liter mercury. After 66 minutes, 47% of the aluminum had dissolved. In a second test, using 5.2 M acid and 1.0 gram/liter mercury, complete dissolution took place in 68 minutes.

The addition of rare earth oxides had no apparent effect on the reaction; the oxides dissolved quickly.

The reaction was carried out without boiling, using relatively large volumes of dilute acid. A test using 2.7 M nitric acid and an initial mercury concentration of 0.33 gram/liter went to completion without boiling.

The acid volume to aluminum ratio was 94 milliliters/gram. This is double that used in the earlier tests. The maximum reaction temperature was 96°C. The time to complete the reaction after initial mercury addition was 44 minutes. A second mercury addition of 0.33 gram/liter was made after 30 minutes reaction time to speed completion. Another test using the same mercury addition schedule and 2.2 M acid was complete in 59 minutes. The acid to aluminum ratio was 109 milliliters/gram. A third test using 1.8 M acid and mercury additions of 0.17 on first addition and 0.11 gram/liter for the second addition required 305 minutes. The acid to aluminum ratio was 126 grams/milliliter. The average temperature was appreciably lower in the third reaction than in the previous two.

Reactions carried out below the boiling point would cause very little load on a reflux condenser, but because of heat dissipation problems, would be difficult to carry out in the large scale operation at FPDL. The ratio of heat generation to surface area will be approximately tenfold greater at FPDL than in the 2-liter beaker. Consequently, later tests were carried out in a vacuum (Dewar) flask. With this equipment, the proportional heat losses to the surroundings were at least as low as those that will occur at FPDL. The data from these tests clearly showed the course of the reactions and allowed estimates of the heat load of the condenser under operating conditions.

Calculations had shown that more than half of the total heat of the reaction would be used in heating the solution to boiling when about half of the FPDL tank volume was used. Consequently, it was expected that the peak reaction rate would have passed before boiling started.

Figure 1 shows the temperature, the rate of heat generation, and the heat load of the reflux condenser as functions of time for two typical tests. In both cases the rate of heat generation peaked sharply well below the boiling temperature. The maximum heat loads of the reflux condenser were much lower than the peak rates of heat generation. The data shown in Figure 1 have been scaled to the full scale operation at FPDL. More details of these tests, runs 3 and 6, are given in Table 1.

The results of all seven tests carried out in the vacuum (Dewar) flask are given in Table 1. All volumes and heats have been scaled to the size of the full scale operation. It was assumed that all values would increase proportionately to the weight of aluminum.

