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CORROSION OF ZIRCALOY-2 BY pH 10 LiOH IN HEATED CREVICES

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CORROSION OF ZIRCALOY-2 BY pH 10 LiOH IN HEATED CREVICES

D. R. Dickinson

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CORROSION OF ZIRCALOY-2 BY pH 10 LiOH IN HEATED CREVICESINTRODUCTION

Both the inner and outer tubes of the N-Reactor fuel elements will have self supports spot welded to the lateral heat-transfer surface of the element. A crevice a few mils thick will exist around the weld between the support tab and the cladding. Because of the heat flux through the cladding at this point and the insulating effect of the support tab, the temperature in this crevice will be higher than that on the free surface away from the support. This can result in boiling in the crevice leading to concentration of LiOH (or impurities in the water) to a level where it can cause severe corrosion of the Zircaloy-2 cladding. The tests described in this report were conducted to determine whether such attack might be encountered in N-Reactor.

SUMMARY

Two electrically heated samples clad in Zircaloy-2 were exposed in an ex-reactor corrosion test loop to recirculating high-purity water with a heat flux of 294,000 Btu/hr ft². The water was adjusted to pH 10 with LiOH. The first test ran 51 days with a bulk water temperature of 332 C; a crevice existed between the Zircaloy-2 and a stainless steel band surrounding the test specimen. The second test ran 113 days at 314 C. Two N-Reactor self-supports were spot welded to the heated surface, producing crevices under four support tabs in addition to the crevice under the steel band as in the first test. The pressure in both tests was 2000 psia, which permitted boiling on the heated surfaces and in the crevices, but suppressed boiling in the bulk water.

Corrosion of the Zircaloy-2 was found in all crevices in both tests with penetrations up to 12 mils. The attack was fairly uniform over all or a large portion of the crevice (i.e., it did not progress by pitting or cracking) and resulted in the formation of a thick layer of white ZrO₂. No corrosion was found except in the crevices. Little hydriding was noticed near the corroded areas.

It is believed that the corrosion resulted from concentration of the LiOH in the crevices by boiling. Since a similar situation will be present in the crevices under the N-Reactor supports, serious corrosion problems may be expected on the N-Reactor fuel elements using the present support design if LiOH is used to control the pH of the primary coolant.

DESCRIPTION OF TESTS

Two separate tests were conducted. In each test, an electrically heated rod clad with Zircaloy-2 and having one or more crevice regions was exposed to pH 10 LiOH under conditions where boiling occurred within the crevices.

A. Test Specimens

In both tests, the test specimen was made from a Watlow "Firerod" heater, rated at 2100 watts, 230 volts, with a heated length of 2 inches and an overall length of 6 3/4 inches, clad in Inconel with an OD of 0.495 inch. A length of Zircaloy-2 tubing was swaged over this, with a final OD of 0.588 inch. A 1/16-inch Zircaloy-2 end cap was welded to the free end of

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the heater rod. The Zircaloy cladding was then machined down to a diameter of 0.514 inch for a distance of 1/2 inch from the free end. This was done to facilitate insertion of a thermocouple in the cladding in the heat-transfer region, as it was difficult to drill a hole for the thermocouple more than a short distance. A hole was then drilled into the Zircaloy cladding from this cut-down region, 0.026 inch diameter and 1/8 inch deep. A specially made thermocouple, clad in stainless steel with a diameter of 0.025 inch, was inserted in this hole. The center of the thermocouple was about 0.025 inch below the surface of the cladding. A band of 304 stainless steel, 0.003 inch thick by 3/8 inch wide, was clamped tightly over the cut-down region to hold the thermocouple in place. A thin crevice was thus created between this band and the Zircaloy cladding. At the other end of the heater the Zircaloy cladding was machined down to 0.562 inch diameter to fit into a 9/16-inch Swagelok compression fitting, which was used to make a pressure seal against the test specimen.

The first test was designed primarily to study the change of cladding temperature due to oxide formation and crud deposition. After serious corrosion was noticed in the crevice during the first test, the specimen for the second test was modified by the addition of supports in order to study the corrosion in the crevices under them. Two "suitcase handle" supports were used of the type to be used on the outer N-Reactor fuel elements. These were 1/4 inch by 1 1/2 inch and stamped from 0.037-inch Zircaloy-2. They were spot-welded 180° apart to the Zircaloy cladding of the test specimen. One support was positioned over the thermocouple with the tip of the thermocouple directly under one weld. The tab at each end of a support in contact with the cladding was about 1/4 by 5/16 inch. The spot weld itself was a region in the center of this tab about 0.08 inch in diameter. In the remaining area a crevice existed between the support and cladding. Before being welded on, the supports were bent to the curvature of the specimen; this produced a thinner crevice more typical of N-Reactor with about 5 mils maximum gap.

