PLANT-SCALE ANODIC DISSOLUTION OF UNIRRADIATED N-REACTOR FUEL

by

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ABSTRACT

Anodic dissolution tests were made with unirradiated N-Reactor fuel to determine the fuel segment length, diameter, and shape required for high throughput electrorefiner treatment for ultimate disposal in a geologic repository. Based on these tests, a conceptual design was produced of an electrorefiner for a full-scale plant to process N-Reactor spent fuel. In this design, the diameter of an electrode assembly is about 0.6 m (25 in.). Eight of these assemblies in an electrorefiner would accommodate a 1.333-metric-ton batch of N-Reactor fuel. Electrorefining would proceed at a rate of 40 kg uranium per hour.

INTRODUCTION

The N-Reactor was operated at the Hanford Site for the production of special nuclear materials. The Zircaloy-clad fuel of the N-Reactor has a heavy metal (HM)-to-zirconium ratio of about 32/1, if cladding and fuel are combined. Electrometallurgical treatment of this spent fuel by anodic dissolution and electrotransport in an electrorefiner is being studied. In processing N-Reactor spent fuel, uranium will be separated from the Zircaloy cladding, transuranic elements, and fission products to produce pure uranium.

In the anodic dissolution process, N-Reactor fuel segments are loaded into anodic dissolution baskets and lowered into the electrolyte of the electrorefiner vessel. The zirconium metal in the N-Reactor fuel cladding will oxidize into the salt at the appropriate voltage and then deposit on the cell cathode. If the dissolution voltage is maintained below 0.5 V, uranium in the spent fuel is oxidized, and the Zircaloy cladding is retained in the anodic dissolution baskets. The uranium in the N-Reactor fuel would be anodically dissolved after the cladding is ruptured by some mechanical means to provide electrolyte access inside the cladding. The ruptured clad slugs are loaded into porous stainless-steel baskets, which become the anode of the cell. Earlier tests of metallic fuels designed for the Integral Fast Reactor (IFR)[1-3] indicated that >99.99% of the heavy metal should be easily dissolved out of the insoluble cladding.

Anodic dissolution of the Zircaloy depends on a number of variables. It is desirable to find conditions that electrotransport uranium, while leaving the Zircaloy behind in the anodic dissolution baskets. In this way, no further separations processing would be needed for the Zircaloy. Appropriate methods
might involve controlling the electrode configuration and the voltage imposed on the cell.

EXPERIMENTAL RESULTS

An engineering-scale electrorefiner [4] that can anodically dissolve a 10-kg batch of chopped, stainless-steel-clad IFR fuel segments was used for the dissolution tests with unirradiated N-Reactor fuel segments. It contained a molten salt electrolyte (LiCl-KCl-UCl₃) and was operated at 500°C. The anodic dissolver used a prismatic-basket design and consisted of multiple baskets hanging from a common anode shaft. After being loaded with fuel segments, the baskets were rotated (typically at 20-75 rpm) to allow the electrolyte to circulate through the segments. After testing, the baskets were raised above the electrolyte and rotated at 250 rpm to remove nearly all of the salt from them.

Seven anodic dissolution tests were completed with unirradiated N-Reactor fuel slugs that had been sawed into pieces of different length, diameter, and shape. These tests were run to determine the electrorefining characteristics of these fuel segments and to determine the type of fragmentation (i.e., exposure of the uranium encased by the Zircaloy cladding) needed to provide spent fuel segments that are suitable for a high throughput (>40 kg uranium per hour) electrorefiner.

Summary of Anodic Dissolution Tests. The unirradiated N-Reactor fuel segments that were used in the anodic dissolution tests are described in Table I. The shapes of these segments were full cylinder, half cylinder, and quarter cylinder. The length ranged from 1.9 to 20.3 cm, and the outside diameter from 3.24 to 6.16 cm. The purpose of these tests was: (1) to determine the N-Reactor fuel element fragmentation needed for high throughput electrorefining and (2) to determine the uranium dissolution rate that could be achieved with different sizes and configurations of anodic dissolution baskets.

The operating conditions and results for the anodic dissolution tests are given in Table II. The average current density measured for these tests (with a cutoff voltage of 0.45 V) was between 0.01 and 0.1 A/cm². The average uranium dissolution rate was 20 to 160 g uranium per hour.
### TABLE I. Description of Unirradiated N-Reactor Fuel Segments Used in the Anodic Dissolution Tests

