

# Mercury-free dissolution of aluminum-based nuclear material: from basic science to the plant

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**Abstract** Conditions were optimized for the first plant-scale dissolution of an aluminum-containing nuclear material without using mercury as a catalyst. This nuclear material was a homogeneous mixture of plutonium oxide and aluminum metal that had been compounded for use as the core matrix in Mark 42 nuclear fuel. Because this material had later failed plutonium distribution specifications, it was rejected for use in the fabrication of Mark 42 fuel tubes, and was stored at the Savannah River Site (SRS) awaiting disposition. This powder-like material was composed of a mixture of ~80% aluminum and 11% plutonium. Historically, aluminum-clad spent nuclear fuels [13] have been dissolved using a mercuric nitrate catalyst in a nitric acid ( $\text{HNO}_3$ ) solution to facilitate the dissolution of the bulk aluminum cladding. Developmental work at SRS indicated that the plutonium oxide/aluminum compounded matrix could be dissolved using boric acid–hydrofluoric acid–nitric acid as a substitute for mercury. Various mercury-free conditions were studied to evaluate the rate of dissolution of the Mark 42 compact material and to assess the corrosion rate to the stainless steel dissolver. The elimination of mercury from the dissolution process fit with waste minimization and industrial hygiene goals to reduce the use of mercury in the United States. The mercury-free dissolution technology was optimized for Mark 42 compact material in laboratory-scale tests, and successfully implemented at the plant.

**Key words** aluminum dissolution • plutonium oxide dissolution • stainless steel corrosion • mercury-free

## Introduction

The SRS mission to recover plutonium for nuclear weapon components stopped in 1992 with the end of the Cold War. However, the United States Department of Energy (US DOE) continued to support SRS processing to stabilize nuclear materials, including corroding aluminum-clad spent nuclear fuels [9] and other legacy materials from previous processing campaigns.

Since the 1950's, dissolution of aluminum-clad spent nuclear fuel at SRS was carried out in  $\text{HNO}_3$  with a mercury catalyst [14]. Under ambient conditions, aluminum forms an oxide layer on the surface, which protects it from further oxidation and corrosion. To dissolve aluminum, a chemical reagent is required to react with the protective aluminum oxide layer (that continually forms under oxidizing conditions) and expose the underlying aluminum metal to attack by  $\text{HNO}_3$ . Mercury fulfills this requirement by forming a mercury-aluminum amalgam that is soluble in  $\text{HNO}_3$ , and once dissolved, liberates mercury and thus, regenerates the catalyst [16]. In boiling 8 M  $\text{HNO}_3$  containing 0.003 to 0.05 M mercury nitrate, the initial dissolution rate of aluminum is greater than 150 mg/min-cm<sup>2</sup>.

In 1956, the toxic effects of mercury were realized when more than 50 people died from fish and shellfish consumption in Minamata, Japan [7]. In that event, inorganic mercury from a chemical factory producing vinyl chloride and acetaldehyde was discharged into the sea, where biological action transformed some of the inorganic mercury

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Received: 16 May 2003, Accepted: 29 July 2003

to methylmercury. The methylmercury accumulated in the fish, which were then consumed by the general population. By 1975, over 15,000 people received compensation for damages caused by the ingestion of the tainted fish. This incident was the catalyst for the international and national regulation of industrial waste streams containing mercury.

Inorganic and organic mercury are known to be toxic, are suspected carcinogens, and tend to bioaccumulate [10]. Mercury is most toxic in the organic form. The primary exposure routes for mercury poisoning are ingestion, inhalation and transdermal passage. Acute mercury poisoning irritates the contacted tissue, while chronic exposure damages the central nervous system and the kidneys. Severe methylmercury poisoning can numb the extremities to the point of non-functionality as well as cause blindness and deafness. With new epidemiological data available, recent legislation in the United States established new limitations for mercury exposure. In 1997, United States Environmental Protection Agency (EPA) lowered the methylmercury "reference dose" to 0.1 micrograms per kilogram of body weight [15]. In 2000, the National Research Council supported the EPA methylmercury standard based on the widely varying neurological impacts on the children born from mothers who were exposed to high levels of methylmercury.