In both tests the specimen was etched (before welding) but not autoclaved before exposure.

A diagram of the test specimen used in the second test is shown in Figure 1. The test specimen in the first test was the same except that there were no supports attached.

B. Test Conditions

Both tests were conducted in the TF-3 Loop at 1706-KE. The heated samples were inserted in a special vertical test section with an ID of 1.000 inch. The specimen was held at the top of the test section by a 9/16-inch Swagelok compression fitting. The electrical leads from the heater were connected to a 230-volt constant-voltage power supply. The thermocouples were run out through a Conax fitting at the bottom of the test section.

The flow entered through a side port 1 inch below the top of the test section, flowed down through the annular space and out a similar side port near the bottom, 6 inches below the inlet. The crevice regions of the specimen were located near the center of this test section. The flow was 6600 lb/hr (16 gpm)

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FIGURE 1

Heated Test Specimen for Second Test

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which gave a mass velocity over the specimen of 1,840,000 lb/hr ft² (10 ft/sec).

The average power generation was 2210 watts, which produced an average surface heat flux of 93 watts/cm² or 294,000 Btu/hr ft² over the 2-inch heated length. (336,000 Btu/hr ft² in the cut-down region because of the reduced surface). The heat flux through the support tabs (in the second test) was of course less than this because the added resistance introduced by the tab deflected some of the heat to the adjacent free surface.

The first test ran for 51 days with a bulk water temperature of 332 C. The second test ran 113 days at 314 C. The pressure was held at 2000 psia in both tests, which corresponds to a boiling point of 336 C. Under these conditions surface boiling but not bulk boiling existed in both tests. Boiling or steam phase also existed in the crevices since they were at a temperature at least as high as the free surface.

In both tests, the water was maintained at pH 10 with LiOH. High water purity was maintained by feed and bleed. Make-up water was passed through lithium-form mixed-bed ion exchange resin to control the pH. Water quality during the tests is summarized in Table I.

TABLE I

TF-3 Water Analyses

	<u>First Test</u>			<u>Second Test</u>		
	<u>(8/29/62 - 11/6/62)</u>			<u>(12/13/62 - 4/14/63)</u>		
	<u>Min.</u>	<u>Max.</u>	<u>Ave.</u>	<u>Min.</u>	<u>Max.</u>	<u>Ave.</u>
pH	9.6	10.3	9.9	7.2	10.5	9.8
Specific resistance, 10 ³ ohm cm	17	134	62	13	168	60
Total solids, ppm	2	14	10	1	28	6
O ₂ , ppm	0	.24	.11	0	2.1	.32
Cl, ppm	<.05	<.05	<.05	<.05	.75	.06
Cold crud, ppb	12	126	51	29	547	169
Fe, ppb	<10	17	<10	<10	320	13
Ni, ppb	<10	190	*	<10	<10	<10
Cr, ppb	< 4	>500	*	< 4	110	9
Cu, ppb	< 4	10	< 4	< 4	96	6
Al, ppb	<10	115	26	<10	230	17
Zr, ppb	< 4	< 4	< 4	< 4	< 4	< 4
Mn, ppb	< 1	< 1	< 1	< 1	25	*
Co, ppb	< 4	< 4	< 4	< 4	< 4	< 4
Ca, ppb	<10	230	*	<10	220	12
Mg, ppb	<10	20	<10	<10	150	<10
Pb, ppb	<50	<50	<50	<50	<50	<50
Zn, ppb	<20	<20	<20	<20	70	*

* All analyses below detection except one high value shown.

The first test was interrupted after completion of the first 17 days in order to run a special test in support of decontamination of the PRTR. The loop was operated for 53 hours at 80 C with CO₂ added to give a pH of 5.0-5.6. During this period the zirconium-clad specimen was left in place but was not heated. The loop was flushed well before resuming high-temperature heat-transfer testing. This period of operation is not believed to have affected the test.

TEST RESULTS

A. First Test

In the first test, an area of extensive corrosion was found on the zirconium next to the crevice under the stainless steel band. Photographs of this corrosion are shown in Figure 2. The maximum penetration was 12 mils; the cut-down cladding in this region had been completely penetrated at some points. In most areas of high corrosion, the oxide was intact and firmly attached to the metal. This oxide was identified as ZrO₂. A pH test of the corroded area showed it to be quite caustic. A maximum of only 75-100 ppm of hydride was found in the zirconium next to the corroded area. No evidence of any preferred orientation of the hydride was observed. Normal corrosion (shiny black oxide) was found on the zirconium in areas free of crevices. The stainless steel band also showed several mils corrosion in the crevice region.

