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REPORT

RADIATION - ENHANCED OXIDATION OF ZIRCALOY - 2
IN pH - 10 LiOH AND pH - 10 NH₄OH

A. B. JOHNSON, JR. AND J. E. IRVIN

JULY 1967

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IN pH-10 LiOH AND pH-10 NH₄OH

By

A. B. Johnson, Jr.
Corrosion and Coolant Chemistry Section
Chemistry Department

and

J. E. Irvin
Metallurgy Research Section
Metallurgy Department

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RADIATION-ENHANCED OXIDATION OF ZIRCALOY-2

IN pH-10 LiOH AND pH-10 NH₄OH

A. B. Johnson, Jr. and J. E. Irvin

INTRODUCTION

In certain reactor environments, zirconium alloys undergo accelerated oxidation,⁽¹⁻⁶⁾ while in other environments, the oxidation rate is essentially unaffected by substantial in-flux exposures.^(6,7) The in-flux tests discussed in this report were conducted in the G-7 pressurized water loop of the Engineering Test Reactor (ETR). Several hundred Zircaloy-2 specimens exposed by W. A. Burns in pH-10 lithium hydroxide underwent accelerated oxidation in the loop.⁽¹⁾ Oxidation of low-nickel Zircaloy-2, Zircaloy-4 and Zr-3Nb-1Sn was also markedly affected by the ETR flux.⁽⁶⁾ Exposures of identical specimens over a range of flux levels (5×10^{12} to 1×10^{14} n/cm² sec, >1 MeV) and in an out-of-reactor loop clearly demonstrated that the accelerated oxidation was flux-induced.

The G-7 loop tests discussed here involve a series of nine exposures of tensile specimens from three lots of Zircaloy-2 that had been machined from tubes supplied for use in the New Production Reactor (NPR). Exposure times were 20 to 354 days at fast fluxes of 3×10^{13} to 1×10^{14} nv, >1 MeV. Eight of the quadrants (specimen holders) were exposed in pH-10 LiOH, ~1 ppm dissolved oxygen; the ninth quadrant was exposed 249 days in pH-10 LiOH. The G-7 loop coolant was then changed to pH-10 NH₄OH, <0.05 ppm oxygen, after which the quadrant was exposed for an additional 105 days.

Weight gain and hydrogen absorption data, reported in part elsewhere,⁽⁸⁾ are interpreted here in terms of neutron flux, time at temperature, alloy lot, and ETR environment. The series of nine exposures provides an opportunity to study characteristics of the in-flux behavior of Zircaloy-2 under conditions where the oxidation rate is greatly accelerated.

SUMMARY AND CONCLUSIONS

To summarize the principal observations of the study:

- Pronounced flux-induced oxidation occurred on all Zircaloy-2 specimens exposed at 280 °C in pH-10 LiOH, ~1 ppm O₂. Rates up to 3 mg/dm² day were observed. Identical specimens exposed out-of-reactor at the same nominal conditions oxidized at normal rates.
- If the data are compared on the basis of exposure time for bulk water temperatures of 270-280 °C, oxidation rates were lower at fast fluxes of 3×10^{13} n/cm² sec than at fast fluxes of 1×10^{14} n/cm² sec.
- A linear relationship was observed between in-flux weight gain and fast neutron fluence* (n/cm², >1 MeV).
- G-7 loop specimens transferred** from pH-10 LiOH ~1 ppm O₂ to pH-10 NH₄OH <0.05 ppm O₂ continued to oxidize at rates characteristic of the lithiated system.
- Marked differences in susceptibility to flux-induced oxidation and hydriding occurred for the three Zircaloy-2 lots. The highest oxidation rate (lot CT) was accompanied by the lowest rate of hydrogen absorption.
- Hydrogen absorption increased almost linearly with the increasing fast fluence in pH-10 LiOH. The percentage of the corrosion hydrogen absorbed was generally in the low range of out-of-flux values for Zircaloy-2.
- Transfer of the heavily-oxidized specimens from the lithiated to the ammoniated G-7 loop environment caused more hydrogen absorption than that predicted from trends established in the lithiated system.

* Fluence is synonymous with integrated neutron flux, n/cm².

** The term "transferred" identifies specimens (Quadrant 140) which were exposed in the loop in pH-10 LiOH and which were returned to the loop after the coolant was changed to pH-10 NH₄OH.

Oxidation rates on the tensile specimens agree in general with rates on other zirconium alloy specimens exposed in the G-7 loop in pH-10 LiOH, ~ 1 ppm oxygen. The highest corrosion rates on Zircaloy-2 cladding in boiling water reactors are somewhat lower than, but of the same magnitude as, the rates reported here. However, rates on the tensile specimens are markedly higher than rates normally encountered on Zircaloy components in the low-oxygen reactor environments. The rates also are higher than rates currently observed in the G-7 loop on specimens exposed only in pH-10 NH_4OH , < 0.05 ppm O_2 . Results of corrosion studies in three G-7 loop environments suggest that dissolved oxygen is a significant factor in the in-flux corrosion mechanism.

EXPERIMENTAL

Typical Zircaloy-2 tensile specimens, quadrants, and the G-7 loop sample hanger assembly are shown in Figure 1. Specimen fabrication is described elsewhere.⁽⁸⁾ Specimen preparation involved the following operations:

- Specimens were machined from NPR tubes. The tube-wall thickness was 0.280 in.; the finished specimen thickness was 0.250 in. Specimen weights were 7.0 to 7.5 g; surface areas were about 0.12 dm^2 .
- Specimens were etched for 3 minutes in 30% HNO_3 - 3% HF - 67% H_2O at 30 °C to remove about two mils per surface.
- Specimens were preautoclaved in deionized water for 72 hr at 300 °C, 1500 psi. Average oxide thicknesses were 11-12 mg/dm^2 .

Specimens were machined from three Zircaloy-2 tubes supplied by three vendors: Allegheny Ludlum Steel Corp. (AT); Harvey Aluminum Co. (HT); and Chase Brass and Copper Co. (CT). Brief fabrication histories and chemical analyses of the tubes are summarized in Tables I and II.

FIGURE 1. *Tensile Specimens, Quadrants, and G-7 Loop Hanger Assembly*

TABLE I. *Fabrication History of NPR Zircaloy-2 Tubes*

<u>Fabrication Step</u>	<u>Allegheny Ludlum Steel Corporation</u>	<u>Chase Brass and Copper Company</u>	<u>Harvey Aluminum Company</u>
	*	*	*
Ingot	12 in. diameter	16 in. diameter	16 in. diameter
Breakdown	Forged to 8 in. ² at 760 °C to 885 °C Rolled to 7 in. round at 790 °C to 930 °C	Forged to 7-1/2 in. round by flat dies at 930 °C, with one reheat	Forged to 11-3/4 in. round by curved dies
Pierced or drilled	Pierced	Drilled	Pierced
Extrusion	Ratio of 8/1 at 790 °C	Ratio of 13/1 at 840 °C	Ratio of 29/1 at 760 °C
Cold work	"Rockrite," 30%, one pass	Draw, 18%, one pass	Draw, 30%, three passes
Welded or Continuous	Welded	Welded	Single Extrusion

* All material was double vacuum melted from reactor-grade zirconium sponge.