In spite of efforts to identify a suitable substitute to the mercury catalyst for dissolution of aluminum-based nuclear materials [3], none had been identified, and mercury remained the catalyst of choice at SRS.

The inventory of the legacy materials targeted for processing at SRS included both unirradiated Mark 42 fuel tubes and reject Mark 42 compact material. The compact material had been rejected for fabrication into fuel tubes because it had failed plutonium distribution specifications. For the fuel tubes [11], the core material consisted of a plutonium oxide/aluminum matrix. Since the fuel tubes had not been irradiated, the plutonium oxide present in the core matrix was much harder to dissolve than if the plutonium oxide had been irradiated. Irradiation causes defects to form in the plutonium oxide crystal, making it more amenable to dissolution. The unirradiated material needed more aggressive dissolution conditions. Fluoride ions were added to the  $\text{HNO}_3$  to promote the dissolution of the refractory plutonium oxide. Calcium fluoride was used as the fluoride source. As plutonium-239 isotope was about 80% of the plutonium, nuclear criticality safety required that a neutron poison be added to the solution. Boric acid was used as the neutron poison. For developmental studies at the Savannah River Technology Center (SRTC) at SRS, to simulate the slower reaction rates after the aluminum cladding and aluminum packaging of the fuel tubes had already been dissolved, aluminum nitrate nonahydrate was added to the dissolving solution without mercury. The mercury-free conditions were initially evaluated to avoid generating a mixed hazardous waste. The core material of the Mark 42 fuel tubes were simulated with a sample of rejected Mark 42 compact material because actual fuel tube material was not accessible. There were concerns that the dissolution of the aluminum in the reject Mark 42 compact material might require mercury. However, the development work for the dissolution of the Mark 42 fuel tubes, indicated that mercury was not needed to dissolve the core material. In the actual SRS plant campaign to dissolve the Mark 42 fuel tubes, mercury was

used to assist with the dissolution of the bulk aluminum cladding and containers in which the fuel tubes were packaged for dissolution.

When SRTC evaluated the dissolution flowsheet for the reject Mark 42 compact material, mercury-free dissolving conditions were considered feasible based on the previous work for the Mark 42 fuel tubes. A literature review indicated that the success in dissolving the aluminum in the matrix of the rejected Mark 42 material was attributed to the formation of fluoroboric acid ( $\text{HBF}_4$ ) from the addition of boric acid and calcium fluoride to the dissolving solution. In 1994, Christian and Anderson [1, 2] at the Idaho National Engineering and Environmental Laboratory (INEEL) discovered an environmentally-benign substitute for the mercuric nitrate catalyst,  $\text{HBF}_4$ . The use of  $\text{HBF}_4$  was optimized for a continuous process on the laboratory-scale that dissolved an aluminum alloy (Al6061) at a rate of  $40 \text{ mg/cm}^2\text{-h}$  at  $100^\circ\text{C}$  using  $0.15 \text{ M HBF}_4$  in  $7 \text{ M HNO}_3$ . The steady state concentration of  $\text{Al}^{3+}$  (aq) and  $\text{HNO}_3$  were  $1.0 \text{ M}$  and  $3.3 \text{ M}$ , respectively. Under these steady state conditions, the corrosion rate of 304L stainless steel was  $0.64 \text{ mm/year}$ . Because  $\text{HBF}_4$  solutions are somewhat corrosive, a proper balance between aluminum dissolution rate and the stainless steel dissolver corrosion rate must be identified for specific materials and conditions.