Another crevice existed between the stainless-steel thermocouple sheath and the hole in the cladding in which it was inserted. The zirconium was found to be corroded along the outer 1/4 to 1/2 of the length of this hole. The maximum penetration was 2 mils. The failure to develop corrosion on the inner half of the hole may have been due to the presence of steam at all times which prevented access of fresh liquid water and thus prevented concentration of LiOH by boiling.

The temperature difference measured between the cladding and the adjacent water was initially 5 C, increased to 14 C in 17 days, and held at about this value for the rest of the test. The period of operation with CO₂ did not significantly change the ΔT . These values, particularly the initial ΔT , are low compared to what would be expected with the heat flux used. The reason for this discrepancy is not known. The rise in cladding temperature during the first part of the test may have been due, at least in part, to build-up of zirconium oxide and crud. However, the area over the thermocouple was generally free of crud, and the region of severe corrosion was sufficiently removed from the thermocouple that it probably contributed little to the measured rise in temperature.

B. Second Test

The heated specimen from the second test was removed after the first 52 days for examination. The stainless steel band was removed and only very slight corrosion of the zirconium was found beneath it. It was not possible to determine whether corrosion had taken place in the crevices under the supports. The steel band was replaced and the test was continued another 61 days.

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When the steel band was again removed at the end of the test, extensive corrosion was found under it, similar to that in the first test. The corroded area extended 0.4 inch along the circumference of the cut-down region. The maximum penetration was 6 mils. In one region, the penetration averaged 3 mils over a length of 0.1 inch. In most places the white ZrO_2 which formed was adherent, but it had flaked off in few spots.

The crevices under the supports were filled with a loose crud deposit, although the free surface was free of crud. It was necessary to section the specimen to see the corrosion under the supports. A cut was made through each of the four welds. Each cut exposed two crevices, one on either side of the weld, except for one cut which apparently passed near but not through the weld and thereby allowed the support to become separated from the metallurgical sample and lost.

Extensive corrosion with formation of thick white oxide was found in each of the crevices. Both the cladding and support were corroded; the corrosion was generally heavier on the cladding. The region of corrosion covered from half to all of the length of the crevice, from its inner tip to a point near its outer edge. The heaviest corrosion in each crevice was usually near the outer edge of the corroded area, rather than down in the tip of the crevice.

The extent of corrosion and thickness of the oxide found in each crevice are shown in Table II. On the basis of the relative densities of metal and oxide, it is estimated that the depth of penetration of the metal equals about $2/3$ of the thickness of the oxide. This ratio was verified in a few instances where the depth of penetration could be measured by comparison to surrounding unattacked metal. The maximum penetration was thus 7 mils. Photographs illustrating the extent of the corrosion are shown in Figure 3.

TABLE II

Corrosion in Crevices Under Supports

Crevice	1a	1b	2a	2b	3a	3b	4a	4b
Position	← downstream →				← upstream →			
Oxide on cladding							}	
Lateral extent, mils	70	90	40	35	50	45		
*Ave. thickness, mils	4	4	1	5	2	2		
*Max. thickness, mils	11	9	3	8	3	5		
Oxide on support								
Lateral extent, mils	60	60	30	35	45	25	-	-
*Ave. thickness, mils	4	3	1	2	1	1	-	-
*Max. thickness, mils	6	5	2	3	3	2	-	-

*Penetration = $2/3$ oxide thickness.

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Region of Moderate Corrosion (150 X)

Severe Corrosion with Complete Penetration of Zr (150X)

FIGURE 2

Corrosion of Zr in Crevice under Steel Band - First Test

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Support

Crevice

Oxide

Cladding

Crevice 1a (100 X)

Support

Oxide

Oxide

Cladding

Crevice 1b (left side) (100 X)

Support

Oxide

Oxide

Cladding

Crevice 1b (right side) (100 X)

FIGURE 3a

Corrosion of Zr in Crevices under Supports - Second Test

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Support

Cladding

Crevice 2a (100 X)

Support

Support

Cladding

Crevice 2b (100 X)

Support

Cladding

Crevice 3a (100 X)

Cladding

Crevice 3b (100 X)

FIGURE 3b

Corrosion of Zirconium in Crevices, under Supports - Second Test

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FIGURE 4

Temperature of Mine-Log-2 (1) 1/2 ft. below top of
directly under rock 1/2 ft.