TABLE II. *Chemical Analysis of NPR Zircaloy-2 Tubes*

<u>Alloy Element</u>	<u>Tube Designation</u>		
	<u>AT-50</u>	<u>HT-37</u> wt%	<u>CT-19</u>
Sn	1.49	1.48	1.51
Fe	0.13	0.11	0.13
Cr	0.10	0.11	0.08
Ni	0.06	0.04	0.05
	<hr/> ppm <hr/>		
N ₂	34	35	46
H ₂	11	20	16
Si	37	47	47
Cu	18	<20	20
W	11	<20	<40
C	390	142	247
O ₂	1330	900	1310

Exposures in terms of flux and time in the ETR G-7 loop are summarized in Table III for the nine quadrants. Loop conditions for the pH-10 LiOH and pH-10 NH₄OH environments appear in Table IV. The G-7 loop coolant was pH-10 LiOH through ETR cycle 74. Beginning with cycle 75, the pH was controlled with ammonium hydroxide. No attempt was made to deoxygenate feed water to the lithiated system, resulting in a dissolved oxygen concentration of ~1 ppm. However, the dissolved oxygen concentration varied between 0.2 and 3.7 ppm, depending on the loop makeup requirements. However, feed water to the ammoniated system was deoxygenated, and radiolytic decomposition of ammonia generated hydrogen, which further reduced the dissolved oxygen level.

The operating bulk water temperature of the loop was 270-280 °C. Stainless steel samples with inserted thermocouples operated at temperatures about 10 °C above the bulk coolant temperature.

TABLE III. Summary of Exposures

Quadrant	No. of ETR Cycles	Fast Flux n/cm ² sec (>1 MeV)	Exposure		
			Time at Temperature, days*	n/cm ² >1 MeV	n/cm ² Thermal
116	1	3.7 x 10 ¹³	21	6.9 x 10 ¹⁹	2.1 x 10 ²⁰
118	1	5.5 x 10 ¹³	21	1.1 x 10 ²⁰	3.0 x 10 ²⁰
124	2	5.2 x 10 ¹³	36	1.6 x 10 ²⁰	4.9 x 10 ²⁰
126	3	1.1 x 10 ¹⁴	58	5.6 x 10 ²⁰	1.3 x 10 ²¹
141	5	9.0 x 10 ¹³	117	9.5 x 10 ²⁰	4.0 x 10 ²¹
122	7	3.0 x 10 ¹³	153	3.5 x 10 ²⁰	1.3 x 10 ²¹
119	8	8.0 x 10 ¹³	174	1.3 x 10 ²¹	4.9 x 10 ²¹
120	11	1.0 x 10 ¹⁴	239	2.4 x 10 ²¹	5.6 x 10 ²¹
140	18	1.0 x 10 ¹⁴	354	3.5 x 10 ²¹	7.2 x 10 ²¹

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* Time at bulk water temperatures of 270-280 °C. Effective full power days are about 10% longer than the time at temperature.

TABLE IV. G-7 Loop Conditions - ETR Cycles 56 through 80Temperatures:

Loop outlet bulk water temperature: 270 - 280 °C.

ΔT of loop coolant across flux zone: 7 to 10 °C.

Estimated maximum sample temperatures: 290 °C.

Nominal Loop Pressure in Sample Section: 2150 psi.

Flow Rate Thru Sample Section: 5 ft/sec (1.6 m/sec), 115 gal/min.

Water Chemistry

A. Cycles 56 through 74 - LiOH pH control:

pH 10 (nominal)
 Oxygen, ppm 3.7 maximum
 0.19 minimum
 0.8 mean

B. Cycles 75 through 80 - NH_4OH pH control:

	<u>Minimum</u>	<u>Maximum</u>	<u>Mean</u>
pH	9.5	10.4	9.8
NH_3 , ppm	1.8	19.7	7.7
H_2 , cc/kg	9	135	32
O_2 , ppm	<0.01	0.055	<0.05
NO_2^- , ppm	<0.002	0.06	0.01
NO_3^- , ppm	<0.05	<0.05	<0.05
Cs^{138} dis/min ml	2.3×10^4	5.2×10^4	3.4×10^4
Total Solids, ppm	Undetectable	7.3	-

Only nonfissile materials were tested in the G-7 loop. However, fuel elements were tested in the companion M-3 loop, which shares common water facilities with the G-7 loop. Table V correlates the M-3 loop fuel element failures and the G-7/M-3 loop decontaminations with the G-7 loop tensile specimen exposures.

TABLE V. Summary of M-3 Loop Fuel Element Failures,
G-7/M-3 Loop Decontaminations, and Tensile Specimen
Exposures

ETR Cycle	Date	Occurrence	Type
50	11-9-62	Fuel Element Failure	Enriched uranium - 1.2% average enrichment. Amount of uranium release unknown.
52	1-7-63	Loop decontamination	1. 10 vol% HNO ₃ 2. NaOH + KMnO ₄ 3. Ammonium citrate, inhibited with nitrilotriethanol
54	3-31-63	Loop decontamination	1. AP-1(a) 2. Sulfamic acid, inhibited
56	7-1-63	First NPR Zircaloy-2 tensile specimen exposure	
61	1-19-64	Loop decontamination	1. NaOH + KMnO ₄ 2. Sulfamic acid (weak solution) 3. Sulfamic acid (strong solution), EDTA, ^(b) inhibited.
62	3-1-64	Loop decontamination	Same as Cycle 61
65	7-19-64	Tensile specimens removed for special G-7 loop test	
65	7-29-64	Fuel element failure	35 g of 0.947% depleted uranium released to G-7/M-3 system.
66	8-16-64	Loop decontamination	1. 10 vol% HNO ₃ 2. AP-1(a) 3. TURCO 4306-D(c)
67	10-9-64	Tensile specimens (Quadrants 120 and 140) returned to G-7 loop.	
68	11-15-64	Loop decontamination	1. AP-1(a) 2. Sulfamic acid (weak solution) 3. Sulfamic acid (strong solution), EDTA, ^(b) 4. Ammonium citrate
68	12-14-65	Fuel element failure	N-Reactor oxide element. Hairline crack. Activity release - no fissionable materials lost.
72	5-10-65	Loop decontamination	1. AP-1(a) + KMnO ₄ 2. Dilute ammonium citrate, inhibited 3. Ammonium citrate, oxalic acid, ferric sulfate, nitrilotriethanol, inhibited.
75	9-12-65	Loop decontamination	1. AP-1(a) + KMnO ₄ 2. Ammonium citrate, oxalic acid, ferric sulfate, inhibited.
75	9-12-65	Loop converted to ammonia pH control	
80	5-22-66	Final NPR Zircaloy-2 tensile specimen quadrant (No. 140) discharged.	

(a) Proprietary alkaline permanganate solution (TURCO 4502).

(b) Ethylenediaminetetraacetic acid.

(c) Proprietary inhibited sulfamic acid.

Fluxes (Table III) were monitored by dosimeters attached to each quadrant. The dosimeters contained wires of iron, nickel, and titanium to measure the fast fluxes; the thermal fluxes were monitored by Al-Co dosimeters. The most reliable fast flux values were obtained from the iron monitors.⁽⁹⁾

Control specimens were exposed in an out-of-reactor loop at Battelle-Northwest. The loop was operated on the G-7 loop time/temperature schedule to provide zero-flux comparisons for in-flux weight gains and hydrogen pickups. Specimens of each Zircaloy-2 lot were exposed at Battelle-Northwest in an autoclave at 390 - 400 °C in 1500 psi steam. Due to a defective thermocouple, the test ran at 390 °C for the first 40 days.

