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PENETRATE-LEACH DISSOLUTION OF ZIRCONIUM-CLAD URANIUM AND URANIUM DIOXIDE FUELS

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ABSTRACT

A new decladding-dissolution process was developed for zirconium-clad uranium metal and UO_2 fuels. The proposed penetrate-leach process consists of penetrating the zirconium cladding with Alniflex solution (2M HF - 1M HNO_3 - 1M $\text{Al}(\text{NO}_3)_3$ - 0.1M $\text{K}_2\text{Cr}_2\text{O}_7$) and of leaching the exposed core with 10M HNO_3 . Undissolved cladding pieces are discarded as solid waste. Periodic HF and HNO_3 additions, efficient agitation, and in-line zirconium analyses are required for successful control of ZrF_4 and/or AlF_3 precipitation during the cladding-penetration step. Preliminary solvent extraction studies indicated complete recovery of uranium with 30 vol % tributyl phosphate (TBP) from both Alniflex solution and blended Alniflex- HNO_3 leach solutions. With 7.5 vol % TBP, high extractant/feed flow ratios and low scrub flows are required for satisfactory uranium recovery from Alniflex solution. Modified waste-handling procedures may be required for Alniflex waste, because it cannot be evaporated before neutralization and large quantities of solids are generated on neutralization. The effect of unstable UZr_3 (epsilon phase of uranium-zirconium system) on the safety of penetrate-leach dissolution was investigated.

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PENETRATE-LEACH DISSOLUTION OF ZIRCONIUM-CLAD URANIUM AND URANIUM DIOXIDE FUELS

INTRODUCTION

A new decladding-dissolution process was developed for zirconium-clad uranium metal and UO_2 fuels as an alternative to Zirflex,¹ electrolytic dissolution,² and shear-leach processing.³ The new process, called penetrate-leach, is an adaptation of the Alniflex process⁴ developed for dissolving zirconium-clad uranium-zirconium alloy fuels in stainless steel equipment. Alniflex dissolvent is used to penetrate the cladding and expose regions of the uranium or UO_2 core for dissolution in nitric acid. The proposed process consists of the following steps:

- Fuel is charged to the dissolver in perforated stainless steel baskets.
- A sufficient amount of Alniflex⁴ dissolvent (initially 2M HF - 1M HNO_3 - 1M $\text{Al}(\text{NO}_3)_3$ - 0.1M $\text{K}_2\text{Cr}_2\text{O}_7$) is added to partially dissolve the zirconium cladding and expose the core. Attack on the cladding is inhomogeneous, and only a portion must be dissolved to expose the core. A portion of exposed core also dissolves during this step.
- Alniflex cladding-penetration solution is removed from the dissolver, and the remaining core is dissolved in nitric acid.
- Undissolved cladding is discarded as solid waste.
- Two uranium-bearing solutions are processed (either separately or as a combined solution) by the Purex solvent extraction process (30 vol % TBP) or by the Savannah River Plant (SRP) enriched uranium process (7.5 vol % TBP), depending on the ^{235}U content of the fuel and the total uranium concentration.

The penetrate-leach process combines several advantages of the Alniflex and shear-leach processes. First, the Alniflex cladding-penetration step is compatible with 304L stainless steel process equipment. Second, dissolution is entirely chemical; therefore maintaining an expensive shear machine in a remote area is not required. Third, liquid waste volumes and solid contents are less than those in processes involving total dissolution of cladding because only a portion of cladding is dissolved; undissolved cladding pieces (hulls) are discarded as solid waste. Finally, UZr_3 intermetallic compound, which may be formed at the core-cladding interface of zirconium-clad uranium metal and UO_2

fuels during fabrication and/or irradiation, cannot accumulate in the dissolver in hazardous quantities. UZr_3 dissolves in fluoride-containing reagents, such as Alniflex dissolvent, but it is insoluble in nitric acid.^{5,6} Thus, UZr_3 not dissolved by the cladding-penetration step is removed with the spent hulls as in the shear-leach process, but in significantly smaller amounts.

EXPERIMENTAL

Dissolution Procedure

Preliminary dissolution of Zircaloy-2, uranium, and UO_2 were conducted with 100 ml of Alniflex dissolvent in 250-ml round-bottomed flasks equipped with a condenser and thermometer. No mechanical stirring was provided, because such agitation is not used in plant equipment. The metal pieces and UO_2 pellet were removed periodically for weight loss determinations. In accordance with the Alniflex procedure,⁴ concentrated HF was added every 2 hr after >40% of the Zircaloy-2 dissolved to increase the total fluoride concentration by 0.5M and to prevent precipitation of ZrF_4 and AlF_3 . HF also was added during the uranium and UO_2 dissolutions to measure the effect of HF concentration on the fuel dissolution rate.