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A moderate amount of hydroxide (about 200 ppm) was found in the neighborhood of the corroded areas. The hydride was particularly concentrated near the outer corners of the support tabs; here the needles of hydride were oriented parallel to the surface. The cladding below the corroded area had less hydride than the adjacent support, but more than on the cladding away from the corrosion.

There was some evidence that the formation of oxide in the crevice tended to extend the crack through the weld. The crevices were completely filled with oxide over most of the region of attack, particularly at the inner ends. Since it is not likely that corrosion would stop when the oxide built up to the width of the original crevice, the build-up of oxide would have tended to force the support and cladding apart. In several instances the tip of the oxide-filled crevice did not match up with what appeared to be the line of demarcation through the weld between the support and cladding. Thus it appears that the strain produced by the oxide build-up extended the crack along a plane other than the weld interface.

No abnormal corrosion or crud deposition was noticed except in the crevices.

The temperature measured by the thermocouple in the cladding under one of the supports rose from 376 C at the start of the test to 429 C at the end. During this time, the adjacent bulk water temperature was constant at 314 C. This variation of cladding temperature with time is plotted in Figure 4. The increase in cladding temperature may be attributed largely to build-up of oxide under the support. The oxide would not only offer increased resistance to heat transfer, but also by filling in the crevice would reduce cooling due to boiling in the crevice. The reason for the discontinuities in temperature shown in Figure 4 is not apparent. The sharp drops in temperature may have been due to sloughing off of crud which blocked free flow of water into the crevice; sloughing off of the ZrO_2 in the crevice hardly seems likely. If these sudden jumps are neglected, the cladding temperature rose at a fairly uniform rate over the test period. This would indicate that the corrosion rate was fairly constant during the test.

DISCUSSION OF TEST DATA

It has been shown by several investigators^(1,2) that at high temperatures zirconium is severely corroded by solutions of LiOH at concentrations above some critical concentration dependent on the temperature. Therefore zirconium is subject to corrosion by dilute solutions of LiOH when some mechanism exists to concentrate the LiOH to above the critical concentration. Such a mechanism is provided by boiling, particularly in a crevice, where the LiOH is left behind as the water is evaporated. The temperature in the crevice under the support before the build-up of oxide started was at or somewhat above the boiling point, 336 C, but certainly below the measured cladding temperature of 376 C. According to the data of Coriou⁽²⁾ the critical concentration of LiOH is 3 g/l at 330 C and 1 g/l at 360 C; below these concentrations, weight gains of Zircaloy-2 in a 3-day test were of the

1. Hillner, E. and J.N. Chirigos, The Effect of Lithium Hydroxide and Related Solutions on the Corrosion Rate of Zircaloy in 680 F Water, WAPD-TM-307, August, 1962 (Unclassified).
2. Coriou, H., et al., Corrosion du Zircaloy Dans Divers Milieux Alcalins a Haute Temperature, Conference on the Corrosion of Reactor Materials, Salzburg, June, 1962.

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order of 10 mg/dm^2 , at higher concentrations they were on the order of 1000 mg/dm^2 . The concentration of LiOH in the coolant at pH 10 was .004 g/l. Thus concentration of LiOH in the crevices by a factor of about 500 would have been required to produce the severe corrosion observed. This degree of concentration could easily have been produced in a boiling crevice.

The higher temperature present in the crevice may also have acted to increase the corrosion, particularly in the later stages when the temperature was raised by oxide formation. However, a rise in the metal temperature due to the temperature drop across the oxide layer was probably not a major factor in promoting corrosion, since the corrosion on the support side of the crevice were the temperature was reduced by oxide build-up was nearly as great as on the cladding side.

Similar corrosion of Zircaloy-2 by LiOH in a boiling crevice was found by Anderson and McGoff.⁽³⁾ Two parallel strips of Zircaloy-2 with a crevice between them were electrically heated to give a heat flux of $500,000 \text{ Btu/hr ft}^2$. The test ran 9 days at pH 10.5 with LiOH with a bulk water temperature of 308°C and incipient bulk boiling. Severe corrosion was found in the crevice region with formation of white oxide and maximum penetration of 5 mils. In a similar test with pH 10.5 NH_4OH , maximum penetration was only 1 mil after 42 days.

Corrosion of Zircaloy-2 due to concentration of LiOH has also been reported by Maffei.⁽⁴⁾ Samples exposed at 300°C to a slow leak of flashing pH 10 LiOH in simulation of a leaking joint showed localized penetration of 4 mils in 1 month in one test and 2 mils in 6 months in another.