Upon discharge from the G-7 loop, specimens were shipped to Battelle-Northwest for postirradiation analysis. Samples were ultrasonically cleaned in a detergent solution, air-dried and weighed on a four-place in-cell Mettler analytical balance. Weight changes due to the cleaning and drying of specimens from Quadrant 140 are summarized in Appendix A. Postirradiation tensile tests were performed on the specimens at room temperature and at 300 °C. Results of tensile tests (not including those for Quadrant 140) are reported elsewhere.⁽⁸⁾ Specimens tensile-tested at room temperature were sectioned for metallography, and samples were taken in duplicate or quadruplicate for hydrogen analysis. Six samples were taken from Quadrant 141 specimens for hydrogen analysis. Hydrogen analyses were performed independently by two laboratories at Battelle-Northwest, using hot vacuum extraction methods. Results of the independent analyses are compared in Appendix B.

RESULTS

APPEARANCE OF IRRADIATED SPECIMENS

Figure 2 shows a section of a specimen after tensile testing. The specimen was exposed in-reactor 174 days in pH-10 LiOH.

The oxide spalled in the region of the fracture and along one edge, but is otherwise intact. The undisturbed oxide surface is medium gray. Where the oxide spalled, the exposed oxide appears white. The thick oxides were surprisingly resistant to spalling, although Quadrant 140 specimens from lot CT show evidence of spalling. In tensile tests on specimens with thick oxides, oxide fragments up to about 0.6 cm square spalled in the region of fracture.

FIGURE 2. Broken Tensile Specimen. Note Oxide Loss in Area of Fracture. Exposure: 174 Days in ETR G-7 Loop, pH-10 LiOH, $\sim 280^{\circ}\text{C}$. Zircaloy-2 Lot CT. Weight Gain - 415 mg/dm^2

Figure 3 shows specimens that have been exposed in the ammoniated system (Quadrant 140) before and after ultrasonic cleaning. Removal of the black crud layer revealed a light

beige oxide. The mean crud layer weight on twelve specimens from Quadrant 140 was 118 mg/dm^2 . Crud removal data for individual specimens appear in Appendix A.

Before Decontamination

After Decontamination

FIGURE 3. *Irradiated Zircaloy-2 Tensile Specimens Before and After Decontamination in an Ultrasonically Vibrated Detergent Solution. In-Reactor Exposure: Quadrant 140; 354 Days; 270-280 °C, pH-10 LiOH and pH-10 NH₄OH*

IN-FLUX WEIGHT GAIN AS A FUNCTION OF TIME

Figure 4a, b and c and Table VI show the relationship of in-flux weight gain to time at temperature for the three lots of Zircaloy-2. Each datum point in Figure 4 indicates:

- The range of weight gains at each exposure.
- The mean weight gain at each exposure.
- The number of samples weighed (shown above each datum point).
- The quadrant number (shown below each datum point).

Flux levels for each quadrant are summarized in Table III. The point at which the G-7 loop environment was changed from pH-10 LiOH to pH-10 NH_4OH is indicated on Figure 4. Mean in-flux weight gains after 354 days were typical of out-of-flux values for Zircaloy-2 in steam⁽¹⁰⁾ at about 445 °C for the CT lot and at about 435 °C for AT and HT lots. Rates were 3.1 mg/dm^2 day for lot CT and 2.0 mg/dm^2 day for AT and HT lots.

TABLE VI. Weight Gain as a Function of Time and Fast Fluence

Quadrant Number	Tube Designation	Time, °C days	Fast Fluence* n/cm^2	Number of Cycles	Mean In-Flux Weight Gain, mg/dm^2	Mean** Out-of-Reactor Weight Gain, mg/dm^2
116	AT	21.2	6.9×10^{19}	1	16	2.2
116	HT	21.2	6.9×10^{19}	1	20	4.1
116	CT	21.2	6.9×10^{19}	1	19	5.2
118	AT	21.2	1.1×10^{20}	1	34	same
118	HT	21.2	1.1×10^{20}	1	32	as
118	CT	21.2	1.1×10^{20}	1	28	Q-116
124	AT	35.8	1.6×10^{20}	2	51	no controls
124	HT	35.8	1.6×10^{20}	2	50	
124	CT	35.8	1.6×10^{20}	2	58	
126	AT	57.7	5.6×10^{20}	3	126	3.7
126	HT	57.7	5.6×10^{20}	3	109	3.9
126	CT	57.7	5.6×10^{20}	3	145	6.0
141	AT	116.8	9.5×10^{20}	5	222	15.6
141	HT	116.8	9.5×10^{20}	5	210	9.9
141	CT	116.8	9.5×10^{20}	5	315	14.3
122	AT	152.6	3.5×10^{20}	7	72	14.7
122	HT	152.6	3.5×10^{20}	7	64	12.3
122	CT	152.6	3.5×10^{20}	7	91	12.7
119	AT	173.8	1.3×10^{21}	8	298	13.1
119	HT	173.8	1.3×10^{21}	8	257	10.7
119	CT	173.8	1.3×10^{21}	8	450	12.3
120	AT	239.2	2.4×10^{21}	11	459	11.3
120	HT	239.2	2.4×10^{21}	11	474	8.4
120	CT	239.2	2.4×10^{21}	11	741	11.5
140	AT	354.4	3.5×10^{21}	18	721	10.8
140	HT	354.4	3.5×10^{21}	18	721	10.0
140	CT	354.4	3.5×10^{21}	18	1042	10.8

* Integrated fast neutron exposure, $\text{n/cm}^2 > 1 \text{ MeV}$.

** Exposed in out-of-reactor loop at Battelle-Northwest. The loop operated under nominally the same conditions as the G-7 loop, including conversion to ammoniated pH control after exposures to 249 days.

The significant effect of flux level is evident from weight gains on specimens from Quadrants 116 and 122, exposed at about 3×10^{13} nv. The in-flux rates for these quadrants were above out-of-flux rates, but were substantially below rates at the higher flux levels. The presence of the flux effect requires that flux levels be taken into account when the shapes of the in-flux corrosion curves are evaluated. The weight gain versus time curves can be interpreted to show two transitions: one at about 25 days, the other at about 200 days. However, inspection of flux levels for each quadrant suggests that adjustment of weight gains to a single flux level tends to eliminate the apparent transitions. The relationship of flux and in-flux weight gain becomes clearer when weight gain is plotted against fast fluence (Figure 5).

IN-FLUX WEIGHT GAIN AS A FUNCTION OF FAST FLUENCE*

The relationship between in-flux weight gain and fast fluence (n/cm^2) is shown in Figure 5 for the three lots of Zircaloy-2, exposed in nine quadrants. The points represent mean weight gains for each lot at each exposure.

The relation between weight-gain and fast fluence is linear for the three lots of Zircaloy-2 in pH-10 LiOH. The slope was highest for the CT lot. Slopes were equal for AT and HT lots. The AT/HT line intersected the CT line at about 1×10^{20} n/cm^2 .

The linear relationship established in pH-10 LiOH continued in pH-10 NH_4OH for AT and HT lots. The mean weight-gain for the CT lot fell below the extrapolated line for pH-10 LiOH.