<table>
<thead>
<tr>
<th>Test No.</th>
<th>N-Reactor Fuel</th>
<th>Cylinder Shape</th>
<th>Length, cm</th>
<th>Diameter</th>
<th>Exposed Uranium Area, cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>148</td>
<td>Full</td>
<td>Full</td>
<td>1.9</td>
<td>Large</td>
<td>357</td>
</tr>
<tr>
<td>148</td>
<td>Full</td>
<td>Full</td>
<td>2.54</td>
<td>Small</td>
<td>357</td>
</tr>
<tr>
<td>149</td>
<td>Full</td>
<td>Full</td>
<td>1.9</td>
<td>Large</td>
<td>122</td>
</tr>
<tr>
<td>151/A/B</td>
<td>Full</td>
<td>Full</td>
<td>1.9</td>
<td>Large</td>
<td>221</td>
</tr>
<tr>
<td>151/A/B</td>
<td>Full</td>
<td>Full</td>
<td>2.54</td>
<td>Small</td>
<td>221</td>
</tr>
<tr>
<td>155/A/B/C</td>
<td>Quarter</td>
<td>Quarter</td>
<td>10.2</td>
<td>Small</td>
<td>535</td>
</tr>
<tr>
<td>157</td>
<td>Half</td>
<td>Half</td>
<td>20.3</td>
<td>Large</td>
<td>180</td>
</tr>
<tr>
<td>158</td>
<td>Full</td>
<td>Full</td>
<td>10.2</td>
<td>Large</td>
<td>61</td>
</tr>
<tr>
<td>162</td>
<td>Quarter</td>
<td>Quarter</td>
<td>10.2</td>
<td>Large</td>
<td>181</td>
</tr>
</tbody>
</table>

*The dimensions of “large” diameter elements are 6.16 cm (2.425 in.) O.D. and 4.32 cm (1.7 in.) I.D.
*The dimensions of “small” diameter elements are 3.24 cm (1.275 in.) O.D. and 1.22 cm (0.480 in.) I.D.
*A cylindrical piece of fuel was sawed axially into four pieces of equal weight.
*A cylindrical piece of fuel was sawed axially into two pieces of equal weight.

### TABLE II. Operating Conditions and Results for Dissolution Tests of Unirradiated N-Reactor Fuel

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Average Current Density, A/cm²</th>
<th>Wetted Anodic Dissolution Basket Area, cm²</th>
<th>Average Uranium Specific Area, cm²/kg U</th>
<th>Quantity of Electricity for Dissolution, Ah/kg U</th>
<th>Uranium Dissolution Rate, g U/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>148</td>
<td>0.022</td>
<td>1116</td>
<td>59</td>
<td>428</td>
<td>60</td>
</tr>
<tr>
<td>149</td>
<td>0.022</td>
<td>1116</td>
<td>66</td>
<td>405</td>
<td>60</td>
</tr>
<tr>
<td>151/A/B</td>
<td>0.016</td>
<td>1116</td>
<td>57</td>
<td>500</td>
<td>40</td>
</tr>
<tr>
<td>155/A/B/C</td>
<td>0.029</td>
<td>3102</td>
<td>186</td>
<td>560</td>
<td>160</td>
</tr>
<tr>
<td>157</td>
<td>0.011</td>
<td>1138</td>
<td>38</td>
<td>356</td>
<td>30</td>
</tr>
<tr>
<td>158</td>
<td>0.10</td>
<td>98</td>
<td>12</td>
<td>560</td>
<td>20</td>
</tr>
<tr>
<td>162</td>
<td>0.012</td>
<td>1442</td>
<td>78</td>
<td>368</td>
<td>48</td>
</tr>
</tbody>
</table>

*The maximum dissolution voltage was 0.45 V.
*Based on wetted anodic dissolution basket area adjacent to the exposed uranium in the fuel segments.
*Area of anodic dissolution basket adjacent to exposed uranium in fuel segments.

The exposed uranium area in the fuel segments was varied between 61 and 535 cm². Tests 148 (357 cm² exposed uranium area) and 151/A/B (221 cm²) show a proportional relationship between exposed uranium area (area of uranium in the
fuel segments that is exposed to the electrolyte) and uranium dissolution rate. The same shape (cylindrical), length, and diameter fuel segments were used. Fewer large diameter fuel segments were loaded in the anodic dissolution baskets for Test 151/A/B than used in Test 148. The ratio of the exposed uranium area for Test 148 to that for Test 151/A/B is 1.6. The ratio of the uranium dissolution rate for Test 148 to that for Test 151/A/B is 1.5.

The effects of anodic dissolution basket area adjacent to the exposed uranium of the fuel segments and of the interelectrode distance can be seen from Tests 157 and 162. A larger (520 cm² facial area per basket) anodic dissolution basket was used in Test 157 compared with that (339 cm² facial area per basket) used in Test 162. The basket area adjacent to the cylindrical wall of the electrorefiner crucible (cathode of the electrorefiner) was masked by the bus bar used for Test 157; thus, the interelectrode distance for this test was measured from the anodic dissolution baskets to the cadmium pool (cathode of the electrorefiner) and was 7.6 cm. For Test 162, the interelectrode distance from the anodic dissolution baskets to the electrorefiner crucible was 0.32 cm (i.e., the basket area adjacent to the crucible wall was not masked by the bus bar).

The exposed uranium area for Tests 157 and 162 was about the same (180 and 181 cm², respectively). The larger anodic dissolution basket area (1442 cm²) adjacent to the exposed uranium in Test 162 (compared with 1138 cm² for Test 157) and the shorter interelectrode distance for Test 162 resulted in a higher uranium dissolution rate in Test 162 (48 g uranium per hour, compared with 30 g uranium per hour for Test 157).