Penetrate-leach dissolutions were demonstrated with 1- to 4-inch sections of unirradiated Zircaloy-2-clad uranium metal fuel. The bare, cut ends of the fuel were protected from Alniflex dissolvent by "Teflon"* end caps. Tests were conducted in a 2-liter "Pyrex"** dissolver equipped with a condenser and thermometer. The temperature was maintained at 70-75°C; in some tests, the solution was agitated by an air sparge. The zirconium dissolution rate was determined by periodic measurements of the weight of the fuel piece and/or by measurement of solution specific gravity. HF and HNO_3 were added periodically during the cladding-penetration step to prevent precipitation of zirconium, aluminum, or uranium. After the cladding was sufficiently penetrated, the remaining core was leached with boiling 10M HNO_3 . Two leaching steps were used in some tests to minimize the volume of HNO_3 required and to decrease the time required for complete leaching.

Any precipitates formed during the cladding-penetration step were filtered, washed, dried, and analyzed by spark source mass spectrometry and x-ray diffraction.

* Trademark of Du Pont for fluorocarbon resin.

** Trademark of Corning Glass Works.

Specific Gravity Measurements

Alniflex solutions containing 2 to 3M HF and 0 to 60 grams of zirconium per liter were prepared. Specific gravities of these solutions were measured at 25, 40, 55, and 70°C in 5- or 10-ml volumetric flasks. The flasks were calibrated to ± 0.002 ml at 25°C with triply distilled water. The cubical coefficient of expansion of borosilicate glass was assumed to be $0.000025^{\circ}\text{C}^{-1}$ for calculations of volume corrections for 40-70°C.⁷ During dissolution tests, dissolvent specific gravities were measured with standard hydrometers.

Distribution Tests

Distribution coefficients were measured for extraction of uranium from Alniflex solution, or a 2 to 1 blend of Alniflex solution and HNO_3 leach solution, into 30 and 7.5 vol % TBP in n-paraffin diluent. Twenty ml each of the organic and aqueous phases were equilibrated by shaking ~15 min at 25°C. After equilibration, samples of each phase were analyzed for uranium.

Analyses

Total fluoride was measured with a specific fluoride ion electrode (Orion Model 94-09*). Phosphoric acid was used to complex cations and free the fluoride for detection.⁸ Acid was determined by pH titration with KF added to complex hydrolyzable cations. Zirconium concentrations were calculated from weight loss measurements and also measured in some cases by atomic absorption spectrophotometry. Aqueous uranium was determined colorimetrically as the uranyl thiocyanato complex; organic uranium was determined similarly after stripping into 0.5M Na_2CO_3 solution.

Materials

For preliminary tests of zirconium dissolution, short sections of 30-mil-thick Zircaloy-2 tubing were oxidized by heating in steam at 400°C and 950 to 1500 psig for 2 days. The oxidized pieces were fitted with a "Teflon" insert to prevent attack on their interior surface. Depleted uranium metal and a UO_2 pellet (density of 9.7 g/cm^3) were obtained from fuel fabrication studies at Savannah River Laboratory (SRL). The Zircaloy-2-clad uranium metal fuel

* Orion Research Incorporated, Cambridge, Massachusetts.

element was a coextruded tube intended for the now decommissioned Heavy Water Components Test Reactor (HWCTR).⁹ The tube was cut into 1- to 4-inch sections for dissolving tests.

Tributyl phosphate (TBP) and n-paraffin diluent (C₁₃-C₁₄ hydrocarbons with an average molecular weight of 191) were obtained from SRP. All other chemicals used were reagent grade.

RESULTS AND DISCUSSION

Dissolution of Zircaloy-2 in Alniflex Solution

Dissolving tests simulating cladding penetration of a Zircaloy-2-clad fuel rod indicated rapid dissolution in boiling Alniflex solution (Figure 1). The dissolution rate decreased significantly when the temperature was decreased to 70-75°C as recommended for corrosion protection (Table 1). With oxidized Zircaloy-2 (especially in the 70-75°C test), an induction period at the beginning of dissolution probably corresponded to the time required to penetrate the ~0.1-mil-thick oxide film. After this period, the dissolvent attacked the Zircaloy-2 and produced severe pitting; the dissolvent completely penetrated the metal after 2-7 hr at boiling and 70-75°C, respectively.