* It is not certain which component of the reactor flux is effective in accelerating the oxidation. There is evidence that β and γ fluxes are not involved.⁽²⁾ Corrosion and mechanical property effects are generally correlated in terms of fast neutron fluxes.^(1,2,7,8)

FIGURE 5. Weight Gain as a Function of Fast Fluence

However, the oxide was thickest on CT specimens. The relatively wide variation in weight gain on CT specimens from Quadrant 140 suggests that the thick oxide has a higher tendency to spall. The Zircaloy-2 tensile specimens oxidized rapidly in pH-10 LiOH, and the high rates continued when the G-7 loop coolant was changed to pH-10 NH_4OH . In contrast, fresh Zircaloy specimens placed in the G-7 loop with the tensile specimens (Quadrant 140) oxidized at rates on an order of magnitude below the in-flux oxidation rates of the transferred specimens.⁽⁶⁾

CHARACTERISTICS OF OXIDES

Figure 6 shows oxide thicknesses on lot CT specimens at four levels of exposure. Cracking of the thick oxides is almost exclusively parallel to the oxide/metal interface. The oxide on a lot HT specimen is shown in Figure 7 at two magnifications. At the higher magnification (1000X) the crack structure is seen to extend very close to the metal/oxide interface. Electron microscopy on thick oxides formed in the G-7 loop indicates a series of horizontal microcracks spaced vertically at about 10 mg/dm^2 .⁽¹⁾

Oxide thicknesses on the tensile specimens are generally uniform, with almost no oxide stringers and no severe localized penetration. However, variations in oxide thickness up to about 35% are sometimes observed on a single specimen (Figure 6c). Oxide thickness measurements were taken around the periphery of a single specimen (140-3) by using a Filar eyepiece. The maximum variation in oxide thickness was 37 percent of the average oxide thickness. However, the average thicknesses along each of the four sides were 0.050, 0.045, 0.047, and 0.048 mm, with a maximum variation of only about 10%. The average of the 20 measurements around the periphery showed a calculated weight gain of $725 \text{ mg}/\text{dm}^2$, compared with a measured weight gain of $750 \text{ mg}/\text{dm}^2$. A factor of $670\text{A} = 1 \text{ mg}/\text{dm}^2$ ($14.9 \text{ mg}/\text{dm}^2 = 1 \mu$) was used to convert oxide thickness to weight gain.

Mount

Oxide

Metal

As-Polished A 250X; Neg. D-6217
 Specimen No. 126-16; Exposure: 58 Days; 5.6×10^{20}
 n/cm^2 , >1 MeV; pH - 10 LiOH; Actual Weight Gain
 148 mg/dm^2 ; Oxide Thickness $0.2 \times 10^{-3} \text{ cm}$; Calculated
 Weight Gain 138 mg/dm^2

As-Polished B 250X; Neg. D-6211
 Specimen No. 119-17, Exposure: 174 Days; 1.3×10^{21}
 n/cm^2 , >1 MeV; pH - 10 LiOH; Actual Weight Gain
 447 mg/dm^2 ; Oxide Thickness $3 \times 10^{-3} \text{ cm}$; Calculated
 Weight Gain 460 mg/dm^2

Mount

Oxide

Metal

As-Polished C 250X; Neg. D-6214
 Specimen No. 120-17, Exposure: 239 Days; 2.4×10^{21}
 n/cm^2 , >1 MeV; pH - 10 LiOH; Actual Weight Gain
 738 mg/dm^2 ; Oxide Thickness $4.1 \times 10^{-3} \text{ cm}$; Calculated
 Weight Gain 616 mg/dm^2

As-Etched D 250X; Neg. D-8180
 Specimen No. 140-15; Exposure: 354 Days; 3.5×10^{21}
 n/cm^2 , >1 MeV; pH - 10 LiOH and pH - 10 NH_4OH ;
 Actual Weight Gain 935 mg/dm^2 ; Oxide Thickness
 $6.3 \times 10^{-3} \text{ cm}$; Calculated Weight Gain 960 mg/dm^2

FIGURE 6. Oxide Thickness as a Function of Fast Neutron Exposure for Lot CT
 Zircaloy-2 Tensile Specimens Exposed in the ETR-G7 Loop at 270-280 °C

Specimen No. 140-3
Zircaloy-2 Lot AT
Weight Gain - 750 mg/dm²
Oxide Thickness - 4.9×10^{-3} cm
Calculated Weight Gain - 730 mg/dm²

FIGURE 7. Oxide on Lot AT Zircaloy-2
at Two Magnifications

The thick oxides are generally adherent to the metal surface. However, metallographic sections of the CT specimens that have thick oxides show areas where the oxide has spalled.*

X-ray diffraction analysis was performed on samples taken from a lot HT tensile specimen exposed in Quadrant 140. Scans were made on three oxide samples from a Quadrant 140 specimen: (1) on an area covered with layers of crud and oxide, (2) on an oxide fragment which had spalled from the specimen, and (3) on the substrate oxide still remaining after spalling. The dual crud/oxide layer scan indicated monoclinic lines and several weak lines which could not be identified. The diffraction pattern from the fragment of oxide which spalled showed only monoclinic oxide lines. The scan on the substrate oxide still remaining after spalling showed monoclinic oxide and several weak lines which could not be identified. A double-diffracting X-ray spectrograph with relatively low sensitivity was used to scan the samples. Therefore the presence of small quantities of the cubic and tetragonal ZrO_2 crystal forms cannot be ruled out. However, a Debye-Scherrer powder pattern on the outer oxide showed only monoclinic ZrO_2 .

HYDROGEN ABSORPTION DURING ACCELERATED OXIDATION

Samples from each of the nine quadrants were analyzed for hydrogen content. Corresponding out-of-flux specimens were also analyzed. The results appear in Table VII. Duplicate analyses on a single sample by two Battelle-Northwest laboratories were averaged in order to obtain the values in Table VII. Comparisons of the individual analyses are given in Appendix B.

* Recent metallographic examination of a fourth lot of Zircaloy-2 tensile specimens shows oxide thicknesses up to 5 mils after a G-7 loop exposure of 894 full power days (8.7×10^{21} n/cm², >1 MeV). The oxide thicknesses are uniform, and there is little evidence of spalling.

TABLE VII. Hydrogen Absorption in Zircaloy-2 Tensile Specimens

Quadrant	Zircaloy-2 Lot	Days at ~280 °C	Fast Fluence n/cm ² , >1 MeV	Hydrogen Absorption*			
				Out-of- Reactor ppm	In-Flux		% of Corrosion Hydrogen
					ppm	mg/dm ²	
116	AT	21	6.9 x 10 ¹⁹	4	7	0.4	21
	HT	21	6.9 x 10 ¹⁹	15	9	0.5	21
	CT	21	6.9 x 10 ¹⁹	0	3	0.2	8
118	AT	21	1.1 x 10 ²⁰	-	10	0.6	14
	HT	21	1.1 x 10 ²⁰	-	21	1.2	30
	CT	21	1.1 x 10 ²⁰	-	7	0.4	12
124	AT	36	1.6 x 10 ²⁰	-	7, 9	0.5	8
	HT	36	1.6 x 10 ²⁰	-	15, 16	1.0	16
	CT	36	1.6 x 10 ²⁰	-	10, 15	0.8	10
126	AT	58	5.6 x 10 ²⁰	3	27	1.6	10
	HT	58	5.6 x 10 ²⁰	3	43	2.6	19
	CT	58	5.6 x 10 ²⁰	2	11	0.7	4
141	AT	117	9.5 x 10 ²⁰	4	46	2.8	10
	HT	117	9.5 x 10 ²⁰	5	74	4.5	17
	CT	117	9.5 x 10 ²⁰	4	23	1.4	4
122	AT	153	3.5 x 10 ²⁰	2	7	0.4	5
	HT	153	3.5 x 10 ²⁰	9	10	0.6	8
	CT	153	3.5 x 10 ²⁰	7	44	2.7	24
119	AT	174	1.3 x 10 ²¹	4	29, 44, 58	2.7	7
	HT	174	1.3 x 10 ²¹	10	59, 74, 120	5.1	16
	CT	174	1.3 x 10 ²¹	4	10, 20, 32	1.3	2
120	AT	239	2.4 x 10 ²¹	4	58, 91, 110	5.2	9
	HT	239	2.4 x 10 ²¹	10	178, 188, 200	11.5	19
	CT	239	2.4 x 10 ²¹	6	27, 32, 45	2.1	2
140	AT	354	3.5 x 10 ²¹	5	175, 183	10.9	12
	HT	354	3.5 x 10 ²¹	5	349, 476	25.1	28
	CT	354	3.5 x 10 ²¹	1	121, 127	7.6	6

* Reported separately for individual samples under ppm; reported as mean values under mg/dm² and % of corrosion hydrogen.