The development of the dissolving conditions of the reject Mark 42 compact material began with the dissolving conditions determined for the Mark 42 fuel tubes. However, as the aluminum concentration of dissolved reject Mark 42 compact material was much less than that of the fuel tubes because it did not contain cladding, it was expected that only a few modifications to the dissolving conditions for the Mark 42 fuel tubes would be required. The proposed  $\text{HNO}_3$  dissolver solution was to contain boron as a soluble neutron poison for nuclear criticality safety and fluoride salts to promote the dissolution of plutonium oxide. Based on the development work for the dissolution of the Mark 42 fuel tubes and on the INEEL studies, it was anticipated that mercury could be eliminated for the dissolution of the reject Mark 42 compact materials. This elimination of mercury from a process flowsheet would support environmental initiatives to reduce mercury emissions in the United States and industrial hygiene initiatives to minimize worker exposure to mercury.

In contrast to the work of Anderson and Christian [1] in which  $\text{HBF}_4$  was added to facilitate the nitric acid dissolution of aluminum, this work approached the same equilibria but from a different direction. Our innovation was to control the dissolver solution chemistry by adding boric acid, calcium fluoride, and nitric acid separately whereas the  $\text{HBF}_4$ -nitric acid dissolution is inherently limited by its fixed B:F ratio of 1:4. We varied the B:F ratio and Al:F ratio to find an acceptable balance between the aluminum dissolution time and the dissolver corrosion rate.

## Experimental

In this work, simulated dissolver solutions were evaluated for their ability to dissolve the Mark 42 compact material in 24 h or less. Subsequently, adequate dissolver solutions were independently evaluated for corrosion potential to the stainless steel. For a given dissolver solution chemistry,

the target was to obtain an acceptable aluminum dissolution with minimal stainless steel corrosion.

### Aluminum dissolution rate studies

Four 500 mL solutions containing calcium fluoride (0.2 to 0.6 M) and boric acid (0.1 to 0.3 M) in 8 M HNO<sub>3</sub> were prepared. The solutions were heated to 85°C in 1000 mL polymethylpentene bottles nested in water-filled 1500-mL beakers. The acidic solutions were stirred at 330 revolutions per minute (rpm) with Teflon<sup>®</sup> stir bars. Once the solutions reached the target temperature, two aluminum coupons were suspended in each polymethylpentene bottle. After 30 min, the coupons were removed from the reaction vessels, dried, weighed, and the dimensions of the coupons were measured with a digital micrometer. Subsequently, the coupons were returned to the reaction vessels and the dissolution proceeded. The mass and dimensions of the coupons were then measured approximately every hour. The corrosive solution continued to be heated when the coupons were removed to maintain a constant reaction temperature. Due to the small mass of the aluminum coupons, the addition of the room temperature coupons to the heated solutions did not significantly affect the reaction vessel temperature. The dissolution rate of aluminum was calculated in mg per cm<sup>2</sup> per minute.

### Stainless steel corrosion rate studies

Stainless steel corrosion tests were performed to evaluate the effect of different mercury-free dissolution solutions on the stainless steel dissolver. Coupon immersion corrosion tests were performed in solutions with chemical compositions that bracketed those specified in the flowsheet. In this work, the effect of boric acid and calcium fluoride concentrations were evaluated for plant-scale processing of aluminum-based nuclear materials in 8 M HNO<sub>3</sub>.

Corrosion rates of AISI Type 304 stainless steel coupons, both welded and non-welded coupons, were immersed in a dissolver solution in week-long corrosion tests [6]. The same range of conditions was evaluated as in the aluminum dissolution rate studies. The stainless steel corrosion experiments were performed in Teflon<sup>®</sup> bottles since it is chemically resistant to HNO<sub>3</sub> and fluoride ions, and can withstand the test temperatures. The coupons were attached to the bottle lid so they could be easily removed from the bottle to be weighed. Each coupon was suspended to ensure complete immersion in the solution. A Teflon<sup>®</sup> tape was used on the bottleneck to minimize evaporation. All bottles were placed on a stainless steel tray and positioned within an oven at 90°C. The mass and dimensions of the steel coupons were determined before the experiment began, after 24 h, and then again after one week had elapsed. The corrosion rate in terms of thickness of steel lost per time in mm/year was calculated for each metal coupon. A corresponding value for the dissolver wall loss was calculated for the entire Mark 42 campaign based on the experimental corrosion rates.