TABLE 1

Corrosion of 304L Stainless Steel
in HF-HNO₃-Al(NO₃)₃ Solution

Solution	<i>(Corrosion Rate, mils/yr)^a</i>		
	50°C	70°C	90°C
2M HF - 1M HNO ₃	>5000	>5000	>5000
2M HF - 1M HNO ₃ - 1M Al(NO ₃) ₃	16	40	212
2M HF - 1M HNO ₃ - 1M Al(NO ₃) ₃ - 0.1M (NH ₄) ₂ Cr ₂ O ₇	2	4	22

a. From Reference 1.

In accordance with the recommended Alniflex procedure,⁴ concentrated HF was added periodically to prevent precipitation of ZrF₄ and AlF₃. However, precipitates were recovered after each dissolution; the precipitation problems were therefore studied more thoroughly, as will be described later.

FIGURE 1 Alniflex Dissolution of Zircaloy-2

Dissolution of Uranium Metal and Uranium Dioxide in Alniflex Solution

Uranium metal and UO_2 were dissolved in Alniflex solution to measure the rate of core dissolution during the cladding-penetration step. The dissolution rate increases after each HF addition, and significant quantities of both core materials will be dissolved during cladding penetration (Figure 2). Therefore, Alniflex cladding-penetration solution, possibly combined with the nitric acid dissolvent, must be processed by solvent extraction to recover uranium and plutonium.

Dissolution of uranium metal in 2M HF - 1M $\text{Al}(\text{NO}_3)_3$ was investigated to determine the effect of omitting HNO_3 and $\text{K}_2\text{Cr}_2\text{O}_7$ from Alniflex solution. After 12 hr, the uranium pieces were coated with a green solid, presumably UF_4 . This was not observed in tests with Alniflex solution; the oxidizing agents ensure formation of U(VI) in solution and prevent UF_4 precipitation.

Dissolution tests with uranium metal and UO_2 were conducted in boiling 10M HNO_3 for comparison with the results in Figure 2. Uranium metal dissolved completely in 5 hr, and the remainder of the UO_2 pellet from the Alniflex dissolution test dissolved in 1/2 hr in HNO_3 . Thus, as expected, the rate of core dissolution during the cladding-penetration step will be considerably lower than during the leaching step.

Dissolution of Zircaloy-2-Clad Uranium Metal Fuel

The penetrate-leach dissolution method was tested with a 4-inch section of Zircaloy-2-clad uranium metal fuel tube (437 g total weight). The section was dissolved in 1200 ml of Alniflex solution at 70°C. The cladding was penetrated after 6 to 8 hr of exposure to the solution (Figure 3); dissolution was continued for 18 hr with HF additions after 8, 12, and 16 hr of dissolving. After 18 hr, the cladding was heavily penetrated, and ~45% of the uranium core had dissolved. Precipitate was noted after 8 hr, and continued precipitation of zirconium was indicated by erratic zirconium analyses for the remainder of the experiment (Figure 4). Solids (42.5 g) recovered after the experiment were predominantly ZrF_4 (shown by spark source mass spectrometry). As discussed below, procedures were developed to prevent precipitation during subsequent experiments.

FIGURE 2 Alniflex Dissolution of Uranium Metal and Uranium Dioxide

a. Before Dissolution

b. After 8 hr in Alniflex

c. After 14 hr in Alniflex

d. After 18 hr in Alniflex

e. After 36-hr HNO_3 Leach

FIGURE 3 Zircaloy-2-Clad Uranium Metal Fuel Piece During Penetrate-Leach Dissolution

FIGURE 4 Penetrate-Leach Dissolution of Zircaloy-2-Clad Uranium Metal Fuel

The cladding-penetration solution was removed, and the remainder of the fuel piece (251 g) was leached with 500 ml of 10M HNO₃ (Figure 4). After 10 hr, >80% of the uranium had been dissolved, but an additional 26 hr was required for complete dissolution because the acid concentration had decreased to an ineffective level (~2.5M). The spent cladding is shown in Figure 3. In another experiment with a similar portion of fuel, only 10 hr was required for complete leaching of uranium when the HNO₃ concentration was maintained near 10M. These results suggest that leaching with two separate volumes of 10M HNO₃ is desirable to minimize dissolvent volume and to decrease the time required for complete dissolution.

Precipitation During Alniflex Cladding Penetration

Conditions for stability of Alniflex solutions against precipitation had been established during Alniflex development;⁴ total fluoride concentration was used as the basis. AlF₃ precipitates if the total fluoride concentration is too high; too low a total fluoride concentration results in ZrF₄ precipitation. The recommended procedure for avoiding precipitation consisted of dissolving the fuel with the initial Alniflex solution to 0.2M Zr and then increasing the total fluoride content by 0.5M every 2 hr until the desired maximum zirconium concentration (~0.5M) was obtained.⁴ However, periodic HF additions on a set time schedule during cladding penetration did not prevent precipitation (Experiments A and B in Table 2). Data summarized in Reference 10 indicated that the precipitation in Experiment B was caused by low acidity. To correct this problem, HNO₃ was added periodically in subsequent experiments to maintain the H⁺ concentration >1M. A coating of white precipitate on the fuel pieces, often observed during weight loss measurements, was attributed to fluoride depletion near the fuel. To correct this, an air sparge was used in Experiments C and D to provide efficient mixing.

