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Corrosion of Zircaloy in Crevices Under Nucleate Boiling Conditions

> W.K. Anderson M.J. McGoff

April 13, 1962

Operated for the United States Atomic Energy Commission by

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CORROSION OF ZIRCALOY IN CREVICES UNDER NUCLEATE BOILING CONDITIONS

W. Kermit Anderson, M. J. McGoff

April 13, 1962

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General Electric Company KNOLLS ATOMIC POWER LABORATORY Schenectady, New York Operated for the United States Atomic Energy Commission Contract No. W-31-109 Eng-52

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ABSTRACT

The MSAR corrosion test loop was used to study the effect of VEE-shaped crevices on the corrosion resistance of Zircaloy under boiling heat-transfer conditions in both ammoniated and lithiated water at pH 10.5. Zircaloy-2 and Zircaloy-4 were compared under identical geometric, thermal, and hydraulic conditions. An effort was made to study the effect of iron oxide crud deposits on crevices of slightly variant geometry.

The tests were run at 586 to 587F (T_{sat} for a pressure of 1390 to 1400 psig). Water velocity was held in the range of 1 to 3 fps. Control was such that the onset of nucleate boiling should, on the average, have taken place at about the middle of the 5-in.-long, thin-walled crevice specimens. Specimens were vertically oriented in an effort to mock up the most common orientation of flow channels in nuclear reactor cores. Heating of specimens was resistive with 60-cycle a-c, at a heat flux of 500,000 Btu/ft²-hr.

The test in ammoniated water was operated successfully for 1000 hr. The test in lithiated water was subject to such drastic corrosion that it had to be terminated at a total exposure of 211 hr.

Two factors tend to obscure the results of this test. First, the previously unsuspected release of alumina into loop water during the ammoniated-water test increased the ionic content of stagnant water in the crevices. Boehmite was deposited in these crevices during boiling. Second, the possible slow thermal dissociation of Teflon seals may have produced minute concentrations of fluorine-containing gases that cause accelerated attack on upstream bus bars.

In spite of these two malfunctions during the experiment, results were quite significant.

Under ammonia pH control, pitting of the Zircaloy specimens and white oxide formation were quite minor. After 1000 hr of testing, the maximum metal penetration found was two mils, observed at the closed edge of a Zircaloy-4 VEE. The maximum penetration depth observed in Zircaloy-2 was one mil.

Under lithium hydroxide pH control, penetrations observed were 5.2 and 5.9 mils for Zircaloy-2 and Zircaloy-4, respectively, during the 211-hr test. Hydrogen pickup in the ammonia chemistry environment was negligible for both Zircaloy-2 and Zircaloy-4. Conversely, in the lithium hydroxide environment, drastic hydrogen embrittlement occurred. Extreme segregation of hydride platelets was demonstrated on all specimens exposed to lithiated water. Very surprising was the fact that 3100 ppm of hydrogen was found in the Zircaloy-4 VEE specimen compared with 1200 ppm for the Zircaloy-2 VEE in this boiling lithium-chemistry environment.

Less corrosion, hydrogenation, pitting, and white oxide formation were observed in both tests on the precrudded, parallel-faced crevice specimens than were seen on either of the comparable noncrudded VEE's. Whether this is attributable to the deposited synthetic crud or to the more open crevice design is not plain from the existing data.

The following conclusions apply in crevice systems under boiling conditions:

Either Zircaloy-2 or Zircaloy-4 will undergo crevice corrosion in closed vertical channels under boiling heat-transfer conditions at temperatures near 587F.

Much more drastic attack occurs in lithiated water than in ammoniated water.

Under either condition, Zircaloy-4 appears less resistant to attack than does Zircaloy-2.

In the presence of lithium hydroxide, extreme hydrogen embrittlement takes place with either Zircaloy. However, Zircaloy-4 is more strongly attacked.

The effect of crud deposition cannot be completely evaluated from this test. The only definite statement justifiable from the relatively ambiguous data is that the presence of crud did not increase the rate of corrosion in either ammoniated or lithiated water.

ACKNOWLEDGMENT

The authors wish to acknowledge contributions to this experiment by several workers at both the Knolls Atomic Power Laboratory and at the Mine Safety Appliance Research Corporation. First to be recognized is the contribution of L. J. Abate in both the design and implementation of the experiment, together with help from D. S. Morris, and his associates, C. H. Beck and A. J. Palmer of KAPL, and Earl King of MSAR. Contributions by the KAPL Chemistry staff, particularly those of F. P. Landis, Vivian Consalvo, and R. W. Merchant, are acknowledged with thanks.

Operation of the loop was ably carried out by Bruce Adams, Robert Bodesheim, James Gallagher, Jesse Magil, Ben Pershing and John Gerken at MSAR. The constant technical support of Earl King of MSAR and William Cashin of KAPL is acknowledged with sincere gratitude.

CORROSION OF ZIRCALOY IN CREVICES UNDER NUCLEATE BOILING CONDITIONS

W. K. Anderson, M. J. McGoff*

INTRODUCTION

In the construction of cores for neutronic reactors, alloys of zirconium are particularly desirable from the standpoint of neutron economy, especially as cladding for fuel elements. Two extensively used alloys of zirconium are Zircaloy-2^{**} and Zircaloy-4.^{**} Compositions of these two alloys are given in Table 1.

It is well known that these two alloys have good corrosion resistance to pressurized water. Extensive testing of these alloys in autoclaves and loops (as well as several years' service in various power reactor cores in the case of Zircaloy-2) has established the adequacy of this resistance to corrosion under normal conditions of pressurized water service.^{1,2}

However, for some time a number of open questions have remained as to the merit of such zirconium-base alloys under nucleate boiling conditions or in boiling reactor service, particularly at higher temperatures and heat fluxes and in long-endurance cores.

In addition, not only for the sake of the Zircaloy, but more particularly for the protection of other structural materials used in the normal power reactor primary system, it has been found desirable to operate such reactors in water whose room temperature pH is maintained well on the basic side.⁹ Agents to maintain this high pH might be any of the alkali hydroxides or ammonia. Although the hydroxides of either potassium or sodium might be used, they have the disadvantage of contributing strongly to the radioactivity of the system. For this principal reason, the field of decision is normally reduced to a choice between LiOH and NH₄OH. To avoid problems arising from radioactivity of the tritium formed in neutron capture by Li⁶, isotopic Li⁷ is normally selected when the reactor operator chooses to use alkali hydroxide rather than ammonia. The question of a choice between Li⁷OH and NH₄OH, therefore, still seems to be open.

^{*}Staff member of the Mine Safety Appliance Research Corporation, Callery, Pennsylvania.

^{**}Trade names for proprietary alloys developed by the Westinghouse Electric Corporation and assigned to the United States Atomic Energy Commission.

TABLE 1. NOMINAL ANALYSIS OF ZIRCONIUM ALLOYS*

Composition	Percent by Weight
Zircaloy-2	Zircaloy-4
1.5	1.5
0.13	0.21
0.1	0.1
0.05	0.007 max
balance	balance
	Composition Zircaloy-2 1.5 0.13 0.1 0.05 balance

*It should be noted that this analysis does not take into account materials such as the gaseous elements (oxygen and nitrogen in particular). Many workers feel that perhaps 2000 ppm of oxygen may be necessary in a properly melted Zircaloy so that the alloy may develop its best mechanical properties; hence, this "impurity" should be included in an analysis as an alloying component.

NOTE: The sum of the iron, chromium, and nickel for each location source within the range is 0.18 to 0.38 for Zircaloy-2 and 0.28 to 0.37 for Zircaloy-4.

Another area of danger from the standpoint of accelerated corrosion on Zircaloy, particularly in the presence of fixed alkalies, has been the presence or deposition of so-called "crud" in areas where high-flux heat transfer occurs. Some workers have proposed that Zircaloy, when maintained at high temperatures and blanketed by crud in high-flux heat transfer applications, is more likely to undergo localized or accelerated corrosive attack if fixed alkali, rather than ammonia, is used to control pH.

Boiling in crevices has always been looked upon with suspicion as a means of concentrating corrosive entities carried in the parts-per-million range in relatively high purity water. It has been felt that such concentration might serve as a means of producing accelerated corrosion in such crevice regions. In nonboiling systems, Zircaloy-4 has been shown to absorb less hydrogen under core operating conditions. However, KAPL proposed to examine the behavior of the two alloys under boiling conditions in crevices with both ammonia and lithium hydroxide pH control.

To contribute at least a partial answer to some of these questions, an experiment was designed in which thin sections of Zircaloy, two per specimen, were used to form specially designed crevices that could be heated electrically in a dynamic loop under nucleate boiling conditions. Two specimen designs, one VEE-shaped in cross section and one with parallel walls, were used. Two of the VEE-type crevice specimens were used, one of Zircaloy-2 and one of Zircaloy-4. In addition, the parallel-walled specimen made of Zircaloy-4 was covered with a layer of deposited magnetite crud before insertion in the loop. Two otherwise identical experiments were run, one with control of pH by ammonia addition, the second with control of pH by LiOH addition. These experiments were performed, therefore, to gain information that might offer at least partial answers to the following questions:

- 1. Do crevices, per se, contribute to the accelerated corrosion of Zircaloy under nucleate boiling conditions?
- 2. In such crevices, operated under nucleate boiling, is there a preference between NH_4OH and LiOH as a pH control agent?
- 3. Is there any preference, under such conditions, between Zircaloy-2 and Zircaloy-4? In particular, is Zircaloy-4 under these conditions superior from the standpoint of its resistance to hydrogen embrittlement?
- 4. Does the presence of a crud layer in crevice situations involving high temperatures, high heat fluxes, and nucleate boiling contribute to acceleration of corrosion reactions?

The experiments described in this report have given at least partial answers to all of these questions. In the case of one of them, namely the selection of a pH agent, it appears to the authors that the answer is clear: only ammonia should be used when boiling occurs. There follow below descriptions of the experiment, the test facility, and the test specimens; a presentation of data and results; and a summary of conclusions, some of which seem inescapable.

GENERAL DESCRIPTION OF THE EXPERIMENT

This experiment, whose purposes have been discussed in the introduction, was carried out in a test loop built and operated for the United States Navy Bureau of Ships by the MSA Research Corporation at Callery, Pennsylvania. This loop, patterned after one designed by Wanklyn and Jones⁴ in England, had been used for several previous experiments, including a series of experiments on stress corrosion of stainless steel. The loop, which has facilities for electrical self-resistance heating of three specimens in parallel-flow channels, operates with forced convection cooling of these specimens at pressures as high as 1500 psig. For a description of this loop, see "Description of the Loop," p. 5.

The specimens used were of two types and are more thoroughly discussed under, "The Test Specimens," p. 13. Both types had crevices that were formed by two mating, flat, dumbbell-shaped Zircaloy ribbons, each 25 mils thick. The first type, designed to study the effects of boiling heat transfer in uncrudded crevices, was so assembled as to produce a VEE-shaped cavity in contact along one edge and four mils apart at the other. Electricity was carried to these specimens by 3/4-in.-diam buses. The second type, designed to study the effects of heat transfer under nucleate boiling on crevices filled with magnetitic crud, was formed by two parallel, 25-mil-thick, dumbbell-shaped specimens whose separation was a nominal four mils. The current-conducting bus design for these crudded specimens was the same as for the VEE-shaped, noncrudded type.

Table 2 describes and numbers all specimens built for both tests. The first test was run under ammonia pH control; the second was controlled by the addition of LiOH. Both tests were run with pH controlled at 10.5 ± 0.1 .

Other significant test conditions were specified as follows:

Bulk water temperature, F	580
System pressure, psig	1400
Water velocity past test specimens, ft/sec	l to 3
Hydrogen content, cm ³ /kg	5 to 15
Oxygen content, ppm	~0.1
Crevice specimen heat flux, Btu/hr-ft ²	0.5 x 10 ⁶
Maximum exposure time, hr	1000

With the preferred operating pressure and heat flux on the specimens, linear velocity and mass flow rate for coolant were so adjusted in the test section that T_{sat} was reached and maintained near the middle of the test section. This fact could be verified instrumentally by means of inlet and outlet high-precision temperature-sensing devices in the test section, in conjunction with a Heise pressure gage and precision flowmetering equipment. Passage into nucleate boiling could be observed by a sharp drop in the reading of a Speedomax indicator that received its signal from a differential couple whose opposing junctions were at the inlet and outlet of the central test section.

Complete descriptions of the loop, test specimens, instrumentation, and method of operation follow.

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Test	Manufacturing			
Descriptive	Serial		pH Agent	
Number	Number	Material	<u>in Test</u>	Type of Crevice
BMD-8A1	2	Zircaloy-2	NH ₄ OH	VEE-shaped crevice specimen.
BMD-8A2	5	Zircaloy-4	NH₄OH	VEE-shaped crevice specimen.
BMD-8A3	3	Zircaloy-4	NH₄OH	Parallel-walled crevice crudded with NH ₄ OH as Fe ⁺⁺ precipitant.
BMD-8B1	14	Zircaloy-2	LiOH	VEE-shaped crevice specimen.
BMD-8B2	15	Zircaloy-4	LIOH	VEE-shaped crevice specimen.
BMD-883	13	Zircaloy-4	LiOH	Parallel-walled crevice crudded with LiOH as Fe ⁺⁺ precipitant.

TABLE 2. LIST OF TEST SPECIMENS

DESCRIPTION OF THE LOOP*

The flow diagram of the loop is shown in Figure 1. The loop was situated in a strong-walled concrete pit below ground-level of the surrounding structure. A 1/2-in.-thick steel wall and door separated the loop proper from the adjoining control room, giving protection to operating personnel. The weak wall of this enclosure consisted of a double, corrugated iron blowout door, oriented away from the loop control room and located in the outer rear wall of the building. Such a design was felt to give completely adequate safety when coupled with sensible operating practices.

Hydraulic Components of the System

The loop, constructed of 1-in.,Sch-80 stainless steel piping, was designed for water at 600F and 1500 psig. A 30-A canned rotor pump was used to circulate the water through the loop. A globe valve upstream of the pump was manually controlled to throttle water flow. Water flow rate was metered by orifice plates. The system was heated by nine 4.167-kw,

Written by M. J. McGoff.



KAPL-2203

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230-volt electrical immersion heaters enclosed in a section of 6-in., Sch-160 stainless steel pipe. Three of the heaters were wired to a variable transformer that was regulated by a temperature controller and thermocouple situated at the outlet of the heater section. Water flowed from the heater through parallel paths to the three test sections.

Piping returning to the pump from the test sections was not insulated, to provide cooling of the circulating water. A flanged section of 2-in. pipe was located upstream of the pump to accommodate a coupon control specimen train. A strainer upstream of the pump removed any particles and prevented them from entering the pump suction. A pressurizer, constructed of 8-in., Sch-160 stainless steel pipe with a flanged heater element, was located out of stream and maintained loop pressure during the run.

Continuous water purification was maintained by a demineralizer in a bypass leg of the loop. Water flow to the demineralizer was cooled before it entered the resin bed. An economizer raised the water temperature before it rejoined the main loop stream. Loop water, cooled to room temperature, was removed at this leg through stainless steel tubing and a valve in the control room. A sampling bomb, also in the cold leg for adding hydrogen to the loop water, was removable for measurement of dissolved hydrogen gas.

The pH control agents were placed into the loop via a chemical feed pump. Makeup water to the loop was supplied by a separate feed-water pump connected to a high-purity water supply. Water for the loop was prepared by distillation and is stored in a heated stainless steel drum to remove dissolved oxygen. Before passing through an HOH effluent resin bed on its way to the feed-water pump, the water was cooled through a heat exchanger. This water supply for the loop had a conductivity below l umbo/cm.

Test Section for Creviced Specimens

Figure 2 is a sketch of the test section that housed the specimens. The test section consisted of flanged sections of 2-in., Sch-160 stainless steel pipe with a 1-in.-pipe inlet at the bottom and outlet at the top. The test sections were vertically positioned in the loop.

The test sections were designed for conducting a previous experiment in which creviced stainless steel specimens were to be stressed. The stressing was accomplished by fixing the specimen bus bar at the top of the test section by a Swagelok nut and permitting free movement of the specimen bus bar through a Teflon-bodied rubber 0-ring seal at the bottom of the test section. To prevent the seal from overheating, a water-cooled copper tubing coil was fixed to the pipe area housing the seal (see Figure 3). In this test, stress on the Zircaloy specimen would be excessive;

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FIGURE 3. Copper Tubing Cooling Coil on Bottom of Test Chamber. Cold water is circulated through this coil to keep the Teflon insulating seal cooled. KS-46236 Unclassified

therefore, a second seal was arranged to counterbalance the force on the specimen. The bus bars on the specimens were designed to limit the stress on specimens to 8000 psi at the operating pressure of 1400 psig. The lower seal was aligned with the test-section seal by mating plates and 3/8-in. all-thread bolts and nuts. The lower seal assembly served a second purpose, i.e., as a stop to prevent ejection of the specimen into the loop area should specimen failure result. The lower seal was out of stream but subjected to pressure through a tubing connection to the loop piping.