### Laboratory-scale dissolution studies with Mark 42 compact material

The material used to simulate the dissolution of unirradiated Mark 42 compacts and sweepings was authentic crushed reject compact material from the Mark 42 program. Inductively-Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) analysis of a HNO<sub>3</sub> solution of a known mass of compact material indicated the material was composed 80% ( $\pm 3$ ) aluminum (as aluminum metal). X-ray diffraction data showed plutonium present as plutonium oxide and the concentration of plutonium was determined as 11% based on alpha and gamma radioactive counting methods. Additional components include oxygen present in plutonium oxide, amorphous aluminum oxide, and adsorbed water. Visibly, the crushed compact material is a homogeneous mixture of fine gray solids and coarse gray chunks as shown in Fig. 1.

Based on nuclear criticality safety evaluation for the Mark 42 compact processing campaign, the HNO<sub>3</sub> dissolver solutions contained boric acid at a minimum concentration of 2 g/L as a soluble neutron poison. Fluoride was added as calcium fluoride. Aluminum and boron complexed fluoride ions, and thus, required high concentrations of fluoride to promote the dissolution of the plutonium oxide. At the high fluoride concentrations using potassium fluoride as the fluoride source, boron precipitated from test solutions as potassium tetrafluoroborate (KBF<sub>4</sub>) [5]. Calcium fluoride proved a suitable source of fluoride ions. The initial HNO<sub>3</sub> concentration was 8 M for each batch test, but 3.75 moles of acid are consumed per mole of aluminum dissolved as reported by Wymer and Blanco [16]. Therefore, dissolution rates decreased as HNO<sub>3</sub> was consumed and as fluoride was complexed by aluminum(III). In this study, dissolver solution contact times required to achieve the mercury-free dissolution of authentic Mark 42 material were determined using a complicated solution matrix that closely simulated the plant matrix.

The following nominal values were expected from the charge of Mark 42 materials to the dissolver for dissolution. Mark 42 rejected compact material composition was 11% plutonium, 80% aluminum. The compact material would



Fig. 1. Mark 42 compact material.

**Table 1.** Laboratory-scale tests to simulate plant-scale dissolution of Mark 42 compact material.

Test no.	Experimental		Simulating		For all solutions: CaF <sub>2</sub> is F-source [Nylon] = 0.1 g/L					[Al]:[F] ratio	Time to dissolve  (h)
	Mass Mark 42 (g)	Volume initial (L)	Mass Pu (kg)	Volume solution (L)	[Pu] (g/L)	[Fe] (g/L)	[B] (M)	[Al] (M)	[F] (M)		
1	3.1272	0.250	11	8000	1.38	1.5	0.19	0.37	0.20	1.9	32
2	3.1383	0.250	11	8000	1.38	1.5	0.19	0.37	0.25	1.5	35
3	3.1314	0.250	11	8000	1.38	0	0.19	0.37	0.30	1.2	7
4	3.1336	0.250	11	8000	1.38	1.5	0.19	0.37	0.30	1.2	7
5	2.8452	0.250	10	8000	1.25	1.5	0.19	0.34	0.23	1.5	>30
6	2.8388	0.250	10	8000	1.25	1.5	0.19	0.34	0.25	1.3	14

be introduced to the dissolver using a can-in-can (carbon steel) configuration. For a single dissolver charge, 32 inner cans in 32 outer cans would be present. The mass of inner and outer carbon steel can be 114.26 g and 158.70 g, respectively. Each inner can would be contained within two linear feet of Nylon bag to give 64 linear feet of Nylon bag per charge. The mass of one linear foot of Nylon bag was 9 grams. Each charge contained 10 kg of plutonium in 8000 liters of solution.