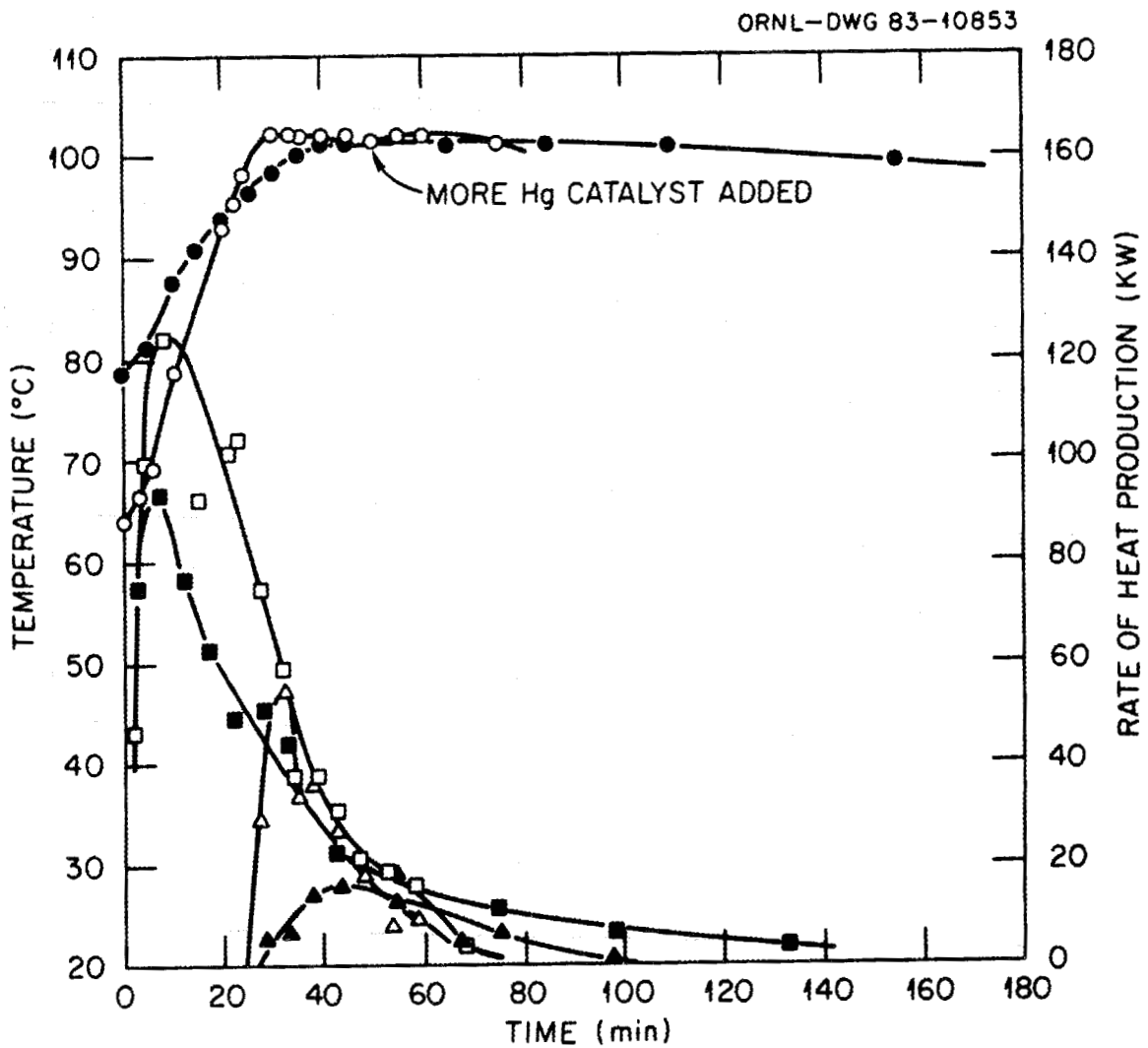

Figure 1. Heat production and condenser load during control plate dissolution.

○ Temperature in Test 3; □ Total rate of heat production in Test 3; △ Heat load of reflux condenser in Test 3; ● Temperature in Test 6; ■ Total rate of heat production in Test 6; and ▲ Heat load of reflux condenser in Test 6.

Table 1. Maximum Rates of Heat Generation and Maximum Condenser Heat Loads During the Dissolution of Control Plate Quadrants

Test	Acid Conc. (M)	Volume (liters)	Starting Temp. (°C)	Max. Rate of Heat Generation KW	Max. Rate of Heat Generation BTU/hr	Max. Heat Load of Condenser KW	Max. Heat Load of Condenser BTU/hr	Hg (g)	g Fe/g Al
1	1.8	978	64	181	6.2×10^5	33	1.1×10^5	520	0.10
2	1.8[a]	903	63	112	3.8×10^5	40	1.4×10^5	479	0.11
3	1.8[a]	877	64	126	4.3×10^5	54	1.9×10^5	310	0.10
4	1.4[a]	876	66	146	5.0×10^5	38	1.3×10^5	310	0.31
5	1.4[a,b]	1036	87	119	4.0×10^5	50	1.7×10^5	249	0.11
6	1.2	1255	79	91	3.1×10^5	16	5.5×10^4	376	0.22
7	1.0[b]	1469	73	50	1.7×10^5	neg	neg	407	0.18

[a]Rare earth oxides were present.

[b]Three liters and 5.7 liters of 30% hydrogen peroxide were added in tests 5 and 7 respectively.

A comparison of tests 1, 2, and 3 show the lowering of the peak condenser load with increased solution volume. Test 5 shows the adverse effect of high starting temperature. Comparison of tests 3 and 4 shows the lowering of the condenser heat load with decreased acid concentration.

The maximum heat load of the condenser did not exceed the estimated capacity of the condenser in any of the tests shown in Table 1, although in test 3 the heat load did essentially equal the estimated capacity of the condenser.

The conditions of test 6 are recommended for use at FPDL. The lower starting temperatures of tests 1 through 4 could not be consistently reproduced. The larger volume of solution used in test 6 compensates for a higher starting temperature. The aluminum was completely dissolved in 135 minutes in this test. The time could have been reduced by a second addition of mercury late in the reaction. The relatively high iron/aluminum ratio may have slowed the reaction. Test 4 is of interest in that essentially all of the acid was consumed. The final pH was 1.1.