The test sections were insulated with rock wool and asbestos tape to lower heat losses. Adjoining piping at the inlet and outlet of each test

section was instrumented with thermocouple wells to measure bulk water temperature of the water coolant. A flow spacer centrally positioned inside the test section surrounded the crevice specimen and was sized for obtaining a flow velocity of 1 to 3 fps.

The Electrical Heating System and Specimen Power Source

The water flow passing through the test sections was preheated by an electrical heater. The heater was constructed of a 5-ft-long section of 6-in., Sch-160 stainless steel pipe with 2-in.-thick flat heads at each end. The shell has a water inlet and outlet of 1-in. pipe, diametrically opposite at each end. Each head contained six 4.167-kw, 230-volt electrical immersion heaters; however, only nine of the 12 available heaters were used. Three of the heaters at the outlet end were wired in a Y circuit to a motor-operated Variac. The motor was regulated by a proportional temperature controller. A thermocouple at the outlet of the heater was the sensing element for the controller. Six of the heaters were directly wired to manual switches.

The Zircaloy specimens were heated by electrical resistance heating. Power to the system was 230-volt, 3-phase, 60-cycle, a-c current. The electrical current was routed through a voltage stabilizer and a sixhigh, manually operated Powerstat to individual current transformers. The current transformers, which energize the bus bars connected to the specimens, were wired in a delta circuit. The bus bars to the specimens were wired in a Y circuit to the secondary of the current transformers. Separate ammeters and voltmeters were instrumented to each specimen for calculation of power dissipated, heat flux, and electrical resistance of each crevice specimen.

Instrumentation and Control System

The loop piping was instrumented with Type K-MA thermocouples. The thermocouples measure bulk water temperature at the inlet and outlet of each test section, heater outlet temperature, and temperatures through the bypass leg of the loop. The pipe wall surrounding the O-ring seal of the test section was equipped with thermocouples to ensure that the seals were adequately cooled. The thermocouples were recorded continuously on a temperature recorder and were read by a potentiometer with an ice-bath junction. Other thermocouples were instrumented to controllers and limit switches to maintain desired operating conditions for the 30-A canned rotor pump, for the water passing through the demineralizer, and for the water supply tank.

A calibrated Heise gage was used for pressure readings. A pressure transmitter and controller regulated the heaters in the pressurizer to obtain the set operating pressure. The pressurizer was equipped with a liquid-level indicator (ratiograph) operated from a dp cell that actuated a feed-water pump and maintained an adequate water level. In conjunction with this control, high and low liquid-level limit switches were provided to shut off the heaters in the pressurizer. A Mercoid switch located on the pressurizer piping was set to interrupt power to all electrical heaters, including the specimen current transformers, if excessive pressure rises occurred.

Flow through each test section was metered by an orifice, with pressure differential sensed by a dp cell (Figure 4). The air-pressure output of the dp cell was instrumented with Mercoid switches to sound an alarm under low-flow conditions in the test sections and subsequently shut off power to the specimens to avoid burnout. Total loop flow was measured by an orifice and a high-pressure mercury manometer. The bypass leg of the loop was also equipped with a low-flow sensing device. This limit switch was arranged to shut off power to the specimen power transformers, the pressurizer heaters, and the electrical preheater.

At operating conditions, constant power was supplied to the specimens by the voltage stabilizer and Powerstat; therefore, such power was not varied during the run. Instrumentation was used to show operating personnel that nucleate boiling conditions were present and that low-quality steam was being generated. Two thermocouples at inlet and outlet ends of test section 2 (the central test section) were wired together in voltagebucking orientation and connected to a millivolt reading instrument with a range of 1.1 mv (Figure 5).

A thermocouple at the outlet of the electrical preheater was connected to a proportional controller with a scale of 400 to 700F. This instrument is also shown in Figure 4. The set point on the controller was adjusted to raise water temperature entering the test sections so that the reading on the millivolt indicating instrument dropped from that at a subcooled or nonnucleate boiling condition. At subcooled conditions, this reading was of the order of ~0.11 mv. The loop operator set the proportional controller to maintain a 0.05- to 0.07-mv reading. Since danger of specimen burnout would arise when only superheated steam containing no liquidphase water was in contact with a major fraction of the specimen area, some provision had to be made for protection of the specimens in case of low-flow or other conditions that would decrease heat removal by coolant. An approach to zero by the differential temperature across a test chamber would indicate this condition. Therefore, as added specimen burnout protection, the millivolt indicator recorder, taking its signal from the differential couple mentioned in the last paragraph, was equipped with a limit switch that tripped off power to the specimens if readings dropped to 0.04 mv and thus prevented the burnout of the specimens. Additional protection from burnout was provided by a high-temperature limit switch on the proportional controller.



FIGURE 4. Proportional Controllers, Power Metering, and Manometers for dp Cells on Separate Flow Channels to Test Chambers. KS-46237

Unclassified



FIGURE 5. Instrument Used with Differential Couples to Detect Nucleate Boiling. Burnout protection was incorporated in the control function of this SPEEDOMAX instrument. KS-46238 Unclassified

Each test section was instrumented with separate ammeters and voltmeters, shown also in Figure 4. Temperatures were measured by a portable Leeds and Northrup potentiometer with an ice-bath reference junction. Flow rate was metered by an orifice plate with differential pressure taps connected to a high-pressure, mercury-filled manometer. The remainder of the control instrumentation described above is shown in the photograph of Figure 6.

THE TEST SPECIMENS*

The use of electrical heating, of course, requires that one end of the electrically heated specimen be isolated from ground potential by an electrical insulator. The seal design (described above) used Teflon insulation. To minimize seal heating, therefore, it was essential that the heavy conducting bars carrying 600 amp or so of current be of minimum electrical resistance. It was essential that the resistance be minimized, since these bars were in intimate contact with the Teflon and the accompanying rubber 0-rings along the inside surface away from the external cooling coils on the stainless steel walls of the loop reaction chamber. It was expected that even minor resistance heating at this point would soften the Teflon and permit it to creep enough to cause seal failure or shorting of the high-current electrical connection to loop ground.

The original design of test specimens (briefly described under "General Description of the Experiment," p. 3) involved the use of pure nickel conductors, to be connected by eutectic diffusion-bonding techniques to Zircaloy hubs holding the thin Zircaloy test specimens. Several of these specimens were fabricated by techniques described in the following text. A parallel corrosion test of a diffusion-bonded Zircaloy-nickel couple (also briefly discussed below) revealed that serious corrosion problems existed. Therefore, the first design was abandoned in favor of Zircaloy-clad copper buses fabricated by coextrusion. A brief description of the two designs, a description of the fabrication techniques developed, and a presentation of results of corrosion tests are included in this section. Details of the methods used to deposit crud on the parallelfaced specimens are also included.

The Original Diffusion-Bonded Design

Figure 7 is a sketch of the original design of test specimens proposed for use. Notice that the Zircaloy hubs carrying the dumbbell-shaped, thinwalled crevice test specimens were threaded into the nickel bus with a very close-fitting Acme thread. This design was selected for two reasons: (1) to minimize play in the joint between the Zircaloy and nickel sections, and (2) to ensure maximum surface contact along the threaded area, to optimize

^{*}Written by W. K. Anderson.

conditions for a eutectic diffusion bond. A brief description of the fabrication methods for these specimens follows.

Fabrication of Diffusion-Bonded Specimens*

<u>Materials Selection</u>. Materials used for fabrication of these specimens built to the original design were carefully selected. The nickel was a commercially pure material in the form of a 3/4-in.-diam rod obtained from the International Nickel Company. Both the Zircaloy-2 and Zircaloy-4 used were from reactor-grade stock found acceptable by the normal tests required by specification MIL-Z-19859.

Outline of Fabrication Process. In all cases, specimens built to the original design were carried through a standardized fabrication procedure essentially as follows.

The parts for each specimen were machined to tolerances specified in shop drawings, then cleaned, and in the case of Zircaloy parts, pickled and thoroughly rinsed. The nickel bus bars were screwed into the Zircaloy holders and diffusion-bonded for 6 to 10 min at 1850 to 1875F. The dumbbell-shaped ribbons were properly shimmed when placed in the holders. The assembly was jigged and placed in a welding box, which was evacuated to 5×10^{-5} mm Hg pressure. The chamber was then back-filled with welding-grade argon. By use of inert-gas tungsten-arc techniques, the creviced ribbon parts were welded to the Zircaloy holders. After the specimens had been removed from the box, oxide formed during welding was removed by a stainless steel wire brush.

It should be noted that normal procedure in Zircaloy component fabrication for nuclear applications requires: (1) a flash-pickle operation, (2) thorough rinsing, and (3) a final acceptance corrosion test for three days in 680F, pH 9 water. The final pickling step had to be waived with these crevice specimens, since it would have been impossible to ensure that all of the fluoride ion from the pickling operation was completely removed from the crevice regions of the specimens. Hence, all Zircaloy components were pickled and rinsed prior to assembly and were tungstenarc-welded into finished assemblies in an atmosphere box. This process made essential the use of white-glove techniques for all assembly and handling operations after pickling and rinsing. Also necessary was the maintenance of such techniques during acceptance corrosion testing, crudding of the parallel-faced specimens, shipment from KAPL to MSAR, and ultimate insertion into the loop.

Details of Corrosion Testing**

Subsequent to fabrication, all specimens were inserted into a large autoclave and corrosion-tested for three days in 680F water at pH 9

**Written by C. Cheng.

^{*}Written by W. K. Anderson and A. J. Palmer.



FIGURE 6. Additional Control and Switching Instrumentation on MSAR Loop.

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FIGURE 7. Original Design of MSA Specimen. KS-45126 Unclassified
(ammonia). Results of these tests on seven specimens gave results which indicated acceptability of the specimens for use. Although some indication of white product appeared during these tests on some specimens near the heat-affected zones, no white product was detected on the faces of any of the ribbon portions of the specimens. Also, no sign of corrosion was detected by these tests in the neighborhood of the nickel-Zircaloy eutectic diffusion bonds.

Hence, based on these tests, it was decided to proceed with the experiment, using specimens of this original design. However, a parallel corrosion test of nickel-Zircaloy eutectic diffusion-bonded specimens was under way in an autoclave in which these diffusion-bonded couples could be connected to the secondary of a seven-volt transformer. By this test, the effect of pH 10.5 lithiated or ammoniated water could be determined while the couple specimen was maintained by the imposed 60-cycle voltage at an a-c potential of seven volts from autoclave ground. Results of these tests, as discussed in the following paragraphs, led to rejection of this original design.

Discussion of Rejection of Specimens

The special corrosion tests mentioned in the paragraph above were carried out in the autoclave sketched in Figure 8. Specimens as sketched in Figure 9 were used. Test details were as follows.

One specimen was suspended in ammoniated, hydrogenated water (5 to 10 cm³ of hydrogen per kilogram of water) at pH 10 with its nickel wire connected to the insulated lead in the autoclave head (Figure 9). Seven volts a-c were impressed between the specimen and the stainless steel autoclave for 93 hr at test temperature.

The second specimen was suspended in lithiated, hydrogenated water (5 to 10 cm^3 of hydrogen per kilogram of water) at pH 10 and corrosion-tested in the same way.

pH Agent	Resistivity,	Average Temperature, F	Average Pressure, psi	emf, rms volts	Average Current,
NH40H	16,000	410	300	7	10
LiOH	14,500	460	500	7	16

Conditions during the autoclave tests were as follows:

<u>Results in Ammoniated, Hydrogenated Water</u>. The test specimen removed from the ammoniated water showed a ring of creany-white corrosion product at the bond and some creany-white patches on the Zircaloy-2 (Figure 10). Under 30X magnification, the creany-white product seemed to originate in







Zircaloy-2



Ammoniated, Hydrogenated Water, - pH-10



Lithiated, Hydrogenated Water, - pH-10

FIGURE 10. Corrosion of Nickel - Zircaloy-2 Diffusion Bond.

KS-45129

Unclassified

the diffusion-bond groove and then deposit out as spots and "whiskers" on the Zircaloy-2 portion of the specimen. This creamy-white corrosion product was not tightly adherent, as was the white corrosion product typical of the Zircaloy. By X-ray diffraction, the creamy-white product was identified as nickel hydroxide $[Ni(OH)_2]$ and nickel oxide (NiO). This analysis was confirmed by a qualitative spectrographic analysis that reported 50-percent nickel and four-percent zirconium as the major elements.

Metallurgical examination revealed that the diffusion bond had suffered galvanic corrosion attack, predominantly at the nickel-rich zone. The attack had penetrated into the nickel-base metal, but not into the Zircaloy-2 (Figure 11).

Results in Lithiated, Hydrogenated Water. The test specimen removed from the lithiated water showed little change at 30X magnification (Figure 10), but metallographic examination at higher magnifications showed that the diffusion bond had again suffered galvanic corrosion attack, predominantly at the nickel-rich zone (Figures 12 and 13). The attack was not as severe as in ammoniated water and did not penetrate into the nickel-base metal.

In addition to the results of these tests, two of these specimens of the original design were observed to corrode badly during application of crud (see "Crud Deposition on Parallel-Walled Crevice Specimens," p. 34). From these results, it was concluded that the specimens of the original design could not possibly be used for the crevice corrosion test; so the design was abandoned. The specimens were redesigned, using Zircaloy-2-clad copper buses, as discussed in the text that follows.

The Zircaloy-Clad Copper Bus-Bar Type Specimens*

This new specimen design, proposed by C. J. Beck of KAPL, differed basically from the original design only in its use of a 0.6-in.-diam copper bar, clad with 0.1-in.-thick Zircaloy, as a current-carrying bus bar.

Figure 14 shows a sketch of the significantly changed parts of these Zircaloy-clad, copper-bus-bar type specimens. The buses, fabricated by a coextrusion and welding technique, permitted any surface intersection of diffusion bonds with Zircaloy to be eliminated completely. Thus it was ensured that the hot water in the loop would see only Zircaloy surfaces that were presumably resistant to corrosion.

The electrical resistance of such a bus can be calculated by means of the parallel resistance laws; it can easily be shown that the resistance of such buses in a test specimen is lower with this design than with

Written by C. J. Beck and W. K. Anderson.

a design that uses a pure nickel rod of the same outside diameter. For example, the calculated resistance of a 24-in.-long piece of nickel rod, 3/4-in. in diameter, is 150×10^{-6} ohms; that of a 1/2-in.-diam, high-conductivity, oxygen-free (HCOF) copper bar, covered with Zircaloy and diffusion-bonded to a 1/8-in.-thick annulus of Zircaloy cladding, is 80×10^{-6} ohms.

The only doubt concerning the performance of such Zircaloy-clad copper buses was based on the fact that the linear coefficient of thermal expansion for copper is ~50 percent higher than that of Zircaloy. However, discussion of the problem with experts in the field of mechanical design of thermally stressed structures led to the opinion that the proposed bimetal couple would be sufficiently ductile under conditions of test to minimize any possibility of rupture of the Zircaloy cladding. Hence this design was selected.

Fabrication and Testing of Specimens

Table 3 shows data on sources of materials selected for fabrication of these specimens to the new design. Fabrication of these specimens of the modified design differed from that of the original design in only two ways, both of which involved fabrication of the current-carrying buses. The two differences were: (1) fabrication of buses by coextrusion, and (2) joining of buses to holders.

The second step, done by inert-gas tungsten-arc-welding, involved only straightforward techniques and will not be discussed at length. This method minimized the difficulty of joining the holders to the buses and permitted use of ordinary pipe threads rather than Acme threads for fastening the holders to the buses.

The first step had enough novelty in its concept to justify a brief description of certain parts of its fabrication and a brief discussion of its performance. This discussion follows immediately below.

Fabrication of Buses by Coextrusion. The required bus bars were to contain a 0.560-in.-diam copper core clad with ~0.100 in. of Zircaloy. These bars were to be cut into 24-in. lengths for the intended application.

Such rods were fabricated by coextrusion of an assembly made up of a copper core 2.38 in. in diameter by 6 in. in length and a Zircaloy sleeve with a 3.375-in. OD $\times 2.88$ in. ID. The copper core was inserted into the Zircaloy sleeve; this assembly, in turn, was inserted into a copper can to make up the extrusion billet assembly. This billet was heated to 800C and held at temperature 1-1/2 hr prior to extrusion through a 0.822-in.-diam die. A pressure of 300 tons was required to make the extrusion. After extrusion, the copper jacket material was mechanically stripped from the rod and the structure machined to final shape and dimensions.