Six tests that were conducted to simulate various dissolution conditions are shown in Table 1. The first four tests simulated an 11-kg charge of plutonium in 8000 liters, and the last two tests simulated a 10-kg charge of plutonium in 8000 liters. Mercury was not added in any of the tests. While the solution chemistry is dynamic throughout the dissolution process, we have found a correlation between the [Al]:[F] ratio and the time required for dissolution.

Dissolver solutions containing HNO<sub>3</sub>, boric acid, calcium fluoride and distilled water were prepared. Samples were taken from the fresh dissolver solution for elemental analyses. The dissolver solution was heated to ≤40°C in glass beakers, and can material and Nylon bag were added, and stirred until dissolution of these materials was complete. Samples were taken from this solution containing dissolved can and Nylon.

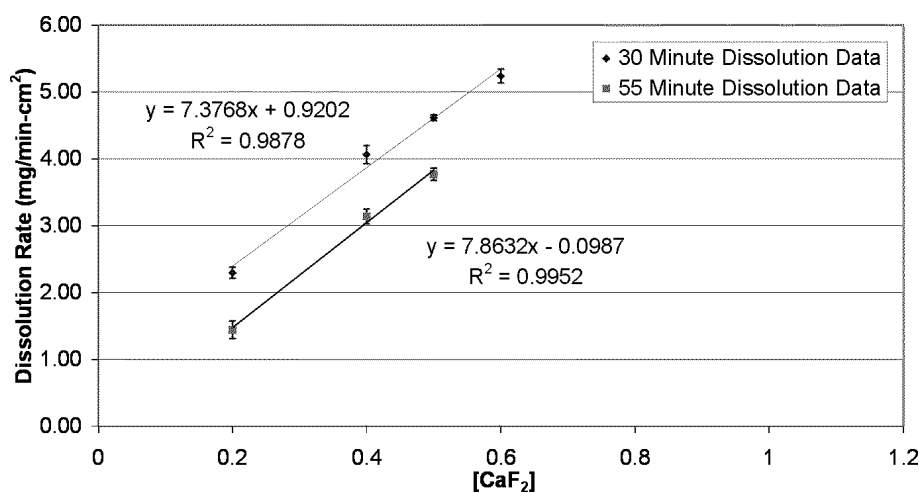
Next, Mark 42 compact material was added to each dissolver solution. A watchglass condenser was placed on the top of each beaker, and loaded with water. Each reaction mixture was stirred at a rate of 300 rpm while heating to

about 65°C. At about 65°C, the hot plate was turned off as the exothermic dissolution of aluminum initiated. The reaction mixture self-heats to a maximum temperature between 85°C and 100°C. After the temperature peaked, the hot plate was turned on again, and the reaction mixture was maintained at 85°C and visually monitored for 8 h shifts. A black solid (PuO<sub>2</sub>) settled to the bottom of the beaker, and slowly dissolved. Samples were taken from the liquid after each heating period to analyze for plutonium by alpha and gamma radioactive counting methods and for elemental composition by ICP-AES. Dissolution was deemed complete when no solids were visually observed. In addition, complete dissolution was confirmed when a Tyndall effect was not observed in a stirred solution. The absence of a Tyndall effect is evidence no solids are suspended in the liquid phase and that a liquid is a true solution.

