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CORROSION OF NICKEL ALLOYS IN NUCLEAR FUEL REPROCESSING

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## INTRODUCTION

Irradiated fuels from nuclear reactors are reprocessed to recover the unused uranium and return it to the fuel cycle. In aqueous reprocessing, the fuel is dissolved in acid, adjusted to proper salting strength, and extracted with tri-butyl phosphate in kerosene diluent to recover the uranium. The waste, consisting of fission products and the alloying constituents in the fuel, is finally calcined to a solid for safe interim storage. Due to the corrosive nature of reagents and radioactivity in the solutions, selection of materials is an important part of process development. This paper describes corrosion studies of high nickel alloys in solutions which will be encountered during reprocessing of fuel from the Core 2, seed 1 and seed 2, of the Shippingport Pressurized Water Reactor (PWR).

## EXPERIMENTAL PROCEDURE

All experiments were of a scoping nature, and therefore, are subject to revision with additional work. The fact that alloys appear to be superior or inferior in these scoping tests does not necessarily prove or disprove their suitability for actual process application

Most experiments were performed with coupons prepared from 1/4-inch plates of the selected alloys. Test coupons were prepared from machined strips with a V-groove on both sides of the weld and were welded by the TIG process using the recommended filler rod; welds were x-rayed to insure full penetration. In addition, data are reported for two welded vessels. Scoping tests were performed at the boiling point using 500 ml of solution for about 4 $in^2$ of coupon surface. Tests were made in plastic containers equipped with condensers; solutions were heated by a fluidized sand bath. Scoping tests of 8 alloys were made for 168 hrs exposure at the boiling point. All rates were determined from loss of weight, and therefore, rates reported in scoping tests were affected by preferential weld attack. Due to the highly corrosive nature of the reagents studied, abnormally high rates and severe weld attack were necessarily considered acceptable. Tests were made using four distinct types of solutions from the dissolution step of the PWR process. (1) Hydrofluoric acid is used as dissolvent for the Zircaloy cladding of the fuel and is present only at the inlet feed line. (2) Zirconium dissolver product (ZrDP) results from the rapid dissolution of the Zircaloy; over 85% of the hydrofluoric acid is complexed by the zirconium in most of the ZrDP used for these studies. (3) Nitric acid is added to the ZrDP solution to facilitate dissolution of the ceramic oxide ($ZrO_2$-$CaO$-$UO_2$) fuel wafers; this is the most corrosive solution as it is a mixture of hydrofluoric acid and nitric acid ($HF$-$HNO_3$). (4) Oxidants, including aluminum nitrate and nitric acid, are required for dissolution of any precipitated uranium tetrafluoride and for removal of fission products from the equipment for decontamination.

EVALUATION OF ALLOYS

Six nickel alloys were tested in each of the four process solutions to determine their potential for construction of pilot plant and process equipment. Figure 1 presents the coupons and the corrosion rates for four Hastelloys manufactured by Stellite Division of Cabot Corporation.

Hastelloy G was rejected from further study due to the severe weld attack in dissolver product containing nitric acid. Hastelloy C-276 had acceptable rates, but the weld suffered preferential attack in dissolver product with and without nitric acid added, and weld decay occurred in the low temperature heat affected zone (HAZ) in the HF-$HNO_3$ mixture. Of the alloys tested early in the process development, this alloy showed the greatest promise and was used to construct a pilot plant dissolver. The newer alloys, Hastelloy C-4 and Hastelloy S both performed well. There was some preferential weld attack, but no visible attack in the HAZ was observed in the HF-$HNO_3$ mixture. Additional work is being performed with Hastelloy C-4, a recommended alloy for this service.

Figure 2 presents coupons and rates for Inconel 625 welded with 625 filler rod and for Incoloy 825 welded both with 625 filler rod and with the recommended 65 filler rod. Both alloys had excessive corrosion, surface flaking, and end grain attack in 8 M hydrofluoric acid. Both weld materials showed preferential weld attack, but the 65 filler rod was more severely attacked. Attack was very severe for Incoloy 825 in the high temperature HAZ of the coupon. The first pilot plant dissolver constructed of Incoloy 825 failed due to weld failure. Even though it performed poorly in 8 M hydrofluoric acid, Inconel 625 has been included in additional testing because it did not suffer weld decay in the HF-$HNO_3$ mixtures.