The bars were cut to the length specified in the drawings. A female thread was cut into the recessed end of the copper insert in the bus, at the

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Nickel



Nickel 750X

FIGURE 11. Corrosion of Nickel - Zircaloy-2 Diffusion Bond in Ammoniated, Hydrogenated Water - pH 10. KS-45130 Unclassified

Zircaloy-2



Nickel

FIGURE 12. Corrosion of Nickel - Zircaloy-2 Diffusion Bond in Lithiated, Hydrogenated Water - pH 10. Unclassified KS-45131

Zircaloy-2



Nickel

FIGURE 13. Corrosion of Nickel - Zircaloy-2 Diffusion Bond in Lithiated, Hydrogenated Water - pH 10. Unclassified KS-45132

TABLE 3. DATA ON MATERIALS USED TO MAKE MSAR LOOP TEST CREVICE SPECIMENS

Group A. Ammonia Chemistry Test

Specimen	Specimen Material	Assembly Design	Certification of Specimen Material	Certification of Bus Material	Certification of Material for Plug and Holder
2	Zircaloy-2	crevice	HCZ1034	Obtained from MDO special stock.	HCZ1062
3	Zircaloy-4	parallel	HCZ733-46	Obtained from MDO special stock.	HCZ1062
5	Zircaloy-4	crevice	HCZ733-46	Obtained from MDO special stock.	HCZ1062
		Gr	oup B. Lithium Chemi	stry Test	
13	Zircaloy-4	parallel	Obtained from C. J. Beck (MDO). Special reactor- grade stock.	Obtained from C. J. Beck (MDO). Special reactor- grade stock.	HCZ1062
15	Zircaloy-4	crevice	Obtained from C. J. Beck (MDO). Special reactor- grade stock.	Obtained from C. J. Beck (MDO). Special reactor- grade stock.	HCZ1062
14	Zircaloy-2	crevice	Obtained from C. J. Beck (MDO). Special reactor- grade stock.	Obtained from C. J. Beck (MDO). Special reactor- grade stock.	HCZ1062



Loop Zircaloy Crevice Corrosion-Test Specimen. KS-45127 Unclassified

end selected for joining to the threaded Zircaloy holder. The opposite (outer) end of each bus was counter-sunk and fitted with a Zircaloy plug of suitable size and design. At this stage, the entire assembly could be inert-gas tungsten-arc-welded in a welding box. With these exceptions, fabrication of these modified specimens followed essentially the same procedures as those described above for the original nickel bus-bar design.

Although properly a portion of the test results, a brief consideration of the condition of these bars after removal from the test chamber forms a logical extension of this description and is therefore included at this point.

Results of Examination of Buses after Completion of Test. One of the Zircaloy-clad copper bus bars used in the first (ammonia pH controlled) test was sectioned and examined metallographically after operating in the MSA loop for 1000 hr at about 585F. Figure 15A shows the 3X appearance of a transverse section of the rod near the holder end of the bus. Figure 15B shows a segment of this same section at 150X. Note that the cladding and core are metallurgically bonded and that the copper-Zircaloy intermetallic compound is intact in this rod. Figures 16A and 16B show longitudinal sections of the rod in approximately the same position. Again, the brittle copper-zirconium intermetallic compound is intact in the rod. Figure 17 shows the cross section of the bus at the juncture of the threaded Zircaloy holder and the copper interior of the bus. Even where the copper has been almost entirely removed by machining, the bond between it and the Zircaloy cladding is still intact.

Acceptance Tests on Specimens*

From the standpoint of acceptance testing of specimens for use in the experiments, two tests were run. These consisted of: (1) corrosiontesting for three days at 680F in pH 9 ammoniated water in a large static autoclave, and (2) gripping the upper and lower bus bars in a tensile machine and pulling until the specimens were held at a tension somewhat

^{*}Written by W. K. Anderson and E. J. Callahan.



A. Cross Section (Macro) 3X FIGURE 15. Transverse Section of Copper-Zircaloy Clad Bus after 1000-hr Loop Exposure at 585F.

KS-46241

Unclassified



A. Longitudinal Section, 3X FIGURE 16. Longitudinal Section Taken from Same Region in Bus Bar as in Figure 11.

KS-46242

Unclassified

greater than that expected to be exerted on the test sections during loop operation (8000 psi). With the specimens under tension, the crevices were examined visually for orientation and structural adequacy.

Results of corrosion tests for all specimens used in the test are shown in Table 4. As a typical photographic exhibit, Figure 18 is presented. This figure shows one side of the last six specimens fabricated (numbers 11, 12, 13, 14, 15, and 17). The white appearance is caused by light reflection rather than white product. Except for the slight staining visible on the right end of some of the dumbbells near the heataffected zone, all of these specimens had a good black film, indicative of acceptable corrosion performance.

Subsequent to corrosion testing, all specimens were photographed. Since no gross differences appear in photographs of the several specimens, only one typical set of pictures will be shown at this point. Figure 19 shows a photograph of one face of specimen 3, one of the earlier specimens used in the ammonia test. The white-appearing area toward the righthand end of the test areas is again caused by light reflection rather than white product. Minor discoloration of a heat-affected zone on an enlarged area of the opposite face of this same specimen is shown in Figure 20. An edge view is shown in Figure 21.

Specimen	Visual Appearance
3	Some gray discoloration in wire-brushed area. Considered acceptable.
2	Same as specimen 3 for flats. Some white product on one hub in previously wire-brushed area.
5	On original test, some white product. Wire-brushed and retested; then same as specimen 3.
13	Acceptable. Only minor staining with slight nodu- lar corrosion in the neighborhood of heat- affected zone.
14	Acceptable. See Figure 18.
15	Same as specimen 14.

TABLE 4. RESULTS OF CORROSION TESTS

Crud Deposition on Parallel-Walled Crevice Specimens*

Prior to discussion of the procedure for deposition of the black iron-oxide crud on the two parallel-walled specimens (specimen 3 for ammonia pH control, and specimen 13 for lithium hydroxide pH control), some basic statements on the behavior of crud need to be emphasized. In the first place, crud deposited with either of the two bases is not compatible with the other base. For example, crud deposited in an ammonia environment will be quickly peptized by lithium hydroxide and dispersed into the loop water. In addition, many workers have felt that the memory effect by metal that has been exposed to lithium ion so alters the nature of the metal surface as to change its behavior in its ability to hold an adherent deposit of, let us say, an ammonia-base crud. Hence, care in keeping the two systems separate and in cleaning the equipment between changes in the pH control agent was considered essential.

The reactions involved in the deposition of crud are written as follows:

For NH₄OH,

$$FeSO_4 + 2NH_4OH \longrightarrow Fe(OH)_2 + (NH_4)_2SO_4$$
 (1a)

$$Fe(OH)_2 + Heat \xrightarrow{170F} \gamma Fe_3 O_4 + Fe + H_2^{**} .$$
 (1b)

For LiOH

$$FeSO_4 + 2LiOH \longrightarrow Fe(OH)_2 + Li_2SO_4$$
(2a)

$$Fe(OH)_2 + Heat \xrightarrow{170F} 7Fe_3O_4 + H_2 + Fe^{**}$$
. (2b)

The deposition of synthetic magnetite iron-oxide crud on the parallel-faced, Zircaloy-4 crevice specimens was carried out by the Experimental Engineering Section at KAPL. Test sections were coated with approximately one-mil layers of crud. Crudding was accomplished in a loop that is described in the next paragraph.

The loop was primarily constructed of surgical tubing and glass fittings in order to minimize crud deposition on the loop. Two 25-liter glass carboys with spigots were used as slurry and ferrous-sulfate containers. The crudding solution was heated with two Variac-controlled immersion heaters and was circulated through the loop by a belt-driven

^{*}Written by B. Selig and J. Samaritano.

 $^{^{**}\}gamma$ is here an arbitrary constant of unknown magnitude to indicate a balance in the equations. The exact state of the iron oxide is not known.



FIGURE 17. 3X Cross Section of Thread Assembly. KS-46243 Unclassified



FIGURE 18. Specimens 11 through 15, and 17 after Corrosion Test. KS-45245 Unclassified



KS-44742 Unclassified



Teel rotary screw pump. A G.E. 200-amp arc-welding motor-generator set was used as a d-c power source to apply flux to the test section.

Figure 22 shows a sketch of the crud deposition loop facility; Figure 23 is a sketch of the special section designed to hold the MSAR loop test specimens during the crud deposition operation.

Temperature was controlled by two iron constantan thermocouples recorded on a G.E. potentiometer. The couples were located at the inlet and outlet of the test section.

Current flow through the test section was continuously recorded on a Leeds and Northrup Speedomax millivoltmeter. Test section voltage was measured by a Weston voltmeter. Slurry pH was measured on P Hydrion test paper which, after immersion in samples of the slurry, was compared with a standard color chart.

Procedure for crudding was as follows. For both ammonia and LiOH pH control, the loop was filled with 16 liters of deionized or distilled water. An equivalent amount of purified water was added to the chemical reserve bottle. Water was deoxygenated by bubbling nitrogen through the system before adding chemicals.

In the case of the ammonia crudding procedure, the water was raised to pH 10 by the addition of concentrated NH_4OH . The procedure for ammonia crudding differed from that for lithium only in the manner of pH control. During crudding, the loop water was kept at pH 10 by periodic addition of NH_4OH .

In the case of the operation with lithium hydroxide pH control, the following procedural description is offered. With the exception noted above, this procedure also applies to the operation with ammonia pH control. Steps are as follows:

- 1. Heat loop water to 170F before circulating.
- 2. When the proper temperature is reached, begin to circulate the solution, maintaining a velocity of 1 to 3 fps at the test specimen.
- 3. Apply power to the test specimen.* Do not allow boiling to take place.
- 4. Add a maximum of 25 ml/min of 0.1 molar of $FeSO_4$ from the chemical reserve bottle to the crud solution.
- 5. Maintain a pH of 10 to 11 for a LiOH environment. This is done by periodically adding LiOH to the crudding solution, or by periodically adding NH₄OH to maintain the loop water at a pH of 10.

^{*}The power supplied to the test section should be just enough to raise the test-section temperature a few degrees above the loop temperature.

6. Keep all solutions deoxygenated by continuously bubbling nitrogen through them.

The mechanism of crudding can be essentially deduced from Equations 1 and 2 for the annonia and LiOH cases, respectively. In both cases, the magnetite crud formed by precipitating out of solution. The crud deposition was obtained by establishing a differential temperature between the test section and the crudding solution (see Equations 1 and 2).

A photograph of the crudded lithium-hydroxide-controlled specimen is shown in Figure 24.



FIGURE 20. Enlarged View of Opposite Face of Specimen 3 to that Shown in Figure 19. (2X reduced 95%.) KS-30640 Unclassified



FIGURE 21. Edge View of Specimen 3. KS-44741 Unclassified



FIGURE 23. Sketch of Chamber Designed to Hold MSAR Loop Specimens during

FIGURE 22. Crud Deposition Facility. KS-46244 Unclassified Crudding Operation. KS-46245

Unclassified



FIGURE 24. Photograph of One Face of Specimen 13 after Crudding with LiOH Precipitated Fe⁺⁺ Ion. KS-30723 Unclassified



OPERATIONAL HISTORY OF THE TEST*

The loop was constructed of stainless steel; however, measures were taken to ensure that scale and other foreign matter were not present before starting the first test. With completion of necessary modifications, the loop was pickled at 200F for several days with a three-percent citric acid solution. Water used in preparing the solution was of high purity, with its conductivity near 0.1 μ mho/cm. The loop was drained after the pickling operation and flushed several times with high-purity water. The loop was again charged and operated several days at 450F. Partial circulation of the loop stream was directed through the bypass demineralizer which was loaded with an HOH effluent resin bed. A water conductivity of less than 1 μ mho/cm and a neutral pH of 7.0 indicated that residual citric acid had been removed.

The data for each day of operation were collected, and the following readings were made: inlet and outlet temperature of each test section, bulk water temperature, loop pressure, water flow rate, specimen amperage, and voltage. These measurements were made six times each day. The temperatures were read from a potentiometer with an ice-bath reference junction; pressure was read from a calibrated Heise gage and water flow rate from an orifice meter and high-pressure mercury manometer. Flow rate through each test section was individually monitored by orifice meters and dp cells (see "Description of the Loop," p. 5). Readings of dp cells indicated equal flow through each of the test sections. Voltmeters and ammeters were used to measure voltage and amperage at each specimen, and the measurements were used to calculate the resistance of each specimen in ohms.

Temperature measurements taken each day showed the presence of nucleate boiling along the specimens. As described previously, instrumentation showed operating personnel that this condition existed. At nonboiling conditions, temperature measurements were taken to determine the average temperature difference, which was about 5F for a flow velocity of ~2 fps across the crevice specimens. (Velocity through the chamber containing the coupon control specimens was also near 2 fps.) At nucleate boiling conditions - the conditions maintained during the test - the average temperature difference was calculated from six sets of readings made each day.

A daily log of loop operations was kept, and data were recorded to observe any noticeable effects during the course of the run. Water samples were removed periodically to check loop pH and conductivity and,

^{*}Written by M. J. McGoff.

at the beginning and the end of each run, to check chloride concentration, total solids, and pH agent concentration. Hydrogen gas was placed in the loop to maintain concentration between 5 and 15 cm³ of hydrogen at STP/kg. Water bombs were removed for analysis of hydrogen-gas concentration.

Ammoniated-Water Run

This test was designated as MDO-BMD-8A. The crevice specimen identification and location in the loop for the ammoniated-water run were as follows:

Specimen I	dentification_		
KAPL Test	Manufacturing	Specimen	Test
Number	Number	Material	Section
BMD-8A-2	5	Zircaloy-4	1
BMD-8A-3	2	Zircaloy-2	2
BMD-8A-1,	3	Zircaloy-4	3
precrudded			

Coupon specimens for Zircaloy-2 were numbered Z-2-1 through Z-2-6, and for Zircaloy-4, Z-4-1 through Z-4-6. During installation and removal from the loop, the specimens were handled with white, lint-free gloves. A log of operational data taken for the run with ammoniated water is given in Table 5. The run was completed after 1000 hr.

The loop was charged with high-purity water (conductivity <1 µmho/cm) that was degassed to nearly 0.2 ppm of dissolved oxygen. Power was applied to the specimens to begin the run. The first 128 hr of operation were interrupted frequently because of the use of steel-bodied rubber 0-ring seals that created short circuits and leakage problems. The steel-bodied rubber 0-ring seals were discarded in favor of Teflon-bodied rubber 0-ring seals. Some strain to the Teflon seals was expected at the operating pressure of 1400 psig. However, a photograph (see Figure 25) of the Teflon removed from the upper seal section shows that deformation was not too severe and that overheating did not occur. The Teflon parts from the lower seals were of like appearance.

The course of the run was plagued with water leakages from the cracked body of the drain valve, throttle valve packing, and high-pressure tubing fittings. These leakages were stopped, and leakage did not appear too extensive until the last week of the run. Water makeup was required each day in the last 200 hr of operation. The leak could not be found during operation since leakage at a 1-in. flexitallic gasket at the inlet flange of test section 1 was absorbed by the insulation and evaporated.