In Figures 8a, 8b, and 8c, the values are plotted in terms of ppm as a function of fast neutron exposure for each of the three lots of Zircaloy-2. Each point on the graphs represents analyses from an individual specimen. Maximum, minimum and mean values are indicated where appropriate. The point of change from lithiated to ammoniated pH control is also indicated on each graph. Out-of-reactor hydrogen absorption values appear below the corresponding in-reactor values for samples having equal exposures at temperature. The relative hydrogen absorption and oxidation characteristics vary markedly for the three lots of Zircaloy-2. The lot having the highest oxidation rate (CT) has the lowest hydrogen absorption rate. Lot HT, having oxidation rates equal to lot AT, has a higher rate of hydrogen absorption.

When plotted as a function of fast fluence, the hydrogen absorption increases linearly with increasing fast neutron exposure in the lithiated coolant. Hydrogen absorption in specimens transferred to pH-10 NH_4OH fell above extrapolations of hydrogen absorption trends established in pH-10 LiOH , suggesting that the combination of thick oxides, flux and hydrogenated coolant increased the rate of hydrogen absorption. Out-of-reactor hydrogen absorption in terms of ppm was low throughout the exposures. Plotting hydrogen absorption as a function of oxygen weight-gain (Figure 9) again shows that the hydrogen absorption was higher for the specimens transferred to the ammoniated environment.

The percentage of the corrosion hydrogen absorbed by the in-flux tensile specimens ranged from 2.3 to 27.8% (Table VII). In the early exposures the relationship between Zircaloy-2 lot and percentage pickup was uncertain. However, at the longer exposures the percentage pickups were consistently highest for lot HT and lowest for lot CT.

FIGURE 8. In-Flux and Out-of-Reactor Hydrogen Absorption in Three Lots of Zircaloy-2 Tensile Specimens. Exposure: ETR G-7 Loop; Temperature, 270 - 280 °C; Coolants - pH-10 LiOH and pH-10 NH_4OH .

FIGURE 8. In-Flux and Out-of-Reactor Hydrogen Absorption in Three Lots of Zircaloy-2 Tensile Specimens. Exposure: ETR G-7 Loop; Temperature, 270 - 280 °C; Coolants - pH-10 LiOH and pH-10 NH_4OH .

FIGURE 9. In-Flux Hydrogen Weight Gain as a Function of In-Flux Oxygen Weight Gain

Percentage pickups on corresponding out-of-reactor specimens were greater than 50%, and in some cases exceeded 100%. The accelerated oxidation contributed to accelerated hydriding, but the percentages of the corrosion hydrogen absorbed were below the values reported for Zircaloy-2 in out-of-reactor autoclaves.⁽¹¹⁾

In Figure 10, microstructures for the three lots of Zircaloy-2 are shown at the highest exposure (Quadrant 140). Microstructures of the as-fabricated NPR Zircaloy-2 are presented elsewhere.⁽⁸⁾ The three lots of Zircaloy-2 contain second phase precipitates distributed as stringers primarily in the grain boundaries, greatly complicating the identification of hydrides in the irradiated structures. In Figure 10, hydrides and stringers occur primarily in the grain boundaries, but visual separation of the two phases is difficult.

OXIDATION CHARACTERISTICS IN 400 °C STEAM

The Zircaloy-2 tube designated CT-19 was extruded at about 845 °C, which is close to the $\alpha + \beta$ region of the phase diagram. Work by Kass⁽¹¹⁾ indicated that Zircaloy-2 which is annealed at about 840 °C has relatively high oxidation rates if slow cooled, and that hydrogen pickup rates for the material annealed near the $\alpha + \beta$ region are low compared to α -annealed Zircaloy-2. Our lot CT in-flux specimens exhibited the high oxidation rates and low hydrogen pickup typical of Zircaloy-2 that has been heat-treated in the $\alpha + \beta$ region.

An out-of-reactor autoclave test at 400 °C in 1500 psi steam was undertaken on the three Zircaloy-2 lots to see whether the relative oxidation characteristics were the same as those observed during in-flux oxidation. It was expected that if the relatively high in-flux oxidation of lot CT involved $\alpha + \beta$ characteristics, the 400 °C test should show similar relative behavior for the three lots. Also included in the 400 °C test

FIGURE 10. Comparison of Microstructures for Three Lots of Zircaloy-2. Exposure: ETR G-7 Loop, Quadrant 140, 354 Days, 3.5×10^{21} n/cm², >1 MeV. Transverse Sections. Etchant: a) 45 Parts HNO₃, 45 Parts H₂O, 8 Parts HF 20 Sec; b) 45 Parts HNO₃, 45 Parts H₂O₂, 8 Parts HF 20 Sec

was HT Zircaloy-2 that had been annealed and cold rolled to 85% reduction in thickness. Weight gains of the 400 °C steam exposures appear in Figure 11. The width of the scatter band for five specimens of each alloy is indicated for the terminal exposures. The lot CT specimens clearly show the lowest out-of-flux oxidation rate, and this tends to rule out $\alpha + \beta$ heat treatment as the explanation for the observed in-reactor behavior. However, after the first transition, the oxidation rates on the tensile specimens were higher than those normally observed for Zircaloy-2.⁽¹⁰⁾

It seems highly significant that the rolled plate from lot HT oxidized at much lower rates than the parent material. Comparison of the microstructures (Figure 12) shows that the rolled plate has a much more uniform distribution of smaller second-phase particles than that of the parent material. The anneal and rolling operation apparently caused the second-phase particles to rupture, redistributing them into a structure that was more favorable from the standpoint of oxidation resistance.

Hydrogen absorption at 400 °C for the three Zircaloy-2 lots and the rolled plate from lot HT is summarized in Table VIII. Hydrogen pickup at 400 °C was low for all three Zircaloy-2 lots.

TABLE VIII. Hydrogen Absorption in NPR Zircaloy-2 Tensile Specimens at 400 °C in Steam Out-of-Reactor*

<u>Zircaloy-2 Lot</u>	<u>Hydrogen Absorption</u>		
	<u>ppm</u>	<u>mg/dm²</u>	<u>% of Theoretical</u>
AT	5	0.3	6
HT	0	0	0
CT	3	0.2	4
HT (Rolled Plate)	8	0.3	7

* Exposed 42 days at 390-400 °C in steam at 1500 psi.