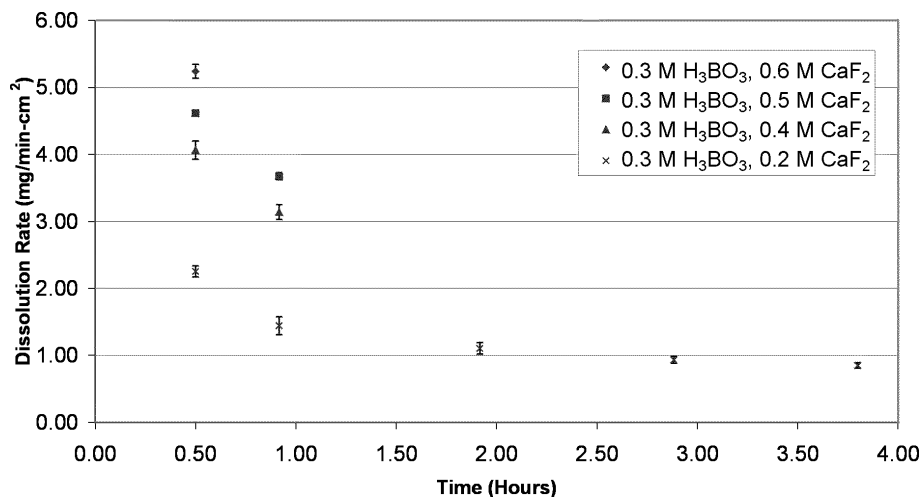
## Results and discussion

### Aluminum dissolution rate studies

The dissolution rates of the aluminum coupons measured in this study were comparable to the aluminum dissolution rates (e.g. 40 mg/cm<sup>2</sup>-h at 100°C using 0.15 M HBF<sub>4</sub> in 7 M HNO<sub>3</sub>) by Anderson and Christian [1]. However, Anderson and Christian described a continuous steady state process while this work evaluated batch dissolution conditions.



**Fig. 2.** Thirty minute and 55 minute aluminum (6063) dissolution rates as a function of calcium fluoride concentration, with [H<sub>3</sub>BO<sub>3</sub>] fixed at 0.3 M.



**Fig. 3.** Aluminum (6063) dissolution rates at various calcium fluoride concentrations as a function of time, with  $[H_3BO_3]$  fixed at 0.3 M.

#### Effect of varied fluoride concentration at fixed boric acid concentration

The evidence of the aluminum dissolution mechanism with the fluoride– $HNO_3$  system has been reviewed [1]. First, HF reacts with the protective aluminum oxide layer to remove it, followed by  $HNO_3$  attack on bulk aluminum. With initial concentrations of 8 M  $HNO_3$  and 0.3 M boric acid, this work verified that the batch process dissolution rate of aluminum increased linearly with calcium fluoride concentration (Fig. 2). However, for each batch dissolution, the dissolution rates decrease with time as shown in Fig. 3 because  $HNO_3$  is consumed by the oxidation of aluminum and because fluoride ions are complexed by the dissolved aluminum cations. These observations are consistent with the proposed mechanism for aluminum dissolution. In the 0.6 M fluoride system (Fig. 3), the coupons were so degraded after thirty min that no subsequent rate measurements were possible. To measure the decrease in reaction rate with time for the more corrosive systems, larger masses of aluminum are necessary. Nitrogen oxides ( $NO_x$ ) gas generation, a measure of reaction rate, qualitatively decreased in all systems as the dissolutions proceeded.

#### Effect of varied boric acid concentration at fixed fluoride concentration

Varying boron concentrations (0.1 to 0.3 M) in the fluoride– $HNO_3$  system had no measurable effect on the dissolution rate of aluminum (measured in  $mg/min\text{-}cm^2$ ) as shown in Table 2. After a given time interval at a fixed calcium fluoride concentration, the dissolution rates were essentially the same.