Other shutdowns resulted because power was interrupted to test section 2 by a loose connection on the power transformer and by the development of

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TABLE 5. DATA LOG ON LOOP OPERATIONS - AMAGNITATED WATER RUN

Specimen Heat Flux ~500,000 Btu/hr-ft2 - Water Velocity ~2 fps

			Heater												Tate	tr Ches	datry			
Operation	Loop	Loop	Erit					T	est Sec	tion			_	_					Total	
Time,	Flow,	Press,	Temp,	Δ τ ,*		1			2			3			Conductivity.	0	H.	CI .	Solida	
<u> </u>	gom	psig	F	F	Amp	Volts	Obms ^{##}	Amp	Volts	Citans ##	Amp	Volta	Ohma ^{##}	рĦ	µ-mbo/cm	0000	ce Ag	, 170m	<u>د</u>	Connects
0	12.7	1/00																	_ <u></u>	
21	12.8	1,00		-	4.77		0.0167	-				-		10.2	44	0.2	-	-	-	Interrupted operations prevailed
43	12.0	1,00	-	-	02)	9.0	0.0157	600	9.8	0.0163	608	9.6	0.0155	10.4	150	0.2	-	-	-	first 128 hr. Seal, valve,
05	12.0	1400	-	-	023	9.7	0.0154	600	9.8	0.0160	608	9.5	0.0154	-	-	0.16	-	-	-	packing, gasket, and fitting
72	13.0	1400	-	-	623	9.8	0.0157	600	9.7	0.0162	616	9.6	0.0156	10.4	150	0.20	-	⊲0.1	0.0004	leakages.
96	13.0	1400	-	-	623	9.8	0.0197	600	9.8	0.0163	616	9.5	0.0154	-	-	-	-	-	-	-
138	12.6	1400	-	-	-	-	-	-	-	-	_	-	-	_	_	_	_			Added II to low makes
162	12.5	1,395	-	-	623	10.0	0.0161	600	9.9	0.0165	623	9-6	0.0154	10.5	195	_	-	0.075	0,0000	Removed states comple
186	12.5	1,395	582	2.7	623	10.0	0.0160	600	9.8	0.0163	616	9.6	0.0156			-	-	0.075	0.0009	WHENARD ASTAL REPTS.
210	12.5	1395	583	2.7	623	9.9	0.0160	600	9.8	0.0163	616	9.5	0.0154	_	-	-	-	-	-	
234	12.5	1390	581	3.7	623	9.9	0.0160	600	9.8	0.0163	608	9.4	0.0154	-	-	-	-	-	-	
										0.0207			0.0274	-	•.	-	-	-	-	Acced museup water.
256	12.5	1395	583	2.7	632	9.9	0.0157	600	9.7	0.0162	616	9.4	0.0153	10.4	160	-	14	-	-	Removed sample for H ₂ analysis.
262	12.5	1395	583	2.8	632	10.0	0.0158	600	9.7	0.0162	616	9.5	0.0154	10.4 [/]	180	-	-	-	-	• • •
306	12.5	1400	584	2.7	623	9.9	0.0160	600	9.6	0.0163	616	9.4	0.0154	10.4	130	-	-	-	-	
330	12.5	1400	584	2.8	623	9.8	0.0160	600	9.6	0.0160	616	9.5	0.0154	10.4	150	-	-	-	-	Added makeup water.
354	12.5	1400	584	1.6	608	9.9	0.0163	600	9.6	0.0160	608	9.4	0.0155	-	-	-	-	-	-	• • • • • • • • • • • • • • • • • • • •
378	12.5	1/00	587	2.0	627	0.0	0 0160	600	96	0 0140	400		0.0166							
402	12.5	1/00	583	2.0	670	30.0	0.0150	400	2.0	0.0160	600	7.7	0.016		-	-	· •	-	-	
426	12.5	1/00	587	1.8	6/0	10.0	0.0154	400	7.1	0.0162	624	7.0	0.0194	20.00		-	-	-	-	Added NH ₄ OH to raise pH.
450	12.5	1,00	504	7.0	640	10.0	0.0150	600	9.7	0.0162	616	9.0	0.0126		-	-	-	-	-	
4.0	12.5	1,000	204	2.1	040	ر.س م	0.0159	600	9.7	0.0162	624	. 9.8	0.0197	10.45	180	-	•	-	-	Added makeup water.
407	12.7	140	رهر	2.)	023	7.0	0.015/	800	9.5	0.0003	908	9.3	0.0192	10.4	170	0.2	-	-	-	Loop down 9 hr to repair trans- former connection.
489	12.5	1400	585	1.8	623	9.9	0.0160	600	9.8	0.0163	606	9.3	0.0152	10.55	210	-	-	-	-	Added NH. CH solution.
513	12.5	1400	583	2.8	623	9.9	0.0160	600	9.8	0.0163	608	9.3	0.0152	-	-	-	-	-	-	
537	12.5	1400	584	2.3	623	9.9	0.0160	600	9.9	0.0165	608	9.3	0.0153	-	-	-	-	-	-	
553	12.5	1400	584	2.5	623	9.9	0.0160	600	9.8	0.0163	608	9.5	0.0154	10.45	195	-	-	-	-	Loop down 8 hr to repair lower seal on test section 3.
577	12.5	1400	584	1.9	623	9.9	0.0160	600	9.8	0.0163	608	9.6	0.0154	10.55	225	0.2	-	-	-	Added NELCOH solution.
601	12.5	1400	583	2.3	623	9.9	0.0160	600	9.8	0.0163	608	9.6	0.0158	10.5	240	-	-	-	-	
625	12.5	1400	583	2.2	623	9.9	0.0159	600	9.8	0.0163	616	9.6	0.0156	10.5		-	-	_	_	
649	12.5	1400	585	1.8	623	9.9	0.0159	600	9.8	0.0163	623	9.6	0.0154		_	_	_		_	
673	12.5	1,00	584	2.7	623	10.0	0.0160	600	9.8	0.0163	616	9.6	0.0156	_	-	-	-	-	-	Added makeum matem
697	12.5	1395	584	2.1	623	9.9	0.0159	600	9.8	0.0163	623	9.5	0.0154	-	-	-	-	-	-	where merech acter.
														. –	-	-	-	-	-	
721	12.7	1400	284	2.0	623	9.9	0.0159	600	9.9	0.0165	623	9.6	0.0154	-	-	-	-	-	-	
745	12.5	1395	583	2.1	623	9.9	0.0159	600	9.9	0.0165	616	9.6	0.0156	10.4	200	-	-	-	-	Added NH ₆ OH to raise pH.
769	12.5	1400	284	2.0	623	9.9	0.0159	600	9.8	0.0163	623	9.5	0.0153	-	-	0.2	15	-	-	Added makeup water and NH ₄ OH solution.
793	12.5	1400	584	1.8	623	9.9	0.0159	.600	10.0	0.0160	623	9.6	0.0154	-	-	— 1	•	•	-	
817	12.5	1400.	583	2.0	616	9.8	0.01 <i>9</i> 9	600	9.8	0.0163	616	9.5	0.0154	10.6	215	0.16	-	-	` -	Added water for makeup and NH ₄ OH to raise pH.
841	12.5	1400	584	1.8	616	9.9	0.0161	600	9.8	0.0163	616	9.5	0.0153	-	-	-	_	-	-	
865	12.5	1400	583	2.0	616	9.8	0.0159	600	9.8	0.0163	608	9.4	0.0155	-	-	-	_	-	-	Added makeum water.
889	12.5	1,00	584	2.1	616	9.9	0.0161	600	9.8	0.0163	616	9.5	0.0153	-	-	-	_	-	-	Added makeum water
913	12.5	1400	584	1.7	616	9.9	0.0161	600	9.9	0.0165	616	9.5	0.0153	10.5	190	-	-	-	-	Added makeup water and NH4CH solution.
9.77	12.5	1/00	582	2.1	616	a .o	0.0161	600	9.9	0.0165	616	04	0.01#4	_	_	0.2	_			
961	12.5	1/00	505 505	1.6	616	7·7	0.0161	400	7.7	0 0164	414	7.0	0.0120	10 65	-	0.3	14	-	-	Added makeup water and MH_OH.
025	12.5	1/00	, C) 80-1	1 4	416	7.7	0.0161	400	7.7	0.0167	414	7.7	0.010	10.77	<u>au</u>	0.2	5	-	-	Added million wither.
1000	10.6	1,00	204	7.0	610	7.7	0.0161	600	0.0	0.0107	010	7.0	0.0156	10.45	212	-	-	-	-	Acced Bakeup Water.
1000	12.7	TAN	764	2.4	010	7.7	0.0101	au	10.0	0.0102	010	9.0	0.0156	-	-	-	-	-	-	Loop shut down - 1000-hr run,

"Average of the three test sections, inlst and outlet temperature difference (at subcooled conditions, AT was 4F, average of three test sections).

a high-resistance contact on the bus bar of test section 3. The latter incident resulted in overheating of the lower Teflon seal assembly. The overheating caused the Teflon to extrude and the rubber O-rings to leak from the deformation. Temperatures of the lower Teflon seal bodies were not recorded since the lower seal assemblies were out of stream and at room temperature. If the overheating resulted in the evolution of hydrogen fluoride, its entry into the loop stream was unlikely because of its out-of-stream location and its more reasonable escape through the surrounding atmosphere. It is worthy of notice that no resistance increase due to decrease in specimen cross section occurred during this test. Figure 26 is a graph of resistance for all three specimens plotted for the duration of the test.

For the entire run, an average of 2.2F temperature difference was measured across the three test sections with a 4F difference being measured at a subcooled condition. The heat corresponding to this 1.8F temperature difference between indicated ΔT and the 4F ΔT determined under subcooled conditions was therefore available to generate and superheat steam. With these temperature difference measurements as a basis of calculation, it was found that boiling existed across the upper 45 percent of the specimen for the run (percent of specimen undergoing nucleate boiling - 1.8/4.0 × 100 = 45 percent).

The crevice specimens and coupon specimens were removed after 1000 hr of on-line testing. No visual damage was noted with the coupon specimens; however, the bus bars of the crevice specimens were covered with a white deposit on the inlet end; the outlet ends had no deposits (see "Presentation and Discussion of Data and Results," p. 50). The white deposit on the buses proved to be zirconia (ZrO_2) . The crevices of all specimens contained white deposit formations; the major formations were identified as hydrated alumina (boehmite). The only source of alumina in the loop structure was in the plunger of the feed-water pump; the chemical feed pump had a stainless steel plunger. The continuous requirement of water makeup presumably resulted in erosion of the alumina from the plunger and concentration in the loop water.

Lithiated-Water Run

This test was designated as MDO-BMD-8B. Before the lithiated-water run began, the loop was operated to remove residual annonium hydroxide. The annoniated resin bed was removed from the bypass demineralizer and replaced with an HOH effluent resin bed. The loop was filled twice with low-conductivity water (~l μ mho/cm), heated to 150F and drained. The loop was charged a third time with water and operated for two days at 450F. Water conductivity was lowered from 1.7 to 0.6 μ mho/cm by the action of the bypass demineralizer. Water pH was a neutral 7.0. The loop piping was considered free of residual ammonium hydroxide. The HOH



A. Side View Showing Outside of Teflon Part with External Rubber O-Rings Visible B. Photograph from Top (Hottest Portion) of Seal Showing Parts of Two Inside Rubber O-Rings.

FIGURE 25. Photograph of Rubber O-Ring Used in Ammonia Test in Test Chamber 2.

KS-46246

Unclassified



KS-46247 Unclassified

effluent resin was removed from the bypass demineralizer and replaced with LiOH effluent resin.

After the system had been drained, the specimens were installed. The greatest care was exercised at this point in order to minimize the possibility of damaging the specimens. For the lithiated-water run, the crevice specimen identification and location in the loop were as follows:

Specimen I	dentification_				
KAPL Test Number	Manufacturing Number	Specimen Material	Test Section		
BMD-8B-3	14	Zircaloy-2	1		
BMD-8B-2	15	Zircaloy-4	2		
BMD-8B-1, precrudded	13	Zircaloy-4	3		

Coupon control specimens for Zircaloy-2 were numbered Z-2-7 through Z-2-12, and for Zircaloy-4, Z-4-7 through Z-4-12. Specimens were installed and removed from the loop with white, lint-free gloves as in the run with ammoniated water.

The system was charged with high-purity water (conductivity $<1 \mu$ mho/cm) and hydrostatically tested at 1450 psig for leaks. Before the power was applied to the specimen, the water charge was degassed until oxygen concentration was lowered to 0.16 ppm. Adjustments were made to obtain a pH of 10.5.

A log of operational data taken for the run with lithiated water is given in Table 6. The run was completed after 211 hr, as increases in specimen resistance and hydrogen-concentration buildup in the loop water were observed.

No makeup water was added during the run. When alumina deposits were found in the crevice specimens in the ammoniated-water run, the ceramic plungers were removed and replaced with Hastelloy plungers. The run proceeded, with one interruption. After several days, amperage decreases and voltage increases were observed at the specimens. Power was turned off for a few hours to check bus-bar contacts for fouling. The buses were cleaned with emery cloth to remove any oxides and ensure good contact. Power was again applied to the specimens. A drop in amperage and increase in voltage that occurred again as the run continued showed that specimen resistance changes were causing this effect.

Hydrogen gas was added to the loop water at the beginning of the run to raise hydrogen concentration to ~5 cm³ of hydrogen at STP/kg of water. Later in the run, a water bomb was removed to determine the concentration

			Istry	r Chem	Tata												Easter			
Commente	Total Solids,	a,	H ₂ ,	0 ₂ ,	Conductivity,		(Brag ##	3		tion .	est Sec 2 Volte	T	Chernetter	1 Volte		<u>م</u> ر,*	Erit Temp,	Loop Press,	Loop Flow,	Operation Time,
							<u></u>	1010			101.00					<u> </u>	<u> </u>			
Added 225 cc H ₂ at STP, calcu- lated concentration = 5 cc H ₂ at STP/kg.	0.0027	<0.1	5	0.14	74	10.0	0.0165	9.6	584	0.0167	10.0	600	0-0162	9.9	608	2.2	586	1 <i>397</i>	12.6	0
Added 400 cc LIGH solution to raise pH-	-	-	-	-	130	10-4	0.0170	9.8	5 76	0.0170	10.0	5 90	0.0167	10.0	600	2.2	586	1400	12.6	24
Added 300 cs LIOH solution to raise pH.	-	-	-	-	201	10.6	0.0167	9.9	5 92	0.0181	10.5	580	0.0173	10.5	608	3.0	585	1400	12.6	48
-	-	-	-	-	152	10.5	0.0170	10.2	600	0.0175	10.5	600	0.0173	10.5	608	2.5	586	1400	12.6	72
-	-	-	-	-	-	-	0.0170	10.2	600	0.0178	10.5	<i>5</i> 90	0.0173	10.5	608	2.7	585	1400	12.6	96
-	-	-	-	-	-	-	0.0176	10.4	592	0.0186	10.6	9 70	0.0175	10.5	600	2.4	585	1,395	12.6	120
-	-	-	-	-	140 °	10.5	0.0182	10.5	5 76	0.0186	10.6	5 70	0.0179	10.6	592	2.8	584	1400	12.6	144
Removed bomb for hydrogen analysis.	-	-	72	-	-	-	0.0177	10.4	585	0.0186	10.6	5 70	0.0130	10.5	585	3.3	584	1400	12.6	168
_ 1	-	-	-	-	190	10.5	0.0181	10.4	576	0.0189	10.6	560	0.0180	10.5	584	2.4	585	1,398	12.6	192
Removed bomb for hydrogen analysis. Removed water sample for complete spectrographic analysis of total solids. Loop shut down - 211-hr run time.	0.0036	≪0.1	66	-	-	-	0.0182	10.4	568	0.0192	10.6	550	0.0181	10.4	5 76	2.6	585	1400	12.6	211

TABLE 6. DATA LOG ON LOOP OPERATIONS - LITHIATED WATER HUN

Specimen Heat Flux ~500,000 Btu/hr-ft2- Water Velocity ~2 fps

""Chas calculated from amperage and voltage readings.

in the loop water. The measurement showed a concentration of 85 cm³ noncondensibles at STP/kg. Because of the high result, a second measurement was made. A concentration of 78 cm³ of noncondensibles at STP/kg was measured. The measurements were made by an evacuation technique. Since the high results were looked upon with aspicion, a sample of gas was removed for identification. Mass spectrographic analysis identified 85 percent of the gases to be hydrogen; the actual hydrogen concentration in the measurements was calculated to be 72 and 66 cm³ of hydrogen at STP/kg of water.

The increase in specimen resistance, as calculated from amperage and voltage readings (see Figure 27), and the high hydrogen concentration prompted the termination of the lithiated-water run. The specimens were removed from the loop. The coupon specimens showed no signs of damage. Crevice specimen BMD-8B-2 in test section 2 was broken during removal, the material appearing to be embrittled. As was the case with the ammoniated-water run, the inlet ends of the crevice specimen bus bars were coated but were of cream-colored appearance, and deposits were much heavier than in the ammonia test. The deposits, which readily flaked off the bus bars, were identified by X-ray diffraction as zirconia. The crevice faces of the specimens appeared to be heavily pitted.

Specimen 13 in test section 3 was precrudded with a black deposit, presumably magnetite (Fe_2O_3 , FeO). After the testing, this crudded area had changed to a red deposit of hematite (Fe_2O_3). Evidently oxidation occurred during this test. A spectrographic analysis of solids in the water showed Fe_2O_3 to be present at 0.7 ppm.

In this run, a 4.8F temperature difference was measured at subcooled conditions, and a 2.6F temperature difference was the average at nucleate boiling conditions. The heat corresponding to this indicated that 2.2F temperature difference was therefore available to vaporize and superheat steam. A calculation of the temperature difference data indicates that boiling occurred over 46 percent of the specimens.

A large amount of corrosion was observed in this test, and extensive white deposits were observed on the lower bus bars for all three specimens (see figures described in "Presentation and Discussion of Data and Results," which follows). Therefore, the question of possible release of hydrogen fluoride gas by the Teflon seals has been raised. Such release of hydrogen fluoride must have been minimal, as is shown by examination of the photograph of the upper (hot) end of the Teflon seal parts used in all three test chambers. This photograph is shown as Figure 28.