Unwelded coupons of Inconel 671, which were tested in the same PWR solutions, had corrosion rates of 75 mpm in 8 M hydrofluoric acid, 111 mpm in ZrDP solution, and only 5 mpm when 0.5 M nitric acid was added to the ZrDP solution. Earlier studies with Inconel 690 and Incoloy 825 in hydrofluoric-oxidant mixtures indicated that the Inconel 625 weld rod used to weld the coupons was more resistant than the parent metal. Additional studies are planned when Inconel 690 filler rod is available.

EFFECT OF PROCESS VARIABLES

Tests were made at the boiling point for one week exposure to determine the effect of variations in solution composition on the corrosion of Hastelloy C-276. Scoping studies with different alloys had indicated that, in general, the relative corrosion in the different solutions tested was similar for most of the nickel alloys tested, i.e., good in ZrDP, poor in hydrofluoric acid, very poor in hydrofluoric acid containing oxidant, and excellent in oxidants alone. Therefore, process flowsheet conditions selected to minimize corrosion of Hastelloy C-276 will probably reduce corrosion of any of the nickel alloys finally selected.

Dissolution of the Zircaloy cladding can be accomplished with various concentrations of hydrofluoric acid; however, lower acidities produce larger volumes of waste per kg of Zircaloy while complete dissolution at high concentrations produces unstable dissolver product solution. Table I presents corrosion rates at total fluoride concentrations of 2, 4, 6, and 8 M. With only hydrofluoric acid present, the corrosion rate was constant at about 30 mpm; additional experiments indicated rates increased linearly with concentration above about 12 M. With dissolved zirconium present, which complexes most of the fluoride, rates were greatly reduced but varied only slightly from 2 to 8 M total fluoride. With 0.5 M nitric acid added to the zirconium dissolver product, the effect of increasing the fluoride concentration is severe, and rates were nearly doubled for each increase of two molar in total fluoride.

The effect of increasing the fluoride-to-zirconium mole ratio in the dissolver product while maintaining a constant total fluoride at 8 M is shown in Table II. With no nitric acid present, the corrosion did not increase until the ratio had increased to 24 (0.33 M zirconium). However, the corrosion rate increased significantly with increasing fluoride-to-zirconium ratio when 0.5 M nitric acid was added. This indicated that the degree of dissolution of the Zircaloy cladding prior to addition of nitric acid could control corrosion of the PWR dissolver vessel during dissolution of the ceramic fuel wafers and additional tests were made with different potential dissolvents. Figure 3 shows that increasing the fluoride-to-zirconium mole ratio in the dissolvent from 5.1 to 6 resulted in about a 3-fold increase in corrosion rate, while an increase from 0.1 M to 0.5 M nitric acid resulted in only a 50% increase in rate. Data for Hastelloy C-276 were similar to that for Inconel 625 in this respect; however, in these tests, rates for Inconel 625 were lower and weld decay was not observed. Based on these data, flowsheet concentrations have been selected to minimize corrosion during dissolution.

Table III presents corrosion data for 3, 6, and 12 M sulfuric acid; this acid is proposed for dissolution of the stainless steel poison pins after the rest of the fuel has been dissolved. These data showed that 12 M sulfuric acid could not be tolerated. While some gain in corrosion resistance was obtained at the 3 M level, it was not sufficient to warrant the decrease in dissolution rates for the stainless steel.

## COMPARISON OF ALLOY HEATS

Since most test coupons of Hastelloy C-276 had been prepared from the same plate of material, welded coupons of different heats, all within limits of specification for composition, were obtained from the manufacturer and tested in the most severe process solution, dissolver product containing 0.5 M nitric acid. Table IV shows that no difference was observed between the four heats tested and results agreed with previous data for this alloy.

