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CHOP-LEACH DISSOLUTION OF COMMERCIAL REACTOR FUEL

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INTRODUCTION

The Advanced Fuel Cycle Initiative (AFCI) program[1] is being developed to address disposal of commercial spent nuclear fuel and improve the performance of the geologic repository. To decrease the volume of waste sent to the repository, commercial fuel would be processed and separated into multiple components: a transuranic (TRU) stream to be converted to AFCI fuel and transmuted by fissioning to generate electrical power; separate ^{99}Tc and ^{129}I streams to be converted into targets for transmutation to short-lived nuclides; a U stream that meets the criteria for Class C low-level waste; and a high level waste stream for repository disposal.

To achieve the AFCI separation objectives, new and innovative processes are under development. One such process is the uranium extraction (UREX) process.[2] The UREX process is based on the well-known PUREX process (Pu extraction from irradiated U); however, in UREX, U and Tc are extracted into the organic phase (U and Tc are subsequently stripped into separate streams), while the other actinides and non-volatile fission products reside in the aqueous raffinate.

The primary goal of the present work was to demonstrate the use of the chop-leach (with nitric acid) process to produce a feed solution for the UREX process (nominally 290 g/L U and 1 M H^+). The secondary goal was to test the efficacy of this treatment for leaching actinides from Zircaloy cladding.

RESULTS

The fuel, approximately 4.5 kg of Zircaloy 2 clad, UO_2 fuel (23,480 MWD/MT burnup) from the Dresden reactor (Morris, IL), consisted of rubble and 3" lengths of clad fuel. It was remotely dissolved in a glass dissolver (as three discreet batches). Each fuel batch was charged into a 1 L heel of 4 M HNO_3. After the initial temperature spike (due to the UO_2-HNO_3 reaction) subsided, the temperature was maintained near 363 K for 8 – 12 hours by addition of heat and/or 10 M HNO_3 until dissolution was complete. After each of the first two dissolutions, the cladding was leached for 2 – 6 hours near 363 K in the 1 L of heel acid added for the next dissolution. After the third dissolution, the cladding was heated in the dissolver product solution for about 7 hours in an attempt to further leach fuel components from the

cladding; 711 g of cladding were recovered subsequent to the three dissolutions. Analysis of a cladding sample (Table 1) showed that actinides are present in the cladding at a concentration of about 5000 ηCi/g.

The combined dissolver product was filtered and 341 g of finely divided residue were recovered; ICP-MS analysis suggested this material was roughly 25% U and 1% Pu. The residue was heated to near 363 K with 140 mL of 10 M HNO_3 in a stainless steel beaker for several hours while stirring. There was no visible sign of reaction during heating, and extensive solids were still present, so KF and 0.5 M HNO_3 were added to form 500 mL of solution, and the mixture was again heated and stirred. This treatment resulted in a solution 424 g/L in U and 17.94 g of filtered residue. The leachate was combined with the products of the three batch dissolutions to produce 7.75 L of solution, which was over 450 g/L in U and 1.45 M in H^+. This combined solution was diluted to produce about 13 L of UREX feed 302 g/L in U and 0.84 M in H^+ (Table 2).

DISCUSSION

While the primary goal of this study was realized, issues that require further study were also identified. These include the secondary goal of actinide removal from the Zircaloy cladding and the large amount of insoluble residue recovered subsequent to the dissolution experiments. The cladding sample analyzed was roughly 50 times too high in actinide content to qualify as a LLW. It is possible that the low HNO_3 concentration in the dissolver product (it was initially 4 – 10 M in H^+, but after dissolution it was 1.45 M in H^+) did not effectively leach the actinides from the cladding. Furthermore, after the HNO_3 dissolutions the amount of insoluble residue was much greater than expected. Analysis of this residue showed that it was high in U and Pu. Treatment with the mixed F^-/NO_3^- media resulted in dissolution of more than 90% of the insoluble material (which included roughly 200 g U).

The greater than expected mass of insoluble residue and the amount of actinides present in the cladding suggest that more aggressive chemistry may be required to completely dissolve the U in the fuel and to extract actinides from the cladding. Future development work on this method should be aimed at addressing these two issues.

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Table 1. Chemical Composition of Zircaloy 2 Cladding (excluding Zr)	
Element	**Result/(μg/g)**
Ag	5340
Al	786
B	5050
Ba	35.4
Ca	<20.2
Cd	<3.70
Cm-244	0.00305
Ce	4380
Co -60	0.00248
Cr	815
Cs-137	1.87
Cu	72.5
Eu-154	0.00426
Fe	1500
Gd	174
K	<826
La	76.3
Li	<37.9
Mg	57.8
Mn	21.0
Mo	461
Na	3410
Ni	<11.9
P	<60.7
Pb	<28.1
Pu-239/240	4.08
Pu-238/Am-241	0.292
Sb	<333
Sb-125	0.00130
Si	44000
Sn	13000
Sr	423
Ti	28.4
U	623
Zn	25.6

Table 2. Chemical Composition of Diluted Feed Solution	
Component	**Result/(g/L)**
H^+	0.85
U	302
Pu	2.16
Np	6.8 E-05
Am	0.23
Cm	0.005
^{99}Tc	1.68 E-04
^{137}Cs	1.31
^{90}Sr	0.070
^{154}Eu	3.87 E-04
Ag	0.78
Ba	0.50
Ce	1.47
Cu	0.37
Fe	0.07
Gd	0.64
La	0.49
Mn	0.02
Na	0.33
Ni	0.60
Sn	0.41
Ti	0.11
Zn	0.05