PRESENTATION AND DISCUSSION OF DATA AND RESULTS*

The MSAR loop crevice-corrosion test has yielded a very complex array of information. Much of this information is the result of visual and metallographic examinations, the record of which is in the form of photographs. The extensive reproduction and use of such photographic evidence is the purpose of the first part of this discussion. The results of chemical analyses of deposits, corrosion products, and specimen surfaces, as well as analyses and mechanical tests carried out on the metal itself, form the content of subsequent parts of the discussion.

Although discussion of observations and data are included where called for, the terminal drawing of conclusions has been relegated to "Conclusions," p. 114.

One logical organization of the data might be to present, first, the information on the part of the test carried out in ammoniated water, followed by a subsection dealing with the test carried out in lithiated water; however, the benefits of direct comparison of information covering a specific aspect of the two parts would be largely lost by such an approach. Hence, for each examination or study of a particular aspect of the test, data on both ammoniated and lithiated water systems will be presented together.

So that the reader may better follow the discussion of all examinations carried out on these crevice-corrosion-test specimens, an outline of the total examination procedure is presented in Table 7.

Visual and Metallographic Examination

Gross Visual Appearance of Specimens after Testing.

The visual appearance of specimens 2, 5, and 3 used in the first (ammoniated water) test prior to insertion are shown collectively in Figure 29. The white areas on the test coupons are light reflections rather that white product. Irregularly shaped dark areas within these reflection areas on specimens 5 and 3 are water-stained regions showing poorer reflectivity than the surrounding areas. Figure 30 is a composite photograph of the same three specimens after testing for 1000 hr in pH 10.5 ammoniated water. In this case, both faces of the specimens are shown. At the right in the photograph, a thin region of nonadherent, brownish-white material is visible on the lower (loop inlet) ends of the exposed specimens. Spectrographic and X-ray diffraction analyses of scrapings of this material identified it as essentially pure zirconium oxide. It has been postulated that minor thermal decomposition of the Teflon portions of the loop test chamber seals may have released

^{*}Written by W. K. Anderson.



FIGURE 28. Photographs of Top (Hottest Parts) of All Three Teflon Seal Members Used in Test Chambers for Lithiated Water Run. KS-46249 Unclassified



Face A of Specimen 3



Face B of Specimen 3

FIGURE 30. Composite Photographs Showing Both Faces of Specimens 2, 5, and 3 after Loop Exposure for 1000 hr in pH 10.5 Ammoniated Water. The lower, inlet end of these specimens is oriented toward the right in the picture. This end, nearest the Teflon seals, was exposed to liquid-phase water. Notice the thin deposits of nonadherent zirconium oxide on these lower ends of all three specimens. KS-46251


TABLE 7. OUTLINE OF EXAMINATION PROCEDURE Description Item No. 1 Throughly examined all specimens visually, making liberal use of photography to record all observations. Removed scrapings of any loosely adherent deposits for chemical 1.1 analysis. Sheared ribbon sections from holders. 1.2 1.3 Examined both faces of both ribbon sections visually and under magnification. Photographed. 1.3.1 Scraped oxide and other material from any significant surface and submitted them for chemical analysis. 1.3.2 Photographed surfaces after scraping. 1.3.3 Selected regions and polished faces in efforts to detect any pitted regions. Photographed. Sectioned and mounted regions suspected of showing pitting for 1.4 transverse photomicrographs. Measured pit depths where found. 1.4.1 First examined polished specimens. 1.4.2 Etched and examined for presence of hydrides. 2 Analyzed oxide deposits or scrapings. 2.1 Analyzed scrapings of deposits or surface oxide layers from outside. 2.2 Determined whether decrudding agents would remove material from surface. 2.3 Removed specimens from interior of all crevice surfaces and analyzed them. 2.3.1 Attempted to determine whether composition varied from surface inward where layers are thick. 2.3.2 Characterized all oxide samples taken by emission spectrography and X-ray diffraction techniques. 3 Determined hydrogen concentrations in metal from each specimen. 4 Determined degree of embrittlement of specimens by mechanical (tension) testing.

sufficient hydrogen fluoride to cause this accelerated corrosion. However, only minor traces of fluoride ion were found in the oxide, and these quantities of fluoride were found ineffective in tests run by Battelle Memorial Institute (BMI)⁴ in causing white corrosion product to appear on Zircaloy. In the case of the similar material found in greater quantity in the run in which LiOH was used as the pH control, the fluoride concentration in this oxide material was almost a factor of 3 higher than that found in the base metal. It can not be definitely stated that this corrosion on the lower bus bars was not caused by fluoride released from the Teflon. (<u>Note</u>: specimen 3 was crudded prior to insertion into the loop. Figure 28 shows this specimen after corrosion-testing and not after crudding.)

Figure 31 shows the opposite faces of those shown in Figure 18 for specimens 14, 15, and 13. These specimens were used in the second test run in which LiOH was used as the pH control agent. At the stage shown in this photograph, the three-day acceptance corrosion test had been completed, but deposition of crud on the parallel-faced crevice specimen (specimen 13) had not been done. The purpose of this photograph is to show that the corrosion test did not significantly mar the surface of these Zircaloy specimens.

Appearance of the same specimens after test is shown by the photographs reproduced as Figure 32. On these specimens, which had been exposed in the loop to lithiated water for only 211 hr, as compared with 1000 hr for the ammoniated-water test specimens shown in Figure 29, the increased damage is very apparent. Much thicker coverings of zirconium oxide are seen on the upstream ends of these specimens exposed to pH 10.5 lithiated water. The high rate of corrosion is certainly attested to by the embrittlement of all specimens, as evidenced by breakage of specimen 15 during its removal from the loop. This highly embrittled Zircaloy-4 specimen shattered during removal from its specimen chamber, despite the fact that all reasonable care was taken to prevent torquing during such removal.

The splotches of white product visible on the exposed inside surfaces of the thin test members in this brittle specimen were definitely $2rO_2$. All the characteristics of the white product observed in in-pile operational failures of Zircaloy surfaces exposed to high heat fluxes were present.

Subsequent to the general visual examination of the specimens from each test described immediately above, the thin, heat-generating, dumbbellshaped parts were sheared from each specimen. Photographs were taken of each face of both halves of each specimen at about 2X enlargement. These photographs (Figures 33, 34, 35) show the appearance of all faces of the crevice specimens after testing in the loop. (Since no corrosion was evidenced on the outer faces of specimens 2, 5, and 3 tested in ammoniated water, and since exposed views of these outer faces have already been shown, the three outer-surface photographs have been omitted.)

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Specimen 15. Zircaloy-4, VEE-Crevice

Specimen 13. Zircaloy-4 Parallel-Faced Crevice, Crudded prior to Insertion

FIGURE 31. Opposite Faces of Specimens Shown as Part of Figure 18 and Used in Lithiated-Water Test. View shows specimens prior to insertion into loop but subsequent to corrosion-testing. Specimen 13 was subsequently crudded prior to insertion. KS-46252

Unclassified



Face B of Specimen 13

FIGURE 32. Specimens 14, 15, and 13 after Loop Exposure for 200 hr in pH 10.5 Lithiated Water. Extreme embrittlement due to hydrogen pickup under accelerated corrosion conditions was indicated by the breaking of the Zircaloy-4 VEE-crevice specimen during removal from the loop. Notice the increased amount of nonadherent white oxide compared with that of Figure 29 on the upstream ends of these specimens. Unclassified KS-46253



Figure 33 shows inner faces of specimens 2, 5, and 3. The white oxide visible in these photographs is largely hydrated alumina (boehmite) of the chemical composition $Al_2O_2(OH)_2$. It has been established that this aluminum oxide deposit probably came from the parts of a charging pump that had been used to pump water into the loop. Spectrographic analyses and X-ray diffraction data have been used to establish the composition of all three of these oxide deposits on specimens 2, 5, and 3.

Figure 34 shows photographs of the interior surfaces of shearedout parts of specimens 14, 15, and 13. All specimens show deeply eroded or corroded surfaces; however, the Zircaloy-2 (specimen 14) appears to have suffered less attack than did the Zircaloy-4 in either the VEEshaped, uncrudded or the parallel-walled, crudded specimens (Figures 33b and 33c, respectively).

A comparison between the ammonia run and the lithia run (Figures 33 and 34) is premature since the heavy deposit of hydrated aluminum oxide on the specimens shown in Figure 32 makes direct observation difficult. However, it should again be pointed out that the white product visible in the photographs of Figure 33 (lithiated-water run) is definitely zirconium oxide and has the general appearance and high degree of adhesion characteristic of white product seen in in-pile occurrences of accelerated attack of Zircaloy. It can further be pointed out that the Zircaloy-2 specimen, in this case, exhibits less white product than do either of the two Zircaloy-4 specimens. No significant difference appears between the crudded and uncrudded specimens in the case of either ammoniated or lithiated water.

White product of an adherent type, resembling the in-reactor formed variety, was apparent on the exterior of specimens 14, 15, and 13. Slightly enlarged photographs of exteriors of these specimens are therefore shown in Figure 35. The caption under these photographs calls attention to the white oxide deposits on the outer surfaces of the specimens used in the 211-hr lithiated-water test. This material is quite adherent and has the same characteristics as those observed in cases of accelerated corrosion in reactors and in-pile loops. The speckled appearance is quite evident. Again, it should be pointed out that the Zircaloy-4 specimens seem to have been subject to greater attack under the conditions of this test.

Figure 36 shows the light, nonadherent, and not very extensive covering of zirconium oxide found on the upstream bus bars in the test run in ammoniated water (test MDO-BMD-8A). Here the possibility has been proposed that this portion of the zirconium corrosion observed may have been due to hydrogen fluoride released by mild thermal decomposition of the Teflon in the insulating seals. However, no fluoride could be detected by chemical analyses on scrapings of oxide from these surfaces. Figure 37 shows 1X views of the heavy, nonadherent zirconium oxide formations on the surfaces of the upstream buses on the specimens exposed to lithiated water. This oxide does not have the appearance or degree of adherence characteristic of "normal" white product. Its flocculent nature and appearance lend some credence to the thesis that its extensive formation may be due, at least in part, to fluoride released by the Teflon seal material. The deposits discussed immediately above, however, even those on the outside of the thin Zircaloy crevice specimen, were of an altogether different appearance. These deposits were quite adherent. If fluoride were even to a partial extent responsible for the formation of white product on these lower Zircaloy bus-bar parts, it seems doubtful that this effect extended up to, and into, the interior of the crevices that were under test in a high-heat flux environment.

Figure 38 shows rather poorly, in black and white photography, the only distinct differences observed in either test. These differences must definitely be attributed to precrudding of specimens. On removal from the loop, specimen 13 (the precrudded test specimen exposed in lithiated water) showed an extensive brownish-red deposit, obviously an iron compound, on many parts of the outer surface. The stain that shows on the photograph of the downstream bus bar in Figure 38 is the most extensive of these deposits. The material has been identified as hematite by the X-ray diffraction technique.

Examination under Magnification*

Subsequent to the examinations just discussed, the thin-walled crevice parts from all specimens were subjected to careful metallographic examination. Specimen 5, the Zircaloy-4, VEE-crevice specimen exposed to ammoniated water for 1000 hr, was the first to be examined. Its examination was typical of that for the other specimens from the ammoniatedwater test.

After the specimens had been sheared from the holders and examined in the manner described in the preceding paragraphs, they were photographed at 12.5X magnification over selected regions to display the appearance of the oxide on the interior surfaces of the crevices. After such photography, the specimens were scraped with a microspatula and samples of the oxide recovered for chemical analysis. Photographs were then taken of the specimens after scraping to exhibit the appearance of the metal surfaces partially laid bare by such scraping. In general, the outline offered in Table 7 was followed.

Figure 39 (A, B, and C) shows the appearance of specimens 2, 5, and 3 in selected regions prior to scraping of oxide. A typical picture, after

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^{*}Written by A. D. McMaster and W. K. Anderson.



Specimen 5. Zircaloy-4, VEE Specimen



Specimen 3. Zircaloy-4 parallel-faced specimen exposed after precrudding with ammonia precipitated iron oxide

FIGURE 33. Slightly Magnified Surfaces of Crevice Interiors from Specimens 2,5, and 3 Used in the 1000-hr Test in pH 10.5 Ammoniated Water. The lower ends were upstream; Upper marks the geometric UP direction in the chambers.

KS-46254

Unclassified



UPPER

A. Interior View of Crevice from Specimen 14. Zircaloy-2, VEE-Specimen



B. Interior View of Crevice from Specimen 15. Zircaloy-4, VEE-Crevice Specimen

UPPER



C. Interior View of Crevice from Specimen 13. Zircaloy-4 Precrudded Parallel-Faced Specimen

FIGURE 34. Interior View of Crevices Exposed for 200 hr to the Action of pH 10.5 Lithiated Water. Tsat was probably reached in these crevices over most of their interior length, making temperature near 587F. KS-46255





A. Specimen 14



B. Specimen 15



C. Specimen 13

:

FIGURE 35. Outside Surfaces of Crevice Specimens Used in Test with pH 10.5 Lithiated Water. The beginnings of white product deposits are visible on the upstream ends of these specimens. KS-46256 Unclassified



A. Specimen 2



C. Specimen 3

FIGURE 36. Nonadherent White Zirconium Oxide Product Formed in Ammoniated Water Test on Upstream Bus Bars. KS-45673 Unclassified





FIGURE 37. Views of Upstream Bus Bars from Test in Lithiated Water Showing Extensive White Oxide on Surfaces. KS-46257



FIGURE 38. Red Iron Oxide Deposit on Upstream Bus Bar of Specimen 13, the Precrudded Test in Lithiated Water (1X). KS-45808







A. Specimen 2, before scraping



C. Specimen 5, before scraping

B. Specimen 3, before scraping



D. Specimen 5, after scraping

FIGURE 39. Typical Appearance of Inner Surfaces of Crevices in Specimens from Test MDO-BMD-8A after Exposure for 1000 hr in pH 10.5 Ammoniated Water. The oxide deposit is boehmite, a hydrated aluminum oxide.

KS-46258

Unclassified



removal of easily detached oxide with a small microspatula, is also shown in Figure 39D. This view is of the same area shown in the unscraped state in Figure 39C.

Figure 40 shows similar unscraped views of selected regions of the inner surfaces of specimens 14, 15, and 13. Here the absence of an extensive alumina deposit is evident. A chemical analysis of bits of oxide removed from these specimens reveals that the white, and very adherent, material seen in these regions is principally ZrO_2 . Because of the general appearance and behavior of the oxide, the authors are of the opinion that it is normal white product caused by the high-temperature reaction of the corroding metal with water. The deep pitting and seriously corroded appearance of the metal visible in areas not covered by oxide strengthen this belief. No remarks on a comparison of Zircaloy-2 vs Zircaloy-4 are thought to be deducible from these pictures. In view of the increased amount of oxide visible in Figure 40C of specimen 13 (the parallel-faced, precrudded crevice), the presence of crud may have increased slightly the rate of oxide formation. However, the deep pits seen in both 40A and 40B make this factor a relatively academic question.

To return to the matter of pitting from an over-all standpoint, a preliminary examination of surfaces such as those shown in Figure 39D had led to the opinion that no pitting with formation of white product had occurred in the ammoniated environment of the first 1000-hr test. However, after a more thorough metallographic examination, this opinion had to be reversed. As evidence, the photographs of Figure 41 are submitted. These are photographs at 250X of transverse mounts taken from specimen 5. Here the Zircaloy-4 specimen, after scraping, hada relatively thin layer of oxide that was quite adherent. By emission spectrographic analysis and by means of the electron-beam microprobe, the oxide on this specimen was shown to contain zirconium as well as aluminum. The outer surfaces of two pieces of specimen 5 had been mounted back to back in the region shown in Figure 41A. Here, only minor deterioration of these outside surfaces is evidenced.

Figure 41 (B and C) shows areas from the inner crevice wall of specimen 5. Here, deterioration of the surface is evident. Picture B, taken at about the center of the crevice, can be estimated to have pitted to a depth of 0.3 mil in the 1000-hr period of exposure. Picture C, taken from the closed edge of the VEE-shaped crevice, had been penetrated to an estimated depth of two mils.

A piece from specimen 2, the Zircaloy-2 crevice specimen tested for 1000 hr in an ammonia environment, was mounted with the inner oxidized face of the crevice wall to be polished. This mount was polished, and a view of an obviously pitted region is shown in Figure 42. Figure 42A, taken at 50X, shows a large pit. Figure 42B is a 250X enlargement of the oxide region within the pit at about 11 o'clock as picture A is oriented. Electron-beam microprobe studies indicate this oxide to be largely ZrO₂.

Figure 43 shows additional pitted regions from inside the crevice of specimen 3. The oxide showing inside these crevices is largely ZrO_2 . The picture with its legends is self-explanatory and further bears out the undeniable fact that crevice corrosion occurred in all three of the specimens tested in ammoniated water.