TESTING OF WELDED VESSELS

In order to simulate process equipment and to obtain long-term corrosion information, small welded vessels were fabricated from Hastelloy C-276 which had been used to construct a pilot plant dissolver. Test vessels have been found to be better than tests in pilot plant equipment because experimental conditions are known and controlled and because more operating time can be accumulated within the study period. The Hastelloy C-276 welded vessel, shown in Figure 4, had not been constructed as a corrosion test vessel, and therefore welds had not been x-rayed.

Rates presented in Table V, which were obtained from weight loss of the vessel, were comparable to rates obtained for coupons at similar conditions. As seen in Figure 5, the factory seam weld exposed to the solutions suffered preferential weld metal attack and attack of the low temperature heat affected zone (HAZ) while the high temperature HAZ was more resistant than the parent metal. Additional studies are being made on heat treated samples of Hastelloy C-276 to determine if these effects can be minimized. Figure 6 shows the weld at the overflow tube which failed due to preferential attack of weld metal.

The Hastelloy C-276 corrosion test vessel, shown in Figure 7, was x-rayed and inspected to insure full penetration of all welds prior to testing. To date, it has been exposed for five months at 80$^{\circ}$C to dissolver product (7 $\underline{M}$ fluoride, 1.32 $\underline{M}$ Zirconium) containing no nitric acid. This zirconium dissolver product solution is of primary importance for long term vessel exposure during plant operation. Figure 8, showing the top of the vessel which has been exposed to the vapor phase, has suffered preferential attack and weld decay similar to the first Hastelloy C-276 vessel tested.

The weld of the overflow tube was constructed by beveling the vessel wall and fillet welding the nozzle into the wall with an overlay of weld metal on the inside of the vessel. This weld metal has suffered preferential attack, but the weld is still in good condition. Figure 9 shows the lower weld of the side arm which was constructed by beveling the nozzle and fillet welding it to the outside of the vessel wall. This weld, which has been contacted by the solution, shows severe preferential attack similar to that seen in Figure 6 which resulted in failure of the vessel. Additional weld designs are being studied using high nickel alloys. When these have been adequately tested and a welder has been qualified, additional vessels will be fabricated from Hastelloy C-4 and Inconel 625 for testing.

TABLE I

EFFECT OF FLUORIDE CONCENTRATION ON CORROSION RATE

(Welded Hastelloy C-276 Coupons Exposed 168 Hours at Boiling Point)

| Process Solution | Total Fluoride Concentration | | | |
|---|---|---|---|---|
| | 2 M | 4 M | 6 M | 8 M |
| Hydrofluoric Acid | 32 mpm | 32 mpm | -- | 30 mpm |
| Dissolver Product (ZrDP) (Fluoride-to-Zirconium Mole Ratio of 6) | 3 mpm | 7 mpm | 5 mpm | 8 mpm |
| ZrDP + 0.5 M Nitric Acid | 10 mpm | 21 mpm | 36 mpm | 70 mpm |

TABLE II

EFFECT OF DISSOLVED ZIRCONIUM ON CORROSION RATE

(Welded Hastelloy C-276 Coupons Exposed 168 Hours at Boiling Point)

| | Fluoride-to-Zirconium Mole Ratio | | | |
|---|---|---|---|---|
| | 6 | 9 | 12 | 24 |
| Dissolver Product (ZrDP) (Total Fluoride of 8 M) | 8 mpm | 6 mpm | 8 mpm | 12 mpm |
| ZrDP + 0.5 M Nitric Acid | 70 mpm | 111 mpm | 156 mpm | 179 mpm |

TABLE III

EFFECT OF SULFURIC ACID CONCENTRATION ON CORROSION RATE

(Welded Coupons Exposed 168 Hours at Boiling Point)

| Alloy Tested | Concentration of Sulfuric Acid | | |
|---|---|---|---|
| | 3 M | 6 M | 12 M |
| Hastelloy C-276 | 5.0 mpm | 7.3 mpm | 23 mpm |
| Hastelloy C-4 | 1.1 mpm | 8.4 mpm | 16 mpm |
| Inconel 625 | 0.3 mpm | 28 mpm | 41 mpm |
| Incoloy 825 | 1.7 mpm | 54 mpm | 200 mpm |