FIGURE 11. *Weight Gains on NPR Zircaloy-2 Tensile Specimens in Steam at 400 °C, 1500 psi, Out-of-Reactor*

FIGURE 12. Comparison of Metallographic Microstructures for NPR Zircaloy-2 Lot HT As-Fabricated (A), Annealed 760 °C - 8 hr, and Cold Rolled, 85% (B)

DISCUSSION

The principal observations from the series of in-flux tensile specimen exposures indicate:

- Consistent and pronounced flux-enhanced oxidation, but with a severity that varies with the Zircaloy-2 lot
- Increased oxidation as flux level increases
- A linear relationship between weight gain and fast fluence
- An apparent "memory" effect for specimens transferred from pH-10 LiOH to pH-10 NH_4OH
- Hydrogen absorption increasing linearly with fast fluence in pH-10 LiOH
- Relatively low fractional hydrogen pickups in pH-10 LiOH
- An apparent increase in hydrogen pickup in specimens transferred from LiOH to NH_4OH
- Different orders of susceptibility to oxidation in-flux and in 400 °C steam for the three lots of Zircaloy-2.

The G-7 loop results reported here are in general agreement with results reported by Burns.⁽¹⁾ But the data reported here include longer exposures, the change in G-7 loop pH control from LiOH to NH_4OH , and comparisons of the in-flux behavior of three lots of Zircaloy-2 at nine levels of exposure.

In comparison with the in-flux zirconium alloy oxidation data from other sites, the rates in the G-7 loop in pH-10 LiOH, ~1 ppm oxygen are among the highest reported. The oxidation rates occurring on the tensile specimens are higher than rates generally encountered in nuclear reactors, which normally operate at a lower dissolved oxygen level. However, since accelerated in-flux oxidation is often observed,⁽¹⁻⁶⁾ the modes of accelerated attack and the conditions which promote it need to be defined.

EFFECT OF ENVIRONMENT ON FLUX-INDUCED OXIDATION

In the G-7 loop pH-10 LiOH system with ~ 1 ppm oxygen, accelerated oxidation has consistently been observed.^(1,6,8) In addition to tests in pH-10 LiOH, ~ 1 ppm O_2 , Burns conducted a test in pH-10 LiOH with a hydrogen overpressure to suppress the oxygen.⁽¹⁾ The test indicated lower oxidation rates than those encountered at higher oxygen levels. Recent G-7 loop experience in pH-10 NH_4OH , <0.05 ppm oxygen indicates that flux-enhanced oxidation is essentially absent on zirconium alloys exposed in the etched condition, but that accelerated oxidation will occur on certain alloys in the prefilmed condition. The results are reported elsewhere,⁽⁶⁾ but are mentioned here since they are highly pertinent to the interpretation of results in the more aggressive system. The recent G-7 loop results in pH-10 NH_4OH , <0.05 ppm O_2 strongly suggest that radiation does not act alone to increase the oxidation rate. Rather, the accelerated oxidation appears to involve a synergistic interaction between flux and some other components in the system.

The first component to suspect is the pH-control cation, since replacement of lithium by ammonia in the G-7 loop coolant generally lowers the flux-induced oxidation rate.⁽⁶⁾ However, high exposures in the Shippingport reactor in pH-10 LiOH did not result in significant accelerated oxidation.⁽⁷⁾ Furthermore, accelerated oxidation without lithium present has occurred at other sites^(2,3,4) and on prefilmed samples in the ammoniated G-7 loop system.⁽⁶⁾ Lithium therefore does not appear to be strongly involved in the flux-induced oxidation mechanism.

Zircaloy oxidation rates in the G-7 loop correlate qualitatively with the dissolved oxygen level in the coolant. However, it is not clear how oxygen enters into the mechanism.

The low-oxygen environment does not necessarily preclude high oxidation rates; this was demonstrated by the quadrant transferred from LiOH to NH_4OH , in that the oxidation rates continued to be characteristic of rates in the lithiated coolant. The observation bears some resemblance to the "memory" phenomenon observed by Thomas and Kass,⁽¹²⁾ viz., that oxidizing specimens transferred from a high temperature to a lower temperature continue to oxidize at rates characteristic of the higher temperature for some time after the transfer. The sustained oxidation on the Quadrant 140 specimens after transfer appears to involve a type of chemical "memory" effect. G-7 loop experiments are underway to see whether the thick film already on the specimens at transfer was involved in the continuing high oxidation rate.

A major controversy in explanations of flux-induced Zircaloy oxidation concerns the role of fissionable contamination. While fissionable materials are not exposed directly in the G-7 loop, fuel element failures from the companion M-3 loop contribute to fissionable contamination in the G-7 system. Evaluation of G-7 loop oxidation results must include consideration of possible effects of uranium contamination and loop decontaminations. Table V summarizes the history of M-3 fuel elements failures and loop decontaminations which have a possible bearing on the nine quadrants of tensile specimens.

Certain problems arise in attempts to explain G-7 loop corrosion results on the basis of fission fragment damage to the oxide. In the first place, the linear weight gain versus integrated flux relationship in pH-10 LiOH (Figure 5) proceeded independently of fuel failures and loop decontaminations.

Secondly, the range of fission fragments in ZrO_2 (about 10 μ) is much less than the thickest oxides (about 70 μ) generated in the lithiated system. The fact that the weight gain/integrated

flux relationship remains linear for the entire exposure (Figure 5) appears to argue against a mechanism that involves fission fragment damage to a rate-controlling oxide at the metal-oxide interface. However, it can be argued that the fission fragments generate rate-controlling species at or near the coolant/oxide interface. It can also be argued that hydrogen may suppress these species, accounting for the drop in rate in the ammoniated system. Preferential adsorption of fissionable contamination to explain prefilm alloy effects seems a somewhat remote possibility. Although fission damage arguments are not compelling, they cannot be ruled out as an explanation for G-7 loop in-flux oxidation. However, the decrease in flux-enhanced oxidation⁽⁶⁾ upon conversion of the loop to ammoniated pH control is substantial evidence that the high rates are related to water chemistry.

FLUX-INDUCED OXIDATION AS A FUNCTION OF TIME AND FLUX

The series of test quadrants examined provides some insight into flux-time interactions. Quadrant 116, which was exposed for 21 days at 3×10^{13} n/cm² sec, had lower weight gains than Quadrant 118, which was exposed for 21 days at 5.5×10^{13} n/cm² sec. Weight gains from Quadrant 122, irradiated at 3×10^{13} nv, fell substantially below the curve for irradiations at 8 to 10×10^{13} n/cm² sec. Previous G-7 loop results suggest that a flux "saturation" effect on oxidation might occur at $\sim 1 \times 10^{13}$ n/cm² sec.⁽¹⁾ However, with the benefit of longer exposures it is apparent that in-flux oxidation continues to increase with flux in the range 3×10^{13} to 1×10^{14} n/cm² sec. This observation indicates that curves of in-flux weight gain versus time must be interpreted with some caution unless it is certain that the exposures were at equal neutron fluxes. Thus, while the weight gain versus time curves (Figure 4) show evidence of transitions, this interpretation must be tempered by the fact that the irradiations were not at equal fluxes.