The depth of the pits shown in Figure 42A was estimated by sectioning the mount in the region shown in Figure 42. Results are shown in Figure 44. View A, at 100 times magnification, shows a fairly wide area (0.04 in.) within the area shown in Figure 42. The depression (pitting) at this point is approximately one mil in depth. View B, at 250 times magnification, shows the thin, broken oxide layer in contact with the metal.

That the pitting of the specimens run in ammoniated water, however, is quite minor can be seen from examination of the two photomicrographs in Figure 45. View A shows a section taken from specimen 3; view B shows a micrograph of specimen 2. The straight edges of metal on which the boehmite deposit appears in these photographs indicate that essentially no metal was lost in this 1000-hr test.

The thin, white layer, however, that is shown in contrasting color on the bottom of view B, is apparently ZrO_2 ; the darker oxide layer, toward the center of the photograph, is alumina. This zirconium-oxide layer can be estimated to have a thickness of 0.5 mil (0.0005 in.) and has the consistency and appearance of normal white-corrosion product of the "general coverage" type. This idea is strengthened by the fact that the ZrO_2 layer is well covered by a relatively thick layer of hydrated alumina. This material would have served as an adsorbent type of protective coating to hinder harmful ionic materials such as hydrogen fluoride from gaining access to the surface. (It was found by Berry, et al.,⁵ at BMI, that high concentrations of iron oxide (Fe₃O₄) that acted in this way so drastically reduced fluoride concentrations as to render them ineffective in accelerating the corrosion of Zircaloy. There would seem to be no reason why alumina, a material with wellknown high-surface activity, would not act in the same way.)

Figure 46 shows a 7X photograph of the mount used to study specimens 14, 15, and 13. The two sections lettered A and B at the bottom of the picture were taken in the vicinity of the bottom and the top, respectively, of specimen 13, the crudded, parallel-walled crevice specimen. (The top of the specimen was exposed to steam, the bottom to water.) Views C and D are, respectively, the same for specimen 14, the Zircaloy-2, VEE-crevice specimen. Views E, F, and G are sections from specimen 15, the Zircaloy-4,

KAPL-2203





A. Specimen 14

B. Specimen 15



C. Specimen 13

FIGURE 40. Views at 12.5X of Selected Regions on Interior of Crevices Tested for 200 hr in 587F pH 10.5 Lithiated Water.

KS-46259

Unclassified









B. Inner crevice wall near center



C. Inner crevice wall near closed edge of VEE

FIGURE 41. Transverse Views of Specimen 5 Photographed after Wet-Polishing at 250X. Corrosion of inner surfaces of the VEE-shaped crevice is more drastic toward the closed edge.

KS-46260

Unclassified





A. View of pit, 50X KS-46261



B. Pit region at 11 0'clock, 250X FIGURE 42. Photographs of Deep Pit in Specimen 2. Unclassified



A. Display of area studied for Specimen 2, 20X

B. Same area, 250X





C. Pitted region at 50X located at intersection D. Intersection of lines XX' and YY' on C, 250X of lines AA' and BB' on A. FIGURE 43. Magnified Views of Pits in Specimen 3, the Zircaloy-4 Crudded Test Specimen. KS-46262 Unclassified



VEE-crevice specimen. Views F and G are bottom and top views, respectively. View E is a mount taken from near the center of the specimen. The numbers in Figure 46 designated locations of correspondingly designated photomicrographs in the ensuing figures.

Figure 47 shows two pictures at 250X magnification of a region marked with the numbers 5 and 7 in Figure 46. These pictures are of a region of specimen 14. View A uses normal illumination; view B is taken with polarized light. Two types of oxide appear to be present in these photographs a thin, outer layer that may be a partial covering of alumina, and the thick, general-coverage oxide that has been determined to be ZrO_2 .

Figure 48 shows four other views of specimen 15 and indicates the increasing depth of penetration of oxide in the direction away from the originally open edge of the VEE crevice. ZrO_2 thicknesses as high as eight mils can be measured in some areas.

Figure 49 shows views of specimens 13 and 14. Locations are indicated on the figure in relation to Figure 46. Again, relatively deep penetrations are shown.

A second look at Figure 46 shows that all of the transverse sections of the specimens from the lithiated-water test are bowed. The convexity can be explained by the assumption that the surfaces of the test pieces had been under compressional stress at the conclusion of fabrication. When the inner surfaces had been eaten away by corrosion, an unbalance was produced which caused the bowing. The strain produced may have caused surface cracks to form. Such cracks are shown in the 250X picture of Figure 50. This area is located at the outer edge of specimen 14 and is indicated by the number 6 in Figure 46.

No such bowing was observed on specimens 3, 5, and 2, the specimens used for the test in ammoniated water.

The previously discussed photomicrographs were taken in the aspolished condition. It was necessary to study the structures more carefully to determine the extent to which hydrogen pickup had occurred by location of the hydrides; therefore, the mounts were subsequently etched, using a solution of 100-ml concentrated nitric acid and five drops of hydrofluoric acid to define the hydride phase.

Studies of the specimens from the ammonia chemistry test showed a more or less even distribution of hydride platelets at very low concentrations. Typical pictures are shown in Figure 51. A highly contrasting situation is displayed in the area of hydride concentration by the photographs of Figures 52 and 53. These pictures display the high concentrations of hydrides found in alloy specimens exposed to lithiated water. Figure 52 shows three views of specimen 15, the Zircaloy-4, VEEshaped specimen, after 200 hr in this lithium hydroxide environment. In this photograph, print A shows the upper (steam phase) effect; print B shows the middle (transition phase) zone, and print C the lower portion of specimen 15, which was exposed to the liquid phase. (The latter region probably reached alkali concentrations considerably above the nominal 10.5 pH, at which the loop water was maintained, because of a distillation column effect of the vertical channel formed by the specimen test chamber .).

Figure 53 shows similar views for specimens 14 and 13. Here again, high concentrations of hydride platelets are in evidence. Specimen 13, a parallel-faced crevice specimen, was precrudded. This specimen shows a lower concentration of hydride than either of the other two specimens. Whether the original presence of magnetitic crud, or the more open structure of the crevice, is responsible for this decrease in hydrogen concentration is a question that can not be answered from the data available.

In summary, the following statements can definitely be made in relation to the metallographic examination whose results have been presented above.

- 1. In an ammonia environment (pH 10.5), with exposure for 1000 hr, only minor pitting and white oxide formation were observed even though the inner surfaces had been covered with a deposit of aluminum oxide, presumably from a previously unsuspected ceramic part in the loop charging pump.
- 2. In a lithium hydroxide environment (pH 10.5) with exposure limited to 200 hr by approaching specimen failure, deep corrosion, pitting, and much white oxide formation have been shown to have taken place.
- 3. In the etched condition, photographs show only the normally expected concentration of hydride platelets after 1000 hr in ammoniated water; extensive hydride deposits are visible in all of the specimens exposed for only 211 hr in lithiated water.
- 4. In the lithiated environment, hydrogen pickup is judged to be as high, or higher, in Zircaloy-4 as in Zircaloy-2, where specimens of identical configuration and preinsertion condition are compared.
- 5. Some indication was found that with more open crevices, which were precrudded prior to loop testing, less hydrogen pickup occurred. No explanation of this aspect of the work can be offered.





A. 100X

B. 250X

FIGURE 44. Views of Pitting Perpendicular to Figure 42. KS-46263 Unclassified





A. Specimen 3B. Specimen 2FIGURE 45.Views of Transverse Sections of Specimens 3 and 2 at 250X.KS-46264Unclassified



FIGURE 46. 7X Photograph of Mount Containing Key to Location for Micrographs of Specimens 14, 15, and 13.

Unclassified



A. Normal illumination



B. Polarized light

FIGURE 47. Photographs at 250X of a Region Near the Outer Edge of Specimen 14 (Regions 5 and 7, Figure 46).

KS-46266

Unclassified





C. Region 9, Figure 46

D. Region 12, Figure 46

FIGURE 48. Various Areas of Specimen 15 at 250X. Note increasing thickness of oxide in moving toward center of crevice. A is toward the originally open edge of the VEE in specimen 15. KS-46267

Unclassified



A. Specimen 14, Region 4, Figure 46 FIGURE 49. Transverse Views of Specimens 14 and 13 at 250X. Unclassified KS-46268





FIGURE 50. View Showing Cracks Along Outside Surface of a Part of Specimen 14 Exposed to Steam. KS-46269 Unclassified







A. View on narrow oxide section of Specimen 5



C. Specimen 2

<section-header><text>

D. Specimen 3

FIGURE 51. Views of the Specimens Exposed to Ammoniated Water for 1000 hr as Etched. Notice the very low concentration of hydride platelets and their even distribution (150X nitric-hydrogen fluoride etch). KS-46270 Unclassified







A. Upper region (steam-blanketed) on Specimen 15

B. Middle region (transition zone) on Specimen 15



C. Lower region (liquid phase) on Specimen 15

FIGURE 52. Etched Views of Specimen 15 at 250X as Etched. The high concentration of hydride platelets is displayed by this etching treatment. No significant difference in hydrogen concentration as a function of elevation on the specimen can be deduced from these photographs. KS-46271 Unclassified





A. Lower portion (water phase) Specimen 14



D. Upper portion (steam phase) Specimen 13 C. Lower portion (water phase) Specimen 13 FIGURE 53. Views of Transverse Sections of Specimens 13 and 14. Specimen 14 was the Zircaloy-2 VEEcrevice specimen; specimen 13 was the precrudded parallel-faced specimen. Both views show high hydride concentrations, but such concentration is unaccountably lower in the precrudded, more open design represented in views C and D. Unclassified KS-46272

B. Upper portion (steam phase) Specimen 14



Test of the Corrosion Environment*

To establish the relationship between quality of loop water maintained in the MSAR loop and the quality of water maintained in other test loops and reactors, and in general to determine the rate of corrosion of Zircaloy in the loop water, corrosion coupons were inserted in a special holder just upstream of the 30-A circulating pump in the loop.

The design of the specimen holder was that of a conventional train. The specimens are shown in Figures 54 and 55, which show the specimens full size, after removal from the loop.

Figure 54 shows one face of the series of specimens that were tested for 1000 hr in the ammoniated environment. These specimens, made from the same Zircaloy stock as for the crevice portions of the test specimens, were precorrosion-tested in 680F water for three days prior to insertion in the loop.

Oxide appearances changed from the glossy black oxide produced in the autoclave test to a dull black oxide produced by the loop test. In addition, the dull black oxide exhibited areas of dull red-brown streaks, which were only slightly visible; these streaks were of a contaminated appearance and would not rub off.

Figure 55 shows one face of the specimens tested in lithiated water at pH 10.5 for 200 hr. The appearance of these specimens is better than that displayed by those shown in the previous photograph, as might be expected from the shorter exposure time.

No significant deterioration of surfaces is visible in any of these specimens. No differences are apparent between Zircaloy-2 and Zircaloy-4 in either test.

Weight gains, both in the autoclave acceptance test and the loop test, are shown in Table 8.

The corrosion rates are the expected rates for both autoclave and loop tests. The rates measured and reported for the loop test are the rates of film growth after the initial corrosion period in the autoclave (three days, 680F water). These rates are reduced rates because the corrosion proceeds through the protective oxide to the metal-oxide interface. There are no significant differences between rates of film growth for Zircaloy-2 and Zircaloy-4 coupons. These rates also indicate that the films are uniform and adherent.

Important conclusions can be drawn from these data. In either lithiated or ammoniated water, under the MSAR loop test conditions in crevices exposed to boiling in vertical channels, crevice corrosion

^{*}Written by E. J. Callahan

Coupon Identity	Autoclave Test*	Loop Test** <u>AW, mg/dm²</u>
Ammon	niated Water Test, ph	<u>i 10.5†</u>
Zircaloy-2		
1	13	4
2	11	4
3	13	5
4	12	6
5	13	5
6	13	5
Zircaloy-4		
1	9	5
2	10	4
3	10	5
4	10	4
5	9	44
6	9	4
Expected Weight Gain - Zircaloy	10 to 15 7-2	4 to 8
Litl	niated Water Test, pl	<u>10.5††</u>
Zircalov-2		
7	12	0.6
8	13	1.6
9	12	0.8
10	12	0.6
11	12	0.8
12	12	0.5
Zircaloy-4		
7	10	1.0
8	9	0.2
9	9	0.6
10	9	1.2
11	10	0.7
12	9	0.5
Expect Weight Gain - Zircalo	10 to 15 y-2	0 to 3
*Three days in 680 **Subsequent to au)F static water. toclave test.	†1000-hr test. ††200-hr test.

TABLE 8. WEIGHT GAINS OF CONTROL CORROSION COUPONS FROM MSAR CREVICE CORROSION TEST



Zircaloy-4



FIGURE 54. Oxide Appearances of Coupons Tested in First MSA Loop Test in Ammoniated Water for 1000 hr. KS-46143 Unclassified



Zircaloy-4



FIGURE 55. Oxide Appearances of Coupons Tested in Second MSA Loop Test in Lithiated Water for 200 hr.

KS-46144

Unclassified



took place. On the other hand, coupon specimens exposed to either lithiated or ammoniated water in the liquid phase (in which crevices are formed between the coupons themselves and the coupon holder structure), showed no effects. This points to the fact that boiling was an essential part of whatever mechanism was active in the corrosion of MSAR loopcrevice test specimens. Further, although lithium hydroxide is a more agressive agent in the boiling crevice-corrosion case, both the photographs of Figures 54 and 55 and the data of Table 8 show, if anything, improvement in corrosion performance when lithium hydroxide is used in pressurized water systems.

Test of Mechanical Properties*

A series of tensile tests was conducted at room temperature on the Zircaloy-2 and Zircaloy-4 specimens used in these tests. The samples still retained some white corrosion product as a result of corrosion tests in ammoniated water (Group A) for 1000 hr at 587F and in lithiated water (Group B) for 211 hr at 587F.

The strip material was machined to contain a 0.245-in.-wide by 2.0-in-long gage section and was tested on an Instron tensile machine at a strain rate of 0.01 in./min. The results of the test are shown in Table 9.

These results show that the increased corrosion and resultant hydrogen generation in the lithiated-water environment caused very bad hydrogen embrittlement of both Zircaloy-2 and Zircaloy-4. In fact, in both of the VEE-shaped crevice specimens run for 200 hr in lithiated water, this embrittlement was so drastic that the material would be useless for reactor service. On the other hand, no such serious results were obtained in the pH 10.5 ammoniated-water test which ran for 1000 hr. Hence, the lithium environment in this respect can be considered much more aggressive.

No significant differences were detected between Zircaloy-2 and Zircaloy-4 specimens in either environment.

The precrudded specimens in the lithium hydroxide environment seemed a bit less drastically attacked than were the other two specimens. Whether this was due to the fact that the coating of crud adsorbed part of the active agents attacking the metal and thus assumed a protective role, or whether the fact that the crevice was open on both sides on this specimen and thus permitted slightly more access by loop water and better scavenging of the crevice, must remain a matter of conjecture.

Chemical Test Data**

This discussion contains data connected with the identification of the various corrosion products as well as analyses of metal from the

**Written by W. K. Anderson and J. Rynasiewicz.

^{*}Written by F. W. Wiesinger.

Specimen Number) Material	Design	Area, in. ²	0.2% Offset Yield Strength, psi × 10 ³	Ultimate Tensile Strength, psi × 10 ³	Elongation in 2.0 in., %	Reduction
		Group A.	Ammoniated	1 Water, 10.5 pH,	1000 hr		
2	Zircaloy-2	Crevice	0.00615	57.2	72.2	17.2	42.6
5	Zircaloy-4	Crevice	0.00651	55.8	67.9	17.9	43.5
3	Zircaloy-4	Parallel	0.00640	56.7	70.3	19.2	43.0
		Group B.	Lithiated	1 Water, 10.5 pH,	200 hr		
14	Zircaloy-2	Crevice	0.00653	-	49.2	0.4	0.31
15	Zircaloy-4	Crevice	0.00672	-	46.4	0.4	0.74
1 <i>3</i> *	Zircaloy-4	Parallel	0.00645	54.6	61.2	1.2	11.8

TABLE 9. MECHANICAL TEST DATA

*This specimen was tested prior to machining of gage section and broke in the grips. The results listed are those after gage had been machined.

specimens after test. These data have been used in the previous discussions, but have been consolidated here for ease of presentation and discussion.

Identification of Coupon Portion of Deposits Taken from Specimens in Ammoniated-Water Test

Copious deposits of white oxide, shown in the photographs of the ammoniated-water-test specimens after shearing from bus-bars, were taken for analysis by scraping with a microspatula. As previously reported, the outer layers of oxide were identified mainly as boehmite, a hydrated form of aluminum oxide of formula $Al_2O_2(OH)_2$. Analyses of the oxides from specimens 2, 5, and 3, using the emission spectrograph, are reported in Table 10.