Tests 148 and 149 indicate that a metal current collector with high surface area can increase the uranium dissolution rate. The ratio of the exposed uranium area in Test 148 (357 cm²) to that in Test 149 (122 cm²) is 2.9. The uranium dissolution rate (60 g uranium per hour) is the same for these tests. Test 149 contained 144 g and 137 g of empty HT-9 cladding hulls (0.25-in. length) in two of the four anodic dissolution baskets, respectively. This additional metal current collector in Test 149 contributed to a higher than expected uranium dissolution rate.

Test 155/A/BC¹ employed a 20-cm diameter electrorefiner designed for high throughput. The higher uranium dissolution rate (160 g uranium per hour) measured in Test 155/A/BC shows the large effect of increased electrode area (3102 cm² wetted anodic dissolution basket area) and shorter interelectrode distance (0.63 cm).

Post-Test Examination of Fuel Segments. Examination of the Zircaloy cladding in the anodic dissolution baskets after electrotransport of the uranium from the fuel segments provided additional information about the dissolution process. These results are discussed below.

¹The letters A, B, and C in the test numbers indicate that the test was interrupted and subsequently continued.
At the start of Test 148, each of the anodic dissolution baskets was loaded with two larger diameter fuel segments and two smaller diameter segments. The smaller diameter segments were nested inside the larger diameter fuel segments. The best electrical contact was provided between the larger diameter fuel segments in contact with the bottom of the basket and one or more of the basket vertical faces. All of the uranium in the larger diameter fuel segments was dissolved. The smaller diameter fuel segments contained some residue. Chemical analysis of samples of this residue showed a composition of about 30 wt % uranium and the remainder salt. The smaller diameter fuel segments contained a lower weight of uranium at the start of the test (2.424 kg uranium compared with 3.68 kg uranium for the larger diameter fuel segments). The lower uranium dissolution rate in the smaller fuel segments is attributed to the poorer electrical contact and lower specific exposed uranium area (47 cm² per kg uranium compared with 66 cm² per kg uranium for the larger diameter fuel segment).

The effect of end pieces on the uranium dissolution rate was seen in the fuel segments dissolved in Test 151/A/B. The end pieces consist of a cap that masks the uranium on one face; thus, uranium dissolution can only occur at the face of the fuel segment where the uranium is exposed to the salt. The specific area of this small diameter end piece is 35 cm² per kg uranium. The length of the small end piece dissolved in Test 151 A/B is 2.2 cm. All of the uranium was dissolved in the larger and smaller diameter fuel segments in which dissolution occurred at two faces. The maximum penetration required in the Zircaloy cladding for the larger and smaller diameter fuel segments was 0.95 and 1.3 cm, respectively. The maximum penetration needed to dissolve all of the uranium in the end piece was 2.2 cm. The depth of penetration required for the end piece was nearly twice that of the other fuel segments. The uranium that was undissolved in the end piece was attributed to the longer penetration depth required in this fuel segment and the lower specific area. Similar results were found with a larger diameter end piece and with another smaller diameter end piece.

The effect of fuel segment length and shape on uranium and Zircaloy dissolution was determined from the results of Test 157. The fuel segments were halved outer slugs, 20.3 cm in length. One of the fuel segments was placed in each of the two large anodic dissolution baskets. About 1 to 2 cm of the Zircaloy cladding was dissolved from the end of the fuel segment that was in contact with the bottom of the anodic dissolution baskets. Uranium was dissolved at each of the exposed surfaces of the fuel segment. The slowest rate of dissolution was at the exposed surface adjacent to the salt-gas interface. An estimated 85% (4.07 kg) of the uranium initially loaded into the anodic dissolution baskets was dissolved in Test 157. The lower uranium dissolution rate (30 kg uranium per hour) and the observed Zircaloy dissolution do not favor use of this shape and length of fuel segment in a high throughput electrorefiner.

High Throughput Electrorefiner (HTER). Based on the above results, a conceptual design was produced of a plant-scale electrorefiner to process spent N-Reactor fuel. In this design, the diameter of an electrode assembly in a HTER is 0.6 m (25 in.). Eight of these assemblies in an electrorefiner with a common electrolyte pool would accommodate a 1.333-metric-ton batch of N-Reactor fuel.
Electrorefining would proceed at a rate of 40 kg uranium per hour. A design effort has been initiated so that the components needed to modify the present electrorefiner to meet the above performance can be fabricated and installed for testing by the summer of 1996.

SUMMARY

The highest uranium dissolution rates were achieved with the following conditions:

1. Direct contact between the fuel segments and the anodic dissolution baskets.
2. Minimum constraint of salt flow through the anodic dissolution baskets.
3. High exposed uranium surface area per kilogram of uranium.
4. High wetted anodic dissolution basket area adjacent to the exposed uranium area.
5. Fuel segments with similar uranium dissolution rates loaded in each anodic dissolution basket.

REFERENCES