The major problem in preventing precipitation is determining the concentration of dissolved zirconium during the cladding-penetration step, so that the proper fluoride concentration can be maintained by HF additions. For processing fuel in a remotely operated facility, a remote sensing method is desirable. A test of such a method was conducted in Experiment D, in which the zirconium concentration was monitored by measuring the specific gravity and temperature of the dissolvent. The zirconium concentration was calculated from Equation 1:

$$\text{Specific gravity} = 1.2297 + (1.4844 \times 10^{-3})(\text{Zr, g/l}) - (7.2336 \times 10^{-4})(\text{temperature, } ^\circ\text{C}) \quad (1)$$

TABLE 2

Summary of Precipitation During Cladding Penetration of Zircaloy-2-Clad Uranium Metal Fuel

Experiment	Fuel Piece, g	Procedures to Control Precipitation	Precipitate, g	Zr/Al ^a Ratio in Precipitate	Cause of Precipitation
A	205	HF additions after 6, 8, and 10 hr; weight loss measurements	21.7	20	Low HF concentration
B	437	HF additions after 8, 12, and 16 hr; weight loss measurements	42.5	7.5	Low H ⁺ concentration
C	302	HF and HNO ₃ additions; agitation; weight loss measurements	21.0	980	Low HF concentration (desired maximum Zr concentration was inadvertently exceeded)
D	96	HF and HNO ₃ additions; agitation; specific gravity measurements; weight loss measurements	0	-	-

a. Uranium concentration of all precipitates was very low (<0.1 wt %).

Equation 1 was derived from least-squares analysis of measured specific gravities of Alniflex solutions containing various concentrations of zirconium at 25 to 70°C. Partial data are shown in Figure 5. Additions of HF and HNO₃ based on calculated zirconium concentrations and the Alniflex stability relationships⁴ maintained a stable solution in Experiment D.

Measurement of zirconium concentration by specific gravity is complicated by variations in acidity and fluoride and uranium concentrations. As shown in Figure 5, varying fluoride concentrations between 2M and 3M does not measurably affect dissolvent specific gravity. However, changes in HNO₃ concentration and in dissolution of uranium core both significantly affect dissolvent specific gravity. Direct measurement of these concentrations is desirable; if it is not possible, semiworks tests with each type of fuel to be processed should be made to develop a schedule of HF and HNO₃ additions. In-line methods should enable control of solution stability.

Semiworks measurement of the total time required for the cladding-penetration step in each fuel is also desirable, because the time will vary with the cladding thickness and the thickness of the oxide coating on the cladding.⁴ Uranium analyses of the Alniflex dissolvent and/or an NO₂ monitor in the dissolver off-gas line could be used to determine when the cladding is sufficiently penetrated to terminate the cladding-penetration step.

FIGURE 5 Specific Gravity of Alniflex Solutions

Preliminary Solvent Extraction Studies

Previous study¹⁰ of the recovery of uranium from zirconium-uranium alloy solutions used 3.5 vol % TBP as extractant. However, the low-enriched uranium fuels that might be processed at SRP would be dissolved to higher uranium concentrations and would require a higher TBP concentration. Uranium distribution coefficients in 7.5 vol % TBP and 30 vol % TBP were measured for both Alniflex solution and a 2 to 1 blend of Alniflex solution and HNO₃ leach solution. These distribution coefficients were used to calculate the range of process conditions over which efficient operation and adequate uranium recovery are obtained.

The results (Table 3) indicate complete recovery of uranium with 30% vol % TBP* from both Alniflex and blended feed solutions.