The samples used in these emission spectrographic tests were also submitted to the X-ray diffraction laboratory for characterization. A microscopic examination of the material on crevice specimens 2, 3, and 5 showed white particles, and also white particles with a reddish-brown layer. The two types of particles were separated and X-ray diffraction patterns made on both. The white particles gave the pattern of boehmite; the white particles with the reddish-brown oxide also gave the boehmite pattern, plus one additional pattern that could not be identified.

The data for the emission spectra of the oxide samples taken from the ammoniated-water tests showed zirconium in low percentage levels. However, during early stages of the examination of these specimens, proper significance was not attached to these qualitative findings. Furthermore, the emission spectrographic results gave only the average composition of the crud that was removed. Subsequently, metallographic and electron-beam microprobe studies proved that minor pitting and white zirconium oxide formation had taken place beneath the copious deposits of white aluminum oxide. Thus it was established that pitting and normal white oxide formation had taken place to a limited extent on all three specimens tested in ammoniated water.

Identification of Oxide Found on Coupon Portions of Specimens from Tests in Lithiated Water

It had been intended that tests similar to those described above for specimens run in ammoniated water be carried out on oxide samples taken from crevice interiors of specimens run in lithiated water. Examination of these specimens, however, showed striking similarity among all three specimens. In addition, specimen 15 had higher, visible concentrations of oxide on its surface than did either specimens 13 or 14. Hence it was decided, in the interest of minimizing total labor, that samples for spectrographic analyses would be taken only from specimen 15.

Element	Sample 5, wt %	Sample 2, wt %	Sample 3, wt %	
Aluminum	750	750	750	
Zirconium	3	3	3	
Silicon	2.5	2.5	2.5	
Lithium	l	1	0.5	
Iron	0.5	0.3	0.3	
Calcium	0.5	0.3	0.3	
Sodium	<0.1 to 0.2	<0.1 to 0.2	<0.1 to 0.2	
Magnesium	<0.1 to 0.2	<0.1 to 0.2	<0.1 to 0.2	
Manganese	<0.1 to 0.2	<0.1 to 0.2	<0.1 to 0.2	
Lead	<0.1 to 0.2	<0.1 to 0.2	<0.1 to 0.2	
Chromium	<0.1 to 0.2	<0.1 to 0.2	<0.1 to 0.2	
Tin	<0.1 to 0.2	<0.1 to 0.2	<0.1 to 0.2	
Copper	<0.1 to 0.2	<0.1 to 0.2	<0.1 to 0.2	
Fluorine	<0.03	<0.03	<0.03	

TABLE 10. EMISSION SPECTROGRAPHIC ANALYSIS OF SCALE-REMOVED MSA CREVICE SPECIMENS*

*The above percentages are qualitative and may vary by a factor of two or three. Analyses were performed by F. P. Landis and D. Del Grosso.

Data are given in Table 11. These data indicate that the oxide was mainly zirconia. The X-ray diffraction data verified this composition. However, subsequent examination with the electron-beam microprobe of a metallographic mount from specimen 15 showed that even in the lithiatedwater test, which was run after removal of the ceramic parts from the loop charging pump, aluminum oxide was deposited in limited quantities over a limited area. Also, as would be expected, iron oxide was visibly present in oxide layers found on specimen 13, the precrudded Zircaloy-4 test specimen.

To return to a further discussion of Table 11, the high aluminum and iron concentrations from the interior of specimen 15 indicated that some crudding with both Al_2O_3 and iron-base crud had taken place. Since this specimen was not the originally crudded specimen (specimen 13), the presence of iron indicates that the usual transport corrosion phenomena had been active. The alumina doubtless came from Al_2O_3 particles or deposits that had hidden out in the loop, since the ceramic plunger in the charging pump had been replaced prior to this test.
Element	Specimen 15	Element	Specimen 15
Aluminum	5	Magnesium	0.005
Boron	<0.003	Manganese	0.03
Calcium	<0.05	Molybdenum	0.05
Chromium	5	Nickel	<0.01
Cobalt	<0.001	Silicon	0.1
Copper	0.03	Silver	0.03
Iron	0.7	Sodium	<0.05
Lead	0.005	Tin	1.
Lithium	<0.05	Titanium	<0.005
		Zirconium	Major

TABLE 11. SPECTROGRAPHIC ANALYSIS OF MATERIAL FROM CREVICE SPECIMENS TESTED IN LITHIATED WATER

Further work on specimens 14, 15, and 13, using the electron-beam microprobe, tends to confirm conclusions discussed above. This work is discussed under "Electron-Beam Microprobe Studies," p. 98.

Identification of Red Desposits on Upper (Downstream) Bus Bar on Specimen 13

This deposit, shown in the photograph of Figure 38, was obviously a compound of iron. Spectrographic analysis (Table 12) confirmed this.

TABLE 12.ANALYS IS OF RED DEPOSITS ON UPPER(DOWNSTREAM) BUS BAR ON SPECIMEN 13

Element	Analyses, %	Element	Analyses, 🖇
Aluminum	0.5	Magnesium	0.1
Boron	<0.003	Manganese	0.4
Calcium	0.05	Molybdenum	0.05
Chromium	0.5	Nickel	0.1
Cobalt	<0.001	Silicon	0.2
Copper	0.05	Silver	0.005
Iron	Major	Sodium	<0.05
Lead	0.15	Tin	0.5
Lithium	<0.05	Titanium	<0.005
		Zirconium	10

Earlier it was thought that this red deposit might be a lithium compound, since no such deposit had been observed on specimen 3, the precrudded specimen from the ammoniated-water run. Less than 0.05 wt % lithium was found in the material, however, when the normal spectrographic analytical technique was used. Table 12 shows the results of the analyses. Characterization by X-ray diffraction proved that the material was hematite.

Identification and Characterization of Oxide Layers on Upstream Bus Bars

Yellowish to brownish-white nonadherent layers of oxide were observed on the upstream bus bars of all specimens used in both the ammoniated- and lithiated-water tests. The oxides formed in ammoniated water were much less extensive than those formed in lithiated water. The oxides contained chiefly zirconium, as shown in Table 13, and were identified as ZrO_2 by X-ray diffraction techniques.

]	Percent by	Weight			
	Ammoniated	Water	Lithiated Water			
	Specimens	2, 5	Specimens 13, 14, 15			
	Light-Colored	Darker				
Element	Deposit	Deposit	Mixed Sample			
Aluminum	-	-	0.2			
Boron	-	-	0.005			
Calcium	-	-	0.05			
Chromium		-	0.5			
Cobalt	-	-	<0.01			
Copper			<0.1			
Iron	1	1	0.7			
Lead	-	-	0.15			
Lithium	-	-	<0.05			
Magnesium	0.02	0.02	0.1			
Manganese	0.01	0.02	0.1			
Molybdenum		-	<0.01			
Nickel	-	. 🛥	0.05			
Silicon	0.05	0.05	0.01			
Silver	-	-	<0.03			
Sodium	-	-	<0.05			
Tin	1	2	1			
Titanium	teo.		<0.005			
Zirconium	Major	Major	Major			
Fluorine	<0.03	<0.03	-			

TABLE	13.	SPEC	TRO	GRAPHIC	C ANAI	LYS IS	OF	OXIDE	FOUND	ON
	UPSTR	REAM	BUS	BARS,	MSAR	LOOP	SPI	CIMENS	5	

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Determination of Hydrogen and Nitrogen in Metals From Test Specimens

The operation of the loop for 1000 hr, with test specimens exposed in ammoniated water, led to no visually or manually detectable embrittlement of the Zircaloy. On the contrary, rupture of one of the specimens during removal from the loop, after 211 hr of test in lithiated water, gave adequate warning that the high levels of hydrogen produced by corrosion reactions in this test had affected the metal. Hence it was felt that some quantitative measure of hydrogen pickup beyond that obtained from metallographic examination of etched specimens would be desirable. Accordingly, analyses of metal from all six specimens tested for both the ammoniated-water and lithiated-water tests were carried out. Determinations were by means of the vacuum fusion method.

Table 14 shows results of these tests. As was expected from the tensile test data and metallographic examination, the specimens run in ammoniated water showed no increase in hydrogen content over that normally found in Zircaloy that had undergone equivalent corrosion testing. On the other hand, material tested in lithiated water showed very great increases in hydrogen pickup, the values ranging from 690 ppm for the Zircaloy-4, precrudded, parallel-faced specimen to 3100 ppm for the Zircaloy-4, uncrudded, VEE specimen. It is interesting to note that specimens 14 and 15 are identical, except that 14 is made of Zircaloy-2 and 15 of Zircaloy-4. Under these conditions, hydrogen pickup was a factor of almost three higher than that for Zircaloy-2. This is contrary to what is normally considered to be the case for these two alloys.

Specimen	Hydrogen, ppr	n Nitrogen, ppn
Ammoniated	Water, pH 10.	5, 1000-hr Test
2	59	51
5	35	30
3	28	26
Lithiated	Water, pH 10.	5, 200-hr Test
14	1200	25
15	3100	47
13	690	24

TABLE 14. HYDROGEN AND NITROGEN CONCENTRATION IN MSA TEST SPECIMENS

Also, the precrudded specimen showed much less hydrogen pickup in lithiated water than did the Zircaloy-4, unprecrudded, VEE specimen, even though made of the same material. No explanation is offered for this effect.

Determination of Fluoride on Test Specimens*

Whether the nonadherent oxide deposits found on the upstream bus bars may have been caused by the presence of trace quantities of hydrogen fluoride is a question that has already been raised. One source of fluoride is Teflon, which is used for the insulating seals. Another possible source is the hydrogen fluoride pickling process, which is used prior to autoclaving the test specimens to obtain the black oxide corrosion film. For example, despite meticulous care in rinsing the pickled specimens, 0.1 to 2 ppm of hydrogen fluoride have been detected in the autoclave waters in which the acceptance corrosion tests on these and similar specimens vere run.⁷ Specifically, the autoclave water from test specimens 2 and 3 contained 0.14 ppm of fluoride. The total volume of the autoclave water was 13,000 ml. Therefore, the total fluoride in the autoclave water amounted to 1820 μ g. Furthermore, fluoride has always been found on normal corrosion-tested Zircaloy specimens.

For example, the Zircaloy ingot (HZC-1027) corrosion coupons, which are routinely pickled and autoclaved as control specimens, contained ~100 μ g of fluoride/dm² of surface. Unfortunately, a portion of test specimens 2 and 3 could not be destructively tested for surface fluoride content, just prior to insertion into the MSA loop. However, fluoride analyses were performed on the surfaces of some of the test specimens at the conclusion of the MSA test (Table 15). The sensitivity of the spectrographic fluoride values (s) in Table 15 is limited by the small amount of oxide available and therefore by the size of the sample taken for analysis. The results indicated that the cruds and white oxides contained no gross amounts of fluoride.

The chemical fluoride analysis, however, is more sensitive because a larger sample of material (if available) can be taken for analysis.** This is especially true in the case of bus bar 2 which contained two distinct areas of white oxide, (A and B in Tables 15 and 16) and a third

^{*}Written by J. Rynasiewicz.

^{**}According to the chemical method, the sample is oxidized in steam at 1100C. Hydrogen fluoride is carried along with the steam, which is then condensed. The hydrogen fluoride in the condensate is analyzed by a colorimetric method which has a sensitivity of 10 μ g of fluoride/100 ml of condensate. For a 1-gm sample, therefore, the sensitivity would be 10 ppm of fluoride.

TABLE 15. LIST OF SPECIMENS FROM MSA TEST CHECKED FOR FLUORIDE

Description	Test	Fluoride Found, ppm
Surface scale from crevice specimen 15 Deposits from upstream end of	ammoniated water	<300 (s)
crevice specimens		
Specimen 2 - light deposit	ammoniated water	<3000 (s)
Specimen 5 - dark deposit	ammoniated water	<3000 (s)
Composite white oxide from bus bars 13, 14, 15	lithiated water	10 (c)
Control sample. Unpickled chips from Zircaloy ingot. Sample NBS-360	not in MSA test	<10 (c)
Millings from bus bar 2, taken below crevice test specimen	ammoniated water	
A. White powder deposit plus adherent surface oxide	ammoniated water	105 (c)
B. White powder deposit plus adherent surface oxide	ammoniated water	127 (c)
C. Steel-gray, adherent sur- face oxide film	ammoniated water	<20 (c)
(s) = spect	rographic analysi	ls

(c) = chemical analysis

area that was steel-gray (C in Tables 15 and 16). For bus bar 2, surface millings, ~0.002 in. thick, were machined from the three areas and analyzed for fluoride by the chemical (pyrohydrolysis) method.

The results (Table 16) show that the white-oxide-covered areas contain at least three times as much fluoride as the normal-appearing, steel-gray surface, which was located under the Teflon seal and not exposed to the loop water. The interpretation of the data of Table 15 would tend to indict the fluoride as a possible culprit in causing the formation of the white surface oxide on the bus bars. Unquestionably, the fluoride content of the white-oxide-covered surfaces is at least three times greater than that of the unexposed virgin surface of the bus bar. However, the corrosion coupons tested during normal procedure at KAPL have been found to contain up to 150 µg of fluoride/dm² of surface compared with the 204

TABLE 16. ANALYSIS OF FLUORIDE ON THE SURFACE OF BUS BAR 2

L. Ta	ocation of Millings aken for Analysis	Total Area	Appearance of Surface from which 0.002-in.	Weight of Millings Taken	Fluor	ide Fou	nd
ab	ove Teflon Seal, cm	Milled, dm ²	Millings Were Taken	from Surface, gm	Total, µg	ppm	µg/dm²
A.	6 to 18	0.72	light white powder	1.3950	147	105	204
в.	21 to 40	1.14	light white powder	2.5768	330	127	290
с.	Specimen taken under Teflon seal	0.66	steel gray	2.2379	<44	<20	<67

Note: Fluoride analysis by pyrohydrolysis and colorimetric analysis of distillate (by Miss VF Consalvo).

and 290 μ g of fluoride/dm² found in this study. Coupled with the buildup of fluoride in the oxide is the fact that the structure, color, appearance, particle size, and degree of adhesion of the oxide to the substrate metal are not characteristics of normal adherent white oxide formed, in pile, by corrosion reactions. Rather, these characteristics are more like those of an oxide which is known to be formed on Zircaloy that has been improperly rinsed after pickling. Hence, one is forced to examine the strong probability that these layers of nonadherent, off-color oxide on the upstream bus bars of both tests may have been caused, at least in part, by the presence of fluoride, either released by decomposition of Teflon or of the original test specimen.

One cannot readily conclude that the source of the corrosive fluoride was from improperly pickled, rinsed, or autoclaved specimens. This possibility is eliminated because the portions of the bus bars that were upstream from the corrosion specimens contained no evidence of white product. Furthermore, the corrosion-tested coupons that were inserted into the MSAR loop as control specimens also contained no white product. This leads to the conclusion that the corrosion by fluoride was a localized phenomenon that was possibly controlled by other factors, such as temperature.

The most plausible theory is that the Teflon gradually released the fluoride at the point of contact with the Zircaloy. A zirconyl fluoride salt was formed at the Teflon seal. A propagation reaction ensued whereby zirconyl fluoride hydrolyzed to release hydrogen fluoride according to the reaction:

$$ZrOF_2 + 2HOH \rightarrow 2HF + ZrO_2$$
.

This, in turn, reacted with a fresh surface of Zircaloy according to the equation:

$$2HF + Zr + H_2 O \longrightarrow ZrOF_2 + 2H_2 O$$

This cycle repeated itself until cyclic losses of fluorine to the coolant and mechanical-hydraulic interruptions inherent in the geometry of the test specimen caused cessation of this cyclic process. It appears to be certain that this fluoride initiated white product, stopped at the end of the upstream bus bar, and did not form either on the crevice specimens themselves or on the downstream bus bar.

Normal appearance and strong adhesion were displayed by the oxide found within the crevices in the lithiated-water test. These same properties of the thinner layers were found over more localized areas beneath the boehmite deposited on specimens used in the ammoniated-water run. Finding these properties led to the conclusion that no fluoride

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effect was apparent in these more significant regions. No gross concentration of fluoride was observed in any oxide samples that were recovered from these regions. This fact lends strong support to the thesis that the ZrO_2 within the crevices and, in general, on surfaces of the thin-crevice test specimens was a "normal white product" type of oxide, as found in inpile tests and on surfaces of components taken from reactors. Further, the only significant concentration of normally adherent white product occurred within the confines of the test-specimen crevices. Therefore, the conclusion is obvious that such white product was formed as a result of crevice-corrosion processes involving some sort of concentration-cell mechanism.