The relatively small amount of hydriding of the zirconium in the area of corrosion is worthy of note since ordinarily one would expect such heavy corrosion to be accompanied by severe hydriding ($>1000 \text{ ppm}$). The most likely explanation is that the hydrogen diffused away from the small areas of corrosion into a relatively large mass of metal so that the resulting concentration was low. The amount of hydrogen picked up from corrosion of one support would be only about 50-100 ppm if spread uniformly throughout the support. The corresponding concentration would be much less for the cladding due to its much larger mass. The average temperature of the support was about 350°C ; at this temperature the diffusion coefficient, D , and solubility of hydrogen in Zircaloy-2 are $2.5 \times 10^{-6} \text{ cm}^2/\text{sec}$ and 190 ppm.⁽⁵⁾ With distances of the order of 1 cm and time of 113 days, the ratio $Dt/L^2 \gg 1$ indicating good distribution of hydrogen by diffusion. Maffei also noted a low concentration of hydride in his test; here also the corroded area was small compared to the total mass of metal. On the other hand, Anderson and McGoff found severe hydriding ($>1000 \text{ ppm}$); in these tests the ratio of corroding surface to sample volume was large. The higher concentrations of hydride at the outer corner of the supports may be attributed to the tendency of hydrogen to diffuse to the cold regions; the outer corners of the support tabs had the best cooling and thus the lowest temperature.

3. Anderson, W. K. and M. J. McGoff, Corrosion of Zircaloy in Crevices Under Nucleate Boiling Conditions, KAPL-2203, April 13, 1962 (Unclassified).
4. Maffei, H. P., Effect of Lithium Hydroxide Leakage on the High-Temperature Corrosion of Zircaloy-2, HW-78819, September 12, 1963 (Unclassified).
5. Sawatzky, A., C.R. Met 826, The Diffusion and Solubility of Hydrogen in Alpha-Phase Zircaloy-2, February, 1959.

DECLASSIFIEDIMPLICATIONS FOR N-REACTOR

The results of these tests show that Zircaloy-2 is subject to severe corrosion by high-temperature pH 10 solutions of LiOH if heated crevices are present in which the solution can boil and become concentrated. Exactly this situation will be present in the crevices around the spot welds of the supports on the fuel elements in N-Reactor. The fuel elements will be exposed to lower temperatures but higher heat fluxes than employed in these tests, and boiling on the free surface, such as was present in these tests, is expected in N-Reactor only under hot-spot conditions. However, because of the impaired heat transfer, boiling will almost certainly be present in the crevices over a substantial fraction of the fuel charge.⁽⁶⁾ Therefore, even with the somewhat lower temperature and lack of surface boiling in N-Reactor, corrosion similar to that encountered in these tests will probably occur if LiOH is used to adjust the pH of the primary coolant. The successful use of LiOH in other pressurized-water reactors does not mean LiOH will be satisfactory in N-Reactor since the heated crevices on the fuel-element surface are a feature peculiar to N-Reactor.

Such corrosion under the supports in N-Reactor may have two highly detrimental consequences. The corrosion may penetrate the cladding, permitting access of water to the uranium, or the build-up of oxide under the support may pry it off from the cladding.

There is very good reason to believe that the problem would be eliminated by the use of NH_4OH rather than LiOH. Being volatile, NH_4OH is not subject to concentration by boiling. Furthermore, the corrosion of zirconium is not accelerated by high concentrations of NH_4OH as it is with LiOH. Coriou⁽²⁾ found no increase in the corrosion at 360 C with concentrations of NH_4OH as high as 20 g/l. As noted above, Anderson and McGoff found corrosion in a boiling crevice to be much less severe with NH_4OH than LiOH.

Redesign of the support weld to eliminate any crevice could also overcome the problem.

FUTURE WORK

A test is now in progress in TF-3 under conditions similar to the second test described in this report except that NH_4OH is used in place of LiOH. This will determine whether the corrosion found in heated crevices with LiOH can be avoided by using NH_4OH . Other tests will be made with NH_4OH and with LiOH duplicating N-Reactor temperatures and boiling-point suppression. In order to extend heat-transfer testing to a second loop, a new test section has been fabricated for TF-2 containing a pair of heat transfer cells similar to that in TF-3.

A number of N-Reactor prototype fuel elements will be examined which have been exposed to LiOH in KER under conditions where surface boiling has been approached and where boiling would be expected in the crevices.

6. Kreiter, M.R., Thermal Hydraulics Operation, personal communication.

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Dean R. Dickinson

D. R. Dickinson
Coolant Systems Development Operation
Engineering Development Operation
Reactor and Fuels Laboratory
HANFORD LABORATORIES

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