A more straightforward relationship appears to exist between in-flux weight gain and fast fluence (n/cm^2). Irradiations performed at fast flux levels from 3×10^{13} to 1×10^{14} $\text{n/cm}^2 \text{ sec}$ correlate with a linear weight gain/fast fluence relationship for any given lot of Zircaloy-2. Expressed in terms of fast fluence, the data from Quadrant 122 fall into line with the data from exposures at higher flux levels. An apparent conclusion from the linear weight gain/fluence relationship is that long exposures at low fluxes are equivalent to short exposures at high fluxes. There are not enough exposures at low fluxes to say whether or not a threshold flux exists below which a flux has no effect. However, the linear relationship passing through the point of origin seems to suggest that under the conditions of these exposures, any flux causes a proportional increase in oxidation. The threshold flux may therefore be a practical matter, dependent on the fact that low fluxes rarely generate integrated exposures causing perceptible accelerated oxidation.

Little is known about flux/temperature interactions in loop systems. It is therefore not clear which of the following relationships is valid:

$$\Delta W_{\phi} = f(\phi) + f(T) \quad (1)$$

$$\text{or } \Delta W_{\phi} = f(\phi, T) \quad (2)$$

where ΔW_{ϕ} is the flux-induced oxidation and ϕ and T are flux and temperature, respectively. Equation 1 expresses independent contributions of flux and temperature to the weight gain. Equation 2 expresses the case in which flux and temperature interact to affect the weight gain.

Taking the view that at G-7 loop temperatures the in-flux weight gain is affected independently by flux and temperature, the total weight gain, ΔW_t , for the tensile specimens is given by:

$$\Delta W_t = \Delta W_{pf} + \Delta W_{th} + \Delta W_{\phi} \quad (3)$$

where ΔW_{pf} is the prefilm weight gain and ΔW_{th} represents thermal oxidation.

Empirically, from Figure 5, the in-flux oxidation is represented by

$$\Delta W_{\phi} + \Delta W_{th} \approx \Delta W_{\phi} = k\phi t \quad (4)$$

where ϕ is effective flux, t is time, and k is a proportionality constant.

Prefilm weight gains were 11 to 12 mg/dm² (not included in the weight gains plotted in Figure 5) and ΔW_{th} was only 2.2 to 15.6 mg/dm², amounting to a small adjustment in the slope of the weight gain/fluence line. The value of k is constant for lot CT, but changes for AT and HT lots at about 1×10^{20} n/cm² sec, >1 MeV.

For Zircaloy-2 lot CT, the value of k is equivalent to one mg/dm² of oxide generation per 3.3×10^{20} neutrons/dm². This corresponds to the generation of one effective oxygen atom for each 10 fast neutrons contacting the oxide. In the case of AT and HT lots, about 13 fast neutrons pass through the system for each oxygen atom generated. While it is not clear what these neutron efficiencies mean in terms of a mechanism, some insight into the mechanism might be gained by comparing these efficiencies to efficiencies for other radiolytic processes, e.g., catalytic site generation or generation of a particular chemical species.

OXIDATION AND HYDRIDING AS A FUNCTION OF ZIRCALOY-2 LOT

The differences in susceptibility to flux-induced oxidation and hydriding among the three Zircaloy-2 lots is not related to alloy composition or impurity level in any obvious way (Table II). Comparing differences in tube fabrication (Table I), cold work level is lower for lot CT than for the AT and HT lots. However, in pH-10 LiOH, cold work effects on

oxidation rate have been minor.^(1,6) Extrusion temperature must be suspected, since the CT lot was extruded near the $\alpha + \beta$ temperature. Burns showed that heat treatment effects were additive to radiation effects.⁽¹⁾ Furthermore, in-reactor oxidation and hydriding characteristics of the CT material were similar to characteristics observed in out-of-reactor tests⁽¹¹⁾ on Zircaloy heat treated near the extrusion temperature for the lot CT Zircaloy-2.

Two observations argue against heat treatment as the explanation for the differences in behavior of the three lots. First, metallographic examination of the CT lot does not reveal evidence of a transformed structure. Secondly, out-of-reactor tests in steam at 390 - 400 °C did not confirm heat treatment as the explanation for the observed differences in the oxidation characteristics of the three alloys.

Microstructure (Figure 12) appeared to influence the oxidation characteristics of lot HT material at 400 °C. The as-fabricated HT specimens oxidized more rapidly than the HT material which was annealed and cold rolled. The second phase was distributed as stringers in the as-fabricated material, but occurred as smaller, uniformly distributed precipitates in the annealed and rolled material. The correlation between oxidation rate and second phase distribution is similar to the results reported elsewhere.⁽¹³⁾

Second phase stringer density was highest for lot HT.⁽⁸⁾ The second phase therefore may have contributed to the increased hydrogen absorption by HT specimens, but apparently does not explain oxidation behavior, since AT and HT lots with similar oxidation characteristics differed considerably in second phase distribution.

In summary, the available elemental compositions for the three Zircaloy-2 lots do not show differences which correlate

with corrosion and hydriding behavior. The high extrusion temperature of the lot CT tube offers a major clue, since lot CT in-flux corrosion and hydriding characteristics correlate with expected behavior.⁽¹¹⁾ However, results of 400 °C out-of-reactor tests render the extrusion temperature hypothesis inconclusive. Cold-work levels do not offer satisfactory correlations with corrosion and hydriding behavior. The fact that HT corrosion characteristics at 400 °C were altered markedly by heat treatment and cold work suggests that the differences in oxidation behavior are more likely due to fabrication than to composition.

IMPLICATIONS OF ACCELERATED OXIDATION TO ZIRCALOY PERFORMANCE IN-REACTOR

While the oxidation rates encountered in this study are higher than the rates generally occurring on zirconium alloy reactor components, it is appropriate to consider briefly some of the consequences of these rates.

Oxide Buildup and Metal Penetration

The highest rate of oxide growth was 1040 mg/dm² per year (lot CT). This corresponds to $\sim 7 \times 10^{-3}$ cm (2.8 mils) of oxide, equivalent to $\sim 5 \times 10^{-3}$ cm/yr (~ 2 mil/yr) of metal penetration. At this rate, on a cladding wall of 7.5×10^{-2} cm (30 mils), $\sim 7\%$ of the metal thickness would be converted to oxide per year. On a tube wall of ~ 0.6 cm (1/4 in.), the tube wall thickness would be reduced by $\sim 15\%$ in a 20-year exposure.

The significance of these metal loss rates in an actual system must be considered in terms of the operating conditions of the given system.

Oxide spallation is another problem arising from the buildup of thick oxides. Oxides up to ~ 700 mg/dm² were quite tenacious,

but thicker oxides ($\sim 1000 \text{ mg/dm}^2$) on lot CT specimens showed some tendency to spall.*

Oxide Buildup and Heat Transfer

Oxide buildup of the magnitude observed in these tests will contribute to temperature increases at the metal/oxide interface of a heat transfer surface.

Taking the case of a $1,000 \text{ mg/dm}^2$ oxide on a fuel-element cladding transferring $1 \times 10^6 \text{ Btu/hr ft}^2$, the calculated** temperature rise across the oxide is $\sim 160^\circ\text{C}$. On a Zircaloy-clad fuel element normally operating at 280°C in a water loop, a temperature rise of this magnitude clearly cannot be tolerated.

On the other hand, at heat fluxes generated in the tensile specimens by gamma heating ($\sim 15 \text{ watts/g}$) the calculated temperature rise across a $1,000 \text{ mg/dm}^2$ oxide is only $\sim 5^\circ\text{C}$.

Temperature increases across crud layers have been calculated.⁽¹⁵⁾ At crud layer thicknesses and heat fluxes similar to those found on the tensile specimens, the calculated temperature rise was $\sim 4^\circ\text{C}$.