**Table 2.** Effect of boric acid concentration on Al dissolution, at fixed  $[CaF_2]$ .

	$[H_3BO_3]$ M	Al dissolution rate ( $mg/min\text{-}cm^2$ )	
		30 min	55 min
0.2 M $CaF_2$	0.1	2.3	1.3
	0.2	2.2	1.4
	0.3	2.3	1.4
0.4 M $CaF_2$	0.2	4.0	3.2
	0.3	4.1	3.1

#### Relative rates of dissolver solutions

The aluminum dissolution rates of various dissolver solutions relative to 6 M  $HNO_3$  are compared in Table 3. Clearly, the fastest dissolution rates are achieved with the addition of mercury. The boric acid–fluoride systems offer much slower rates relative to the mercury system, however, the surface area of the material will have a large effect on the time required to achieve complete dissolution. For example, a high surface area material (e.g. reject Mark 42 compact material), the dissolution time would be considerably shorter than for bulk material (i.e. aluminum cladding or packaging).

#### Stainless steel corrosion rate studies

The corrosion rates for 304 and 304L stainless steel in the dissolution solutions were calculated from the coupon weight losses. The weight losses were determined from the initial, one-day, and final weight measurements. The corrosion rate in  $mm/year$  was calculated from the following equation:

**Table 3.** Relative aluminum dissolution rate experiments.

Dissolver solution		Relative dissolution rate
6.0 M $HNO_3$	[8]	1.00
10% DW-560, 6.0 M $HNO_3$	[8]	1.58
0.10 M $H_3PO_4$ 0.01 M K, Mg, Cu, Zn, Sn 6.0 M $HNO_3$	[8]	2.50
0.25 M $ZrF_4$ , 6.0 M $HNO_3$	[8]	3.33
0.10 M NaF, 6.0 M $HNO_3$	[8]	3.67
0.33 M $Al^{3+}$ (average) 0.2 M $H_3BO_3$ , 0.2 M $CaF_2$ 8 M $HNO_3$	[this work]	6.75
0.99 M $Al^{3+}$ (steady state) 0.20 M $HBF_4$ 7.0 M $HNO_3$	[1]	11.3
0.001 M Hg, 6.0 M $HNO_3$	[16]	83.3
0.002 M Hg, 6.0 M $HNO_3$	[16]	1416

**Table 4.** Corrosion rate of 304 welded stainless coupons in 0.2 M  $\text{H}_3\text{BO}_3$  – 8 M  $\text{HNO}_3$  at 90°C.

[CaF <sub>2</sub> ], M	Corrosion test	
	24-h (mm/year)	168-h (mm/year)
0.10	0.64	0.64
0.15	0.71	0.86
0.20	0.84	1.07
0.25	1.02	1.35
0.30	1.27	1.78
0.35	1.65	2.36

$$(1) \quad \text{Corrosion rate} = [C \cdot (W)] / [\rho \cdot A \cdot t]$$

where:  $C$  – corrosion constant ( $3.45 \times 10^6$ );  $W$  – weight loss (g);  $\rho$  – density of stainless steel ( $\text{g/cm}^3$ );  $A$  – surface area of coupon ( $\text{cm}^2$ ),  $t$  – time (h).

For both the one day and the one week data, the corrosion rates indicated a relatively mild corrosion on the dissolver vessel (Table 4). Corrosion rates for the welded coupons were consistently higher than the corrosion rates for the non-welded coupons. However, the difference between the two decreased as the solution aggressiveness decreased. In these tests, solution aggressiveness corresponded with the fluoride concentration.

The mild corrosion damage expected by the dissolution processes is evidence of the affinity of boron and aluminum for the fluoride anions, and is consistent with the “buffer” theory of Anderson and Christian [1].

#### Laboratory-scale dissolution studies with Mark 42 compact material

For the PUREX processing of nuclear materials, complete dissolution is important to prevent the transfer and buildup of fissile solids into the solvent extraction system and other downstream processes. The prevention of solid accumulation is important for process efficiency, but most importantly for nuclear criticality safety. The rate of dissolution of materials in the canyon dissolver is of practical concern because of the large inventory of legacy material targeted for processing, limited facilities available for processing, and programmatic incentives aimed at accelerated stabilization and additional facility closures [12]. During the processing campaigns, the rate of corrosion to the dissolver is also a primary concern because the dissolver equipment used is aging and approaching the end of its useful life. For a single charge in a canyon dissolver, a maximum dissolution time of 24 h was set for as an arbitrary target for processing efficiency. Within this time interval, the dissolver had to be charged, heated, and the material had to be dissolved completely while the corrosion rate for the dissolver must be less than 1.3 mm/year.