## TABLE IV
## COMPARISON OF HEATS OF HASTELLOY C-276
(336-hr exposure at 80°C in dissolver product with 0.5M $HNO_3$)

| Alloy Heat Number | Carbon, w/o | Corrosion Rate, mils per month: Rate for First Week | Rate for Second Week | Avg. for Two Weeks |
|---|---|---|---|---|
| 2760-3-3236 | 0.009 | 5.8 | 7.6 | 6.7 |
| | | 5.8 | 7.3 | 6.6 |
| 2760-2-3238 | 0.009 | 6.8 | 5.8 | 6.3 |
| | | 6.5 | -- | -- |
| 2760-2-3241 | 0.007 | 5.6 | 7.2 | 6.4 |
| | | 6.7 | 5.8 | 6.3 |
| 2760-2-3242 | 0.008 | 6.3 | 6.1 | 6.2 |
| | | 6.4 | | |

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## TABLE V
## CORROSION OF WELDED C-276 VESSEL
(8.5 Weeks Exposure at 80°C in Vessel fabricated from 3-inch dia. pipe)

| Solution Composition | Exposure, weeks | Rate, mpm |
|---|---|---|
| Zirconium Dissolver Product (8M F, 1.36M Zr) | 2½ | 7.7 |
| Complexed Dissolver Product [$Al(NO_3)_3$ added] | 1 | 5.1 |
| Hydrofluoric Acid, 8M | 1 | 17.2 |
| Complexed Dissolver Product [$Al(NO_3)_3$ added] | 1 | 5.7 |
| Dissolver Product +0.5M Nitric Acid | 1 | 45 |
| Aluminum Nitrate, 2.2M | 1 | 0.4 |
| Hydrofluoric Acid, 8M | 1 | 6.1 |
| Dissolver Product (Boron Added) | 1 | 1.0 |
| Total Corrosion | 8½ | 10 |

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# CORROSION COUPONS AND RATES