The molar ratio of nitric acid consumed to aluminum dissolved varied in the range of 3.6 to 3.8 for the rapid reaction rates in 4 to 6 M nitric acid. These are average values for several reactions that occur simultaneously. Some of the reactions carried out below the boiling point gave

lower ratios. There is some uncertainty in all of these values because of the problems involved in titrating acid in solutions containing aluminum nitrate and because of possible losses of acid vapor. The reaction producing NO has a molar ratio of 4. The low values observed may indicate the formation of substantial amounts of N_2O, N_2, and H_2, or they may indicate appreciable reoxidation of NO to NO_2 and the reaction of NO_2 with water to form nitric acid.

The production of nitrogen oxides was not directly investigated, but certain observations were made. The gas, NO_2, which is present as $(NO_2)_2$, is visible because of its brown color. NO quickly oxidizes to visible NO_2 on contact with air. Large amounts of NO_2 were never observed at temperatures much below the boiling point of the solution. Large amounts of NO_2 were seen in the fast reactions using 4 to 6 M nitric acid after the solutions reached the boiling point.

A small amount of NO_2 was observed in the condensation cylinder during the vacuum flask runs. This probably resulted from the oxidation of NO. When hydrogen peroxide was added in the vacuum flask runs, the NO_2 was barely detectable. Thus, hydrogen peroxide may be of value in reducing nitrogen oxide production. However, no problem is anticipated.

The stainless steel corrosion samples showed very little attack. Weight losses were in the range of 10^{-8} to 10^{-7} $g/cm^{-2}hr^{-1}$.

The tantalum samples were not dissolved to any measureable degree in the acid dissolution tests. The tantalum in the control plates will not dissolve but will accumulate in the tank.

Tests were made of the final steps of the process. The solution from a dissolution test was diluted and neutralized with sodium hydroxide. The particle size distribution of the resulting precipitate was determined. The pH of the solution was measured after each of a series of dilutions. The results are given in Table 2. If this solution had been produced by the dissolution of a 3.5-year-old plate, a 41-fold dilution would have been required to reduce the radionuclide content to 2 curies/gallon. The solution initially contained 7.9 grams/liter of aluminum, 0.82 gram/liter of iron, and 0.64 mole/liter of hydrogen ion.

Table 2. Influence of Dilution on the Acidity of Waste Solution

Degree of Dilution	pH
10 to 1	1.20
20 to 1	1.55
40 to 1	1.87
50 to 1	2.00

The pH values are close to those predicted by simple dilution calculations. This indicates that the hydrolysis of the Al^{3+} and Fe^{3+} ions did not make a significant contribution to the acidity.

The addition of 37.5 milliliters of 1 M sodium hydroxide per liter of the diluted solution (50 to 1) caused precipitation and increased the pH to 9.9. The particle size distribution of this precipitate was determined using a Leeds and Northrup MICROTRAC. The results, given in Table 3, indicate that the precipitate could be pumped as a slurry.

Table 3. Particle Size Distribution of Precipitate

Particle size range (μm)	Percent of particles falling in range
16-22	4.2
11-16	12.5
7.8-11	11.1
5.5-7.8	24.5
3.9-5.5	18.9
2.8-3.9	11.7
<2.8	5.6

A study and estimate report for the facility for the HFIR control plate dissolution and other very high activity wastes was published July 30, 1982, by the UCC-ND Engineering Division.[3]

SUMMARY OF CONCLUSIONS

1. The maximum rate of the mercury-catalyzed reaction of nitric acid with aluminum is too great for use in tank P45 at FPDL because of the limited capacity of the reflux condenser.

2. The reaction rate is slowed by the presence of iron, but the reaction rate can be made adequate with additional mercury.

3. The load of the reflux condenser can be reduced to a safe level if a large volume of dilute acid is used for the reaction.

4. The solution resulting from the dissolution of a control plate quadrant can be diluted and neutralized with sodium hydroxide. The resulting slurry is satisfactory for disposal by the hydrofracture process.

5. The following procedure is recommended for the dissolution:
   1) The control plate quadrant is dropped into FPDL tank P45 which will contain 1236 liters of 1.2 M nitric acid.
   2) The tank is heated to 79°C.
   3) Three hundred seventy-six grams of mercury added as mercuric nitrate solution will cause the reaction to go to completion.

6. Laboratory work indicates satisfactory operation of the process. However, a full-scale test is needed before a procedure is adopted.

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