In this work, the dissolution time for Mark 42 material was determined under various conditions in laboratory-scale tests (Table 2, Fig. 2). The fluoroboric acid matrix was evaluated as a mercury-free dissolver solution by separate additions of calcium fluoride and boric acid. Boron

(added as boric acid) is used in the dissolver as a neutron poison and as a nuclear criticality safety control, however, boric acid also complexes fluoride anions, thus, complicating the solution chemistry.

Fluoride is corrosive and enhances the dissolution rate of aluminum and also catalyzes the dissolution of plutonium oxide. A successful dissolution will require that both aluminum metal and plutonium oxide are dissolved. In this work, the bulk of the aluminum components were dissolved within the first hour of reaction time, and the dissolution time was principally determined by the dissolution of the plutonium oxide. The best predictor of a batch dissolution time of Mark 42 compact material within the 24 h limit was identified as the Al:F ratio. In the laboratory-scale test results shown in Table 1, complete dissolution within 24 h was achieved with the Al:F ratio of 1.3 or less. For higher Al:F ratios, the dissolved aluminum ions complexed most of the fluoride anions, thus, inhibiting the rate of plutonium oxide dissolution. Test number 6 showed that 0.25 M fluoride (0.125 M  $\text{CaF}_2$ ) achieved dissolution in 14 h.

#### Plant-scale dissolution studies with Mark 42 compact material

Based on the laboratory-scale dissolution and corrosion rate studies, a full-scale mercury-free co-dissolution of plutonium oxide and aluminum was performed at SRS on Mark 42 compact material, showing that mercury-free fuel processing is feasible for high surface area material. While laboratory-scale tests in 8 M  $\text{HNO}_3$  dissolution indicated a 0.25 M fluoride solution would be adequate for complete dissolution within 24 h [4], a higher fluoride concentration of 0.38 M was actually employed because of uncertainties in the fluoride determination. The fluoride concentration was more than adequate for complete dissolution and the corrosion rates of stainless steel were still acceptable for the duration of the dissolution campaign. In the coupon immersion tests, the corrosion rates were calculated for both one day and one week weight losses. The values ranged from 0.07 to 0.83 mm/year. These corrosion rates correspond to an actual surface damage of 0.000188 to 0.000226 mm for each 24 h dissolution. A maximum of seven dissolution runs was expected giving a cumulative damage of 0.00132 to 0.0157 mm for the overall unirradiated Mark 42 dissolution campaign. These corrosion rates indicate a relatively mild corrosion on the dissolver vessel.

#### Conclusions

Based on the development of a dissolution flowsheet for unirradiated Mark 42 fuel tubes, the potential for a mercury-free dissolution of reject Mark 42 compact material (aluminum and plutonium oxide) was identified. The minimum fluoride requirements for the dissolution of the reject Mark 42 compact material were identified. While the aluminum dissolution rates in the laboratory studies were much slower than the traditional mercury-catalyzed process, the high surface area of the Mark 42 compact material enabled acceptable processing rates. Based on our laboratory studies which were focused on batch processing, a mercury-free dissolution of aluminum-based nuclear

material was achieved on a plant-scale using a corrosive calcium fluoride–boric acid–HNO<sub>3</sub> solution, and the corrosion rate to the stainless steel dissolver was within acceptable limits. The elimination of mercury from this dissolution process supports environmental initiatives for reduction of mercury use within the chemical industry in the United States.

**Acknowledgment** JPC acknowledges the U.S. Department of Energy for funding through the Radiochemistry Education Award Program.

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