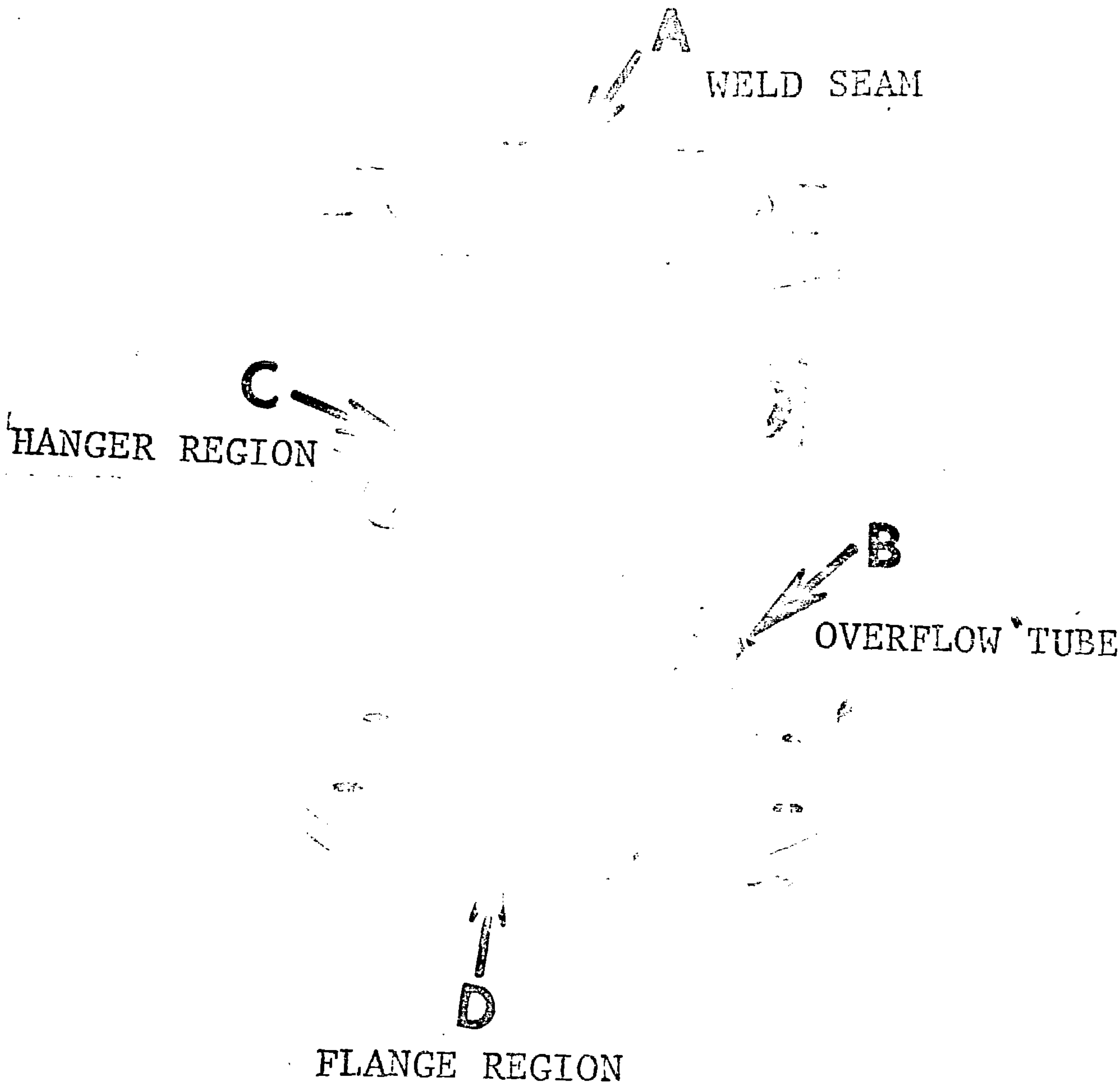
| | HASTELLOY C-276 | HASTELLOY C-4 | HASTELLOY S | HASTELLOY G |
|---|---|---|---|---|
| ACID FEED 8 M HF | 37 MPM | 7.2 MPM | 29 MPM | 59 MPM |
| DISSOLVER PRODUCT 8 M HF 1.3 M ZR | 8.2 MPM | 3.6 MPM | 3.1 MPM | 19 MPM |
| DISSOLVER PRODUCT WITH 0.5 M $HNO_3$ | 61 MPM | 46 MPM | 49 MPM | 102 MPM |
| ALUMINUM NITRATE 2.2 M | 1.6 MPM | .07 MPM | .20 MPM | .015 MPM |

# CORROSION COUPONS AND RATES

| | INCONEL 625 | INCOLOY 825 65 WELDED | INCOLOY 825 625 WELDED |
|---|---|---|---|
| ACID FEED<br>8 M HF | 124 MPM | 162 MPM | 133 MPM |
| DISSOLVER PRODUCT<br>8 M HF<br>1.3 M ZR | 8.0 MPM | 4.3 MPM | 3.8 MPM |
| DISSOLVER PRODUCT<br>WITH 0.5 M $HNO_3$ | 10 MPM | 34 MPM | 64 MPM |
| ALUMINUM NITRATE<br>2.2 M | 0.19 MPM | 0.14 MPM | 0.17 MPM |

# CORROSION COUPONS AND RATES

| | | MOLE RATIO 5.1 F/Zr | MOLE RATIO 6.0 F/Zr |
|---|---|---|---|
| HASTELLOY C-276 | 0.1 M $HNO_3$ | 13 MPM | 36 MPM |
| | 0.5 M $HNO_3$ | 19 MPM | 51 MPM |
| INCONEL-625 | 0.1 M $HNO_3$ | 7 MPM | 22 MPM |
| | 0.5 M $HNO_3$ | 10 MPM | [illegible] MPM |



A
WELD SEAM
C
HANGER REGION
B
OVERFLOW TUBE
D
FLANGE REGION