TABLE 3

Extraction of Uranium from Alniflex and Blended Alniflex-HNO₃ Solutions

	<u>Alniflex^a</u>		<u>Blended Alniflex-HNO₃^b</u>	
	30	7.5	30	7.5
Distribution coefficient				
Extraction section	22.7	0.638	1.73	0.147
Scrub section	1.8 ^c	0.70 ^d	1.8 ^c	0.70 ^d
Number of extraction stages	8	8	8	8
Number of scrub stages	8	8	8	8
Relative flow				
Aqueous feed	1.0	1.0	1.0	1.0
Aqueous scrub	0.17	0.55	0.5	0.55
Organic extractant	0.83	5.0	2.5	5.0
Aqueous waste	1.2	1.55	1.5	1.55
Organic product	0.83	5.0	2.5	5.0
Calculated Recovery, %	99.99	99.81	99.98	43.12

a. Alniflex solution containing 68.7 g U/l.

b. Blended solution containing 238 g U/l.

c. Estimated for 3M HNO₃ as aqueous scrub.¹¹

d. Estimated for 4M HNO₃ as aqueous scrub.¹²

* Purex processing (30 vol % TBP) of Alniflex solutions with uranium concentrations as low as 80 g/l would require either modifications to the Purex process or blending with dissolved UO₃ to increase the uranium concentration.

With 7.5% TBP, high extractant/feed flow ratios and low scrub flows were required for uranium recovery of >99% from Alniflex solution containing 68.7 g U/l. The uranium concentration in the blended solution, 238 g U/l, is too high for adequate uranium recovery with 7.5 vol % TBP. These uranium concentrations are higher than may be allowable for some fuels because of nuclear safety considerations, and dilution before processing may also be considered.

Dilution of the Alniflex or blended feed with $\text{Al}(\text{NO}_3)_3$ (as permitted by solution stability requirements) before extraction with 7.5 vol % TBP would: (1) complex fluoride and decrease corrosion of stainless steel equipment and (2) dilute the uranium and allow higher recovery with less extreme extractant/feed flow ratios. Further tests are required to determine whether satisfactory plutonium recovery is possible with either 7.5 or 30 vol % TBP, because significant $\text{Pu}(\text{IV})$ -fluoro complex forms in Alniflex solutions.

Preliminary Waste Neutralization Studies

Tests were conducted to determine compatibility of spent Alniflex solutions with SRP waste handling procedures. In most cases these solutions require evaporation before neutralization with NaOH. Alniflex cladding-penetration solution from the solvent extraction tests were extracted several times with 30 vol % TBP to remove all uranium. This solution was neutralized by adding it to 50% NaOH. An excess of NaOH ($\sim 1\text{M}$) was used above that required by stoichiometry for H^+ , Al^{3+} , and Zr^{4+} . A thick, blue-green slurry was formed; solids did not settle overnight.

Conclusions were: (1) Alniflex waste must be neutralized without evaporation because the high fluoride concentration would corrode evaporators, and (2) the large volume of solids produced on neutralization (~ 50 vol % after centrifugation) may present problems in pumping the waste to storage tanks.

Behavior of UZr_3 During Penetrate-Leach Dissolution

Studies were conducted to assess the effect of UZr_3 (epsilon phase of U-Zr system) on the safety of penetrate-leach processing of zirconium-clad uranium metal fuels. These fuels may contain UZr_3 , an unstable intermetallic compound known to react rapidly, sometimes explosively, under oxidizing conditions. UZr_3 forms at the core-cladding interface during fabrication of zirconium-clad uranium metal and U-Zr alloy fuels, and may be formed in zirconium-clad UO_2 fuels during fabrication and reactor operation at temperatures exceeding 350°C .^{5,6}

Pieces of Zircaloy-2-clad uranium metal fuel were examined with a scanning electron microscope before and after partial dissolution in Alniflex solution and in 10M HNO₃. Before dissolution, a thin layer of UZr₃ was observed at the core-cladding interface or bond zone. During Alniflex dissolution of uranium metal fuel, the bond zone was attacked faster than the cladding or the core (Figure 6a). Uniform dissolution of the bond zone was indicated by smooth, even surfaces; there was no sign of fracturing of the bond zone layer. Thus, Alniflex dissolution of this fuel is safe because no mechanism was identified for accumulation of hazardous UZr₃. Alniflex dissolution of zirconium-clad UO₂ fuels should be safer still because of lower UZr₃ content. However, this could not be tested because UO₂ fuels containing UZr₃ were not available.

During chemical dissolution in HNO₃, the UZr₃ layer of the bond zone did not dissolve or break into small pieces, but remained attached to the undissolved Zircaloy-2-cladding (Figure 6b). Therefore, UZr₃ could be removed from the dissolver with spent cladding as in the shear-leach process. Penetrate-leach dissolution actually presents fewer safety problems than shear-leach processing because part of the UZr₃ dissolves during cladding penetration. Further study is necessary to evaluate the safety of handling waste cladding with UZr₃ present.

FIGURE 6 Behavior of UZr₃ During Penetrate-Leach Dissolution of Zircaloy-2-Clad Uranium Metal Fuel

ACKNOWLEDGMENT

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