Hydrogen Absorption

Considering the worst case, hydrogen pickups up to ~ 500 ppm were observed on a specimen from lot HT exposed in the lithiated and ammoniated environments for approximately one year, reaching a fast fluence of $3.6 \times 10^{21} \text{ n/cm}^2$. Had the exposure continued for one year in pH-10 LiOH, ~ 1 ppm oxygen, the predicted hydrogen pickup would be ~ 300 ppm. Canadian investigators report that fuel cladding containing up to 400 ppm hydrogen successfully reached 10,000 MWd/ton burnup.⁽¹⁶⁾ Therefore, even the highest hydrogen pickups occurring in pH-10 LiOH during the

* See the footnote on page 20.

** The thermal conductivity of the oxide was taken as $0.8 \text{ Btu/hr ft}^2 \text{ }^\circ\text{F/ft}$.⁽¹⁴⁾

accelerated oxidation would not have reached critical values in terms of effects on fuel cladding. In pressure tubes with a wall thickness of 0.6 cm (0.25 in.) and an inside diameter of 7.6 cm (3 in.) the annual hydrogen pickup will be 70 ppm, based on a value of 500 ppm absorbed by the tensile specimens. The terminal concentration for a 20-year tube life would then be 1400 ppm.

Hydrogen pickup increased linearly with exposure, in agreement with results of other G-7 loop tests.⁽¹⁷⁾

FUTURE WORK

Specimens of the three lots of Zircaloy-2 tensile specimens have been charged into the ammoniated G-7 loop environment without prior exposure in the aggressive high-oxygen pH-10 LiOH system. The tensile specimens are exposed in pH-10 NH_4OH in the following conditions:

As-fabricated

As-etched

Prefilmed

400 °C steam to 190 - 250 mg/dm²

400 °C steam to 20 mg/dm²

300 °C water to 11 - 12 mg/dm²

Annealed

α -annealed

β -quenched

The ammoniated exposure of the specimens prefilmed at 300 °C will provide a comparison of G-7 loop environmental effects, since all NPR tensile specimens previously exposed were in that prefilm condition.

The specimens with thick oxides were exposed to investigate whether the oxide contributes to accelerated oxidation and

hydriding in the low-oxygen environment. The result will be pertinent to the interpretation of the accelerated oxidation on specimens transferred from the lithiated to the ammoniated G-7 loop environment.

Some as-fabricated specimens were heat treated to "erase" the effects of the extrusion conditions.

The tests also will help to clarify the role of prefilm and heat treatment conditions on flux-induced oxidation.

Other G-7 loop tests, conducted under a cooperative USAEC/AECL* program, are designed to investigate effects of alloying agents on flux-induced oxidation.

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* AECL: Atomic Energy of Canada, Ltd.

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APPENDIX A

APPENDIX A

EFFECT OF POSTIRRADIATION CLEANING PROCEDURES
ON SPECIMEN WEIGHT CHANGES.

Quadrant 140

Exposure: ETR G-7 loop

354 days - 249 days - pH-10 LiOH

105 days - pH-10 NH₄OHFlux: 1 x 10¹⁴ nv; 3.53 x 10²¹ nvt

Temperature: 270 - 280 °C

Sample Area: 0.1227 to 0.1210 dm²

TABLE A-1. *Effect of Postirradiation Cleaning Procedures
on Specimen Weight Changes*

	Total In-Flux Weight Gain, mg	Weight Loss in Ultrasonic Cleaning,* mg	Weight Loss in Oven Drying, mg	Weight Loss in 2nd Ultrasonic Cleaning,* mg	Crud Weight mg/dm ²
HT 1	105.1	11.3	0.5		
2	105.5	10.2	0.3		
3	104.8	10.2	0.6	2.6	109
4	99.4	11.3	0.4	6.6	156
5	98.4	11.1	0.4	2.0	107
6	105.4	8.7	0.4	2.3	92
AT 1	112.7	11.5	0.3		
2	109.2	13.3	0.4		
3	100.5	12.8	0.2	1.1	119
4	103.9	10.5	0.4	1.0	116
5	99.8	11.7	0.3	1.7	102
6	102.2	11.7	0.2	1.8	112
CT 1	135.7	8.0	1.1		
2	142.9	9.4	1.8		
3	125.6	9.7	0.8	1.3	97
4	144.9	9.4	1.3	1.9	103
5	147.6	10.8	0.9	1.9	110
6	139.8	8.6	1.3	2.2	100

*Detergent Solution

APPENDIX B

APPENDIX B

COMPARISON OF HYDROGEN ANALYSES
ON IRRADIATED TENSILE SPECIMENS

Selected tensile specimens from the nine quadrants were cut into sections approximately 1/4 in. long. Up to six specimens were cut from a single specimen. Specimens were submitted in duplicate to two laboratories (Radiometallurgy and Physical Analysis) at Battelle-Northwest. Samples from Quadrant 116, 118, 124, and 126 were analyzed only by Physical Analysis. Quadrant 122 was analyzed only by Radiometallurgy. Quadrants 119, 120, 140, and 141 were analyzed by both laboratories. Hydrogen determinations were made by hot vacuum extraction methods in induction-heated equipment maintained at approximately 1200 °C during extractions. Both systems were calibrated periodically with National Bureau of Standards titanium samples of known hydrogen content.

Blank hydrogen contents for the three lots of Zircaloy-2 were:

AT-25 ppm
HT-20 ppm
CT-35 ppm

Results of analyses on individual samples are summarized in the table.

TABLE B-1. Comparison of Hydrogen Analyses on Irradiated Tensile Specimens

Total Hydrogen, ppm												
Quadrant	Zircaloy-2 Lot	Sample No.	Radiometallurgy Analyses					Physical Analysis Analyses			Combined Average ppm	
			Run	#1*	Run	#2*	Ave.	Run	#1	Ave.		
116	AT	2						30	33	32		
	HT	8						29	29	29		
	CT	14						37	38	38		
118	AT	1						34	35	35		
	HT	7						50	32	41		
	CT	13						41	43	42		
124	AT	1						31	33	32		
	AT	2						33	35	34		
	HT	7						33	36	35		
	HT	8						36	36	36		
	CT	13						48	51	50		
	CT	14						44	45	45		
126	AT	2						50	53	52		
	HT	8						61	64	63		
	CT	14						47	44	46		
141	AT	1	66	72	60	71	67	88	61	75	71	
	HT	7	97	113	86	73	92	103	88	96	94	
	CT	13	87	45	53	63	62	56	51	54	58	
119	AT	1	56	52			54					
	AT	2			80	58	69					
	AT	4						77	88	83		
	HT	7	77	80			79					
	HT	8			161	119	140					
	HT	10						88	100	94		
	CT	13	43	46			45					
	CT	14			86	47	67					
120	CT	16						59	50	55		
	AT	1	104	129			116					
	AT	2			148	123	135					
	AT	4						77	88	83		
	HT	7	230	186			208					
	HT	8			194	255	225					
	HT	10						219	176	198		
	CT	13	56	68			62					
140	CT	14			79	54	67					
	CT	16						84	75	80		
	AT	3	216	199			208	202	211	207	208	
	AT	4	238	183			211	186	142	189	200	
	AT	9	528	562			545	475	478	477	496	
	HT	10	343	366			355	393	370	382	369	
	CT	15	149	165			157	154	155	155	156	
	CT	16	171	168			170	154	154	154	162	

* Samples from the same tensile specimen were run on different days.

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