Electron-Beam Microprobe Studies

<u>Surface Scans.</u> The surface scale on the high-heat flux regions of specimens used in the MSAR loop test was examined, using the electron-beam microprobe. Qualitative scans were made on distinctly different areas. Data in the previous parts of this report have made use of information from these qualitative scans when the information was deemed valuable. Zirconium, aluminum, iron, and chromium were found in varying amounts in oxide layers of all specimens.

Specimen 13, however, was examined in detail for concentration in the varying strata of significant elements that could be observed under the optical microscope. On this precrudded specimen, a brownish-gray top layer seemed to contain the principal elements expected from the deposited iron-base crud. In addition, this layer contained some aluminum that presumably came from trapped alumina particles that had been carried into the loop from the charging pump during the previous run, before the ceramic parts in this pump had been replaced.

A second layer consisted largely of the elements from iron-base crud, with some increase in zirconia and apparently (Table 17) less alumina. The third layer examined consisted mainly of iron-base-crud residues with some aluminum oxide. For some unknown reason, a deeper layer below the iron contained a high aluminum deposit which was probably localized. (It is likely that this layer was exposed to coolant during a part of the short 200-hr run.) Beneath this layer, the material contained zirconium oxide as its principal ingredient, with some contamination by aluminum in admixture with the off-colored zirconium oxide.

If one reconstructs the action that probably occurred in this crevice during its 200-hr operative history, it is seen that the originally deposited synthetic crud may have been partly washed off and dislocated as the water boiled and diffused in and out of the crevice. Distillation probably raised the LiOH concentration to a pH near 12 or so, and some hydrated alumina was deposited from the loop water in admixture with the iron-base crud. At the high temperatures existing in the crevice (between 587 and 700F) and at the high pH, pitting took place and white

from Surface	Layer Identification	Zircaloy	<u>Iron</u>	Chromium	Aluminum
l	Brown-gray Brown-gray Brown-gray	10 12 -	22 20 8	25 24 7	- 33
2	Steel-gray				
	Top Middle Lower	2 16 1	8 1 4	29 8 7	- -
3	Red-brown Red-brown Red-brown	6 7 11	<0.5 47 66	- 8 5	15 - -
4	Red-white	m	t	-	М
5	Grains, white Grains, white Grains, white	77 82 74	0.7 0.7 <0.5	<0.5 <0.5	- - <0.5
6	White areas on base				
	Gray Fluffy Fluffy	M M M	<0.5 <0.5 <0.5	- - -	M M m
7	Base metal	98	t	t	ND
	Code: M - ma; m - mir t - tra ND - not	jor constit nor constit ace (1 to 2 detectabl	uent (ov uent (un percent e.	ver 10 perce nder 10 perc , estimated)	ent) cent)

TABLE 17. TABULATION OF ELECTRON-BEAM-MICROPROBE X-RAYRELATIVE INTENSITIES FOR SPECIMEN 13

Position

product began to form under these oxide deposits. A concentration-celltype, crevice-corrosion mechanism was probably set up, resulting in pitting and white oxide formation. Judging by the relative scarcity of zirconium oxide, unmixed with other oxides in the pits, some of this zirconium oxide may have reacted with LiOH to form a zirconate that subsequently decomposed throughout the crud layer. This action accounts for microprobe results that in some locations indicated the existence of relatively higher concentrations of zirconia in oxide layers farther from the base metal than would be expected on the basis of the following: (1) all zirconium oxide being formed in situ by corrosion, (2) all alumina being transported and deposited by coolant, and (3) all iron being a part of either the original synethetic crud deposit or a coolant-transported corrosion product from metal walls of the loop.

Profile Scans of Transverse Metallographic Mounts of Specimens 14, 15, and 13. To establish more firmly the composition of oxide layers that were found on metallographic mounts for specimens 14, 15, and 13, electron-beam microprobe profile scans were run across selected regions

of the transverse faces of some of these mounted specimens. Such profile scans also permitted precision location of boundaries between different oxide layers and hence aided in determining depths of metal penetration by oxidizing agents in the coolant at these selected points.

In order to locate the regions that were scanned with the electron beam, reference is again made to Figure 46. The electron beam was scanned across selected profiles of areas marked as 3, 4, and 10 on this figure.

Figure 56 localizes the lines surveyed in these profile scans. Picture A of Figure 56 shows a 250X magnification of region 3, which is a portion of specimen 13. Picture B in the same figure displays the area marked 4 on Figure 46. This picture shows the location and direction of an electron-beam scan across the deep oxide layer found in this region; this layer was deposited on the surface of the lower part of specimen 14 (this was the Zircaloy-2, VEE-crevice specimen). Picture C shows the orientation and location of the electron-beam scan across the oxide layer on the lower portion of specimen 15 (Zircaloy-4, VEE, Region 10, Figure 46).

Graphical representation of data from one electron-beam scan, described by Figure 56C on specimen 15, is given in Figure 57. For example, the Y-axis of the grid superimposed on Figure 56C shows that the major metallic component in the first 4.5 mils of oxide above the metal is zirconium; hence this portion of the oxide is ZrO_2 . From 4.5 mils on this grid to 5.5 mils, the material has aluminum and chromium as its major metallic components and is therefore undoubtedly Al_2O_3 , contaminated by crud from the stainless steel loop.

Data for all three of the profile scans shown in Figure 56 are given in Table 18.

Table 19 summarizes the results of the data of Table 18 in terms of the thickness of the zirconia layer at the trace-plane on these transverse mounts. In addition, on the assumption that the $2rO_2$ was originally 100-percent dense, calculations were made to determine the thickness of the

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	Co	mposition*	Distance above Metal-Oxide	
Specimen	Zirconium	Aluminum	Chromium	Interface, mils
13	Major	Minor	Minor	0 to 4.75
	Minor	Major	Major	4.75 to 5.5
14	Major	Minor	Minor	0.to 7.5
	Minor	Major	Major	7.5 to 7.8
15	Major	Minor	Minor	0 to 4.5
	Minor	Major	Major	4.5 to 5.5

TABLE 18. ELECTRON-BEAM MICROPROBE SCAN OF OXIDE LAYERS DISPLAYED IN FIGURE 56

*Judged by height of graphical trace on original recorder version of graphs similar to that of Figure 57.

	T	Thickness, mils				
Specimen	Zirconia	Zircaloy	Alumina			
13	4.75	3.3	0.75			
14	7.5	5.2	0.3			
15	4.125	2.9	1.0			

metal that was eaten away. These numbers are also recorded in Table 19. The third column of data given in Table 19 shows thicknesses of alumina or iron-base crud deposited on top of the zirconia layer.

Water Analysis for Loop Coolant Used in Test with Lithiated Water

The data of Table 20 were obtained by Spectrochemical Laboratories, Inc. of Pittsburgh, Pennsylvania; this laboratory was retained by MSAR to analyze a water sample taken from the loop during the test with lithiated water, after removal of the alumina parts from the charging pump.

OF SOLIDS WITHOUT STANDARDS Loop Water January 25, 1962 Percent of Total Solids* Composition Li_20 Major 25.0 Al_20_3 Cr_2O_3 1.0 2.0 Fe₂0₃ MgO 0.10 MnO 0.002 $Si0_2$ 0.25 Pb0 0.01 Sn02 0.005 Mo03 0.01 V205 0.001 0.05 CuO ZnO 0.01 NiO 0.001 CaO 0.50 Note: not detected; Cd, As, Te, P, Be, B, Ge, Ti, Zr, Ba, Sr, Bi, Co, F. *Data given as percent of total solids which were 0.0036 percent by weight in water sample.

TABLE 20. QUALITATIVE SPECTROGRAPHIC ANALYSIS



A. Specimen 13

Scan Vector



B. Specimen 14



FIGURE 56. Photomicrographs Locating Electron-Beam Microprobe Scans on Specimens 14, 15, and 13, 250X.

KS-46273

Unclassified





FIGURE 57. Sketch of Recorder Trace for Electron-Beam Microprobe Analysis for Specimen 15, Figure 56C. KS-46274 Unclassified



DISCUSSION*

This MSAR loop test was a crevice-corrosion test of Zircaloy-2 and Zircaloy-4. The test was run under conditions simulating reactors that boil in hot vertical channels. The effect of crud deposition was simulated on one specimen in each test. Water conditions were those most commonly found in modern boiling reactor plants or, more especially, those pressurized, water-cooled plants where some nucleate boiling is permitted or where bulk boiling occurs in the hot channels.

The test was divided into two parts. The first part was a 1000-hr run in water whose alkalinity was controlled at pH 10.5 \pm 0.1 with ammonium hydroxide; the second part was a test limited to 211 hr by rapid corrosion, in which the pH was maintained in the same range as for the ammoniated-water test, using lithium hydroxide.

A study of the effects of crevices on corrosion of these zirconium alloys under the specified conditions was the primary purpose of these tests. Therefore, a brief summary of the theory of crevice corrosion is of interest. This theory is discussed by de Paul⁶ at some length for iron-base alloys and similar structural materials. Since Zircaloy, like stainless steel, normally protects itself from water attack by the formation of a thin oxide film, the same mechanisms discussed by de Paul for crevice corrosion of stainless steel might be assumed to become active.

According to de Paul, the three types of corrosion active in metal crevices are (1) the metal-ion cell, (2) the oxygen cell, and (3) stagnant area corrosion.

The first mechanism named, the metal-ion cell, results from galvanic currents arising in a region where differential concentrations of metal ions can be built up and maintained. "Corrosion occurs at those points where the current leaves the metal. In metal-ion cell corrosion in crevices, the current travels from the metal outside the crevice to the metal inside the crevice. Therefore, the corrosion products will form at the mouth of the crevice or at the perimeter of the contact area."**

The second type, oxygen-cell corrosion, results from corroding currents that arise at those points where a differential oxygen concentration results. In this case, the corroding current travels from the oxygen-starved region to the metal surface. Therefore, in contrast to the metal-ion cell, the accelerated attack would be expected to occur at the entire interface surfaces of both walls of the crevice, rather than at the mouth of the crevice.

*Written by W. K. Anderson. **Direct quote from Reference 6, p. 148. Both of these forms of cell-type crevice corrosion can be controlled only by elimination of crevices from the design or by ensuring a maximum flow of fresh water through the crevice.

The third type, stagnant area corrosion, is not normally considered a form of crevice corrosion. However, it should certainly be a factor in corrosion of metal in crevices not subject to forced coolant flow. Stagnant area corrosion, as specifically related to crevices, may be defined as a generally accelerated attack that may occur within the crevice. This type of corrosion results primarily from an accumulation of higher concentrations of ionic species than exist in surrounding regions. Any mechanism that tends to produce such a difference in concentration of ionic species within a restricted flow area should likewise contribute to an increase in corrosion rate within the crevice or stagnant region.

The modifications in behavior implied by the Chirigos and Thomas mechanism.¹ as compared with the behavior of stainless steel under corrosive attack by water. may deserve some consideration. However, there are inadequate theoretical grounds and certainly inadequate data from this experiment on which to base any firm statements as to the mechanisms involved. The data, however, surely point to the fact that the corrosion observed would not have taken place in the absence of boiling. This fact is essentially verified by lack of any significant attack on the control coupons previously discussed. That the crevice geometry was significant is strongly indicated by the following: (1) the presence of white product and pitting in crevices, (2) the lack of significant observable pitting on the outside of the crevice specimens, and (3) the lack of observable accelerated corrosion on downstream bus bars that must have been kept at temperatures only slightly lower than at the outer surfaces of the crevices themselves.

One aspect of this experiment must be questioned, i.e., the effect that electrically heated specimens may have on the results. This question is always raised when corrosion tests are carried out with electrical self-heating of specimens. Wanklyn and Jones⁴ discussed this question and concluded that, with alternating-current heating, no significant electrolytic effects would occur.

This general discussion should point out the two other areas of uncertainty that have been mentioned in the body of this report.

The effect of aluminum oxide crud in the crevice interiors of the specimens used in the ammonium-hydroxide-controlled test is quite difficult to assay. Certainly this compound is soluble to some extent in water and hence would furnish either OH⁻ ions or aluminate ions to implement a concentration-cell mechanism. The point has already been made, however, that in actual reactor operation over longer periods of time, there would be other sources of ions if aluminum were absent. The implication is that a crevice would be likely to cause accelerated corrosion even without the presence of aluminum in the system. The alumina may have intensified or accelerated the effect, however. There is an encouraging aspect of this test: even with the potentially accelerative effect of the alumina present during the test, penetration of Zircaloy (particularly Zircaloy-2) by coolant attack in the ammoniated-water test was quite insignificant.

Attention is directed next to the effect of small quantities of hydrogen fluoride that may have been released by thermal dissociation of Teflon. The thermocouples located near the Teflon seals in the MSAR loop (Figure 1) showed an average temperature of 240F with the loop on stream. A dead-water space tended to cool the bus bars that emerged from the reaction chamber through the Teflon seal. However, the temperature of the inside surfaces of the Teflon in contact with the lower bus bars should have been in the range 240 to 580F. An estimate of 400F should be fairly accurate. Based on the duPont information at this temperature, no significant thermal decomposition should have occurred. The nature and fluoride content of the oxide deposit on the upstream bus bars, however, cast some doubt on this question. No exact estimate on the extent of this effect can be made with existing data. However, the appearance, composition, and properties of all zirconium oxide layers, other than the "chalky" areas on the upstream bus bars, were conclusively those of normal white product seen in in-pile loops. Therefore, the conclusion is obvious that fluoride ion had no part in their production.

In the following discussion on the extent of such dissociation, duPont sales literature on the stability of Teflon may be quoted: "It (Teflon) can be used at temperatures from -265 to $+315^{\circ}$ C. It is inert, even at elevated temperatures to practically all chemicals except fused alkali metals, and fluorine and chlorine tri-fluoride at elevated temperature and pressure. Excellent durability has been indicated by accelerated aging tests, including heating for prolonged periods at 315° C. When heated above 260° C, it is recommended that Teflon be used under a hood or in a well-ventilated area as traces of the tetrafluoroethylene monomer may be given off. The plastic changes to a transparent gel above 325° C, and significant decomposition occurs above 400° C. Vessels (made of Teflon) can be heated by means of ovens, baths, and hot plates with a protective asbestos pad, provided the temperature of the plastic is not allowed to exceed 315° C."

No information has been found on the behavior of Teflon in the presence of high-temperature water. However, at temperatures in the

range in which the fluorocarbon monomer is given off, it seems reasonable that this compound might react with water by some scheme such as

$$\begin{array}{c} \overset{H}{\operatorname{RCF}} + \operatorname{HOH} & \longrightarrow \overset{H}{\operatorname{RCOH}} + \operatorname{2HF} \\ \overset{H}{\operatorname{OH}} \end{array} .$$

Thus, hydrogen fluoride gas would be released. By such means it would be possible to initiate the zirconyl fluoride oxidation chain proposed by Rynasiewicz under "Determination of Fluoride on Test Specimens," p. 94.

Literature (duPont) insists that such dissociation "does not begin until 260°C (500F)." However, no information is available on the method used by duPont chemists to assay the extent of this dissociation. The possibility certainly exists that some fluorine or fluorine compounds might be slowly released at temperatures significantly below 580F, the operating temperature of the loop test sections.

The photomicrographs presented throughout the text are thought to contain maximum penetration depths for each specimen tested. Reasonable care, consistent with other needs for metal from the crevice specimens, was exercised to ensure this to be true.

Two methods were used in measuring these penetration depths. In the case of the tests in ammoniated water where pitting was quite localized, where the specimens were not distorted, and where such measurements were obviously valid, direct measurement of metal loss was undertaken. On the other hand, with the specimens from the lithiated-water tests, where general-coverage attack had taken place and where gross distortion of the specimens made the first method difficult or impossible, the alternate scheme of measuring oxide thicknesses and converting to metal penetrations was necessary.

Although many such measurements were made, absolute assurance cannot be extended to the reader that the maximum depth of penetration was actually found in each case. Particularly for the specimens from the lithiatedwater test, this point may be in some doubt. However, the conclusions are believed to be reasonably accurate.

On a good contact print of the negative, differentiation between alumina crud deposits and ZrO_2 corrosion product was not difficult, particularly after the negative had been taken by careful observation of its field under polarized light. Verification of several points by use of the electron-beam microprobe has already been discussed.

Data are presented in Table 21. These data show that with VEE-shaped crevices, penetration was a factor of three to five greater for the lithiated-water test. This statement is based on the data as presented in Table 21 and ignores the difference in exposure time. When this additional factor is considered, another factor of five becomes involved

Specimen	Material	Specimen Type	Water Chemistry, pH Agent	Depth, mils
2	Zircaloy-2	VEE	NH₄OH	1.0 *
5	Zircaloy-4	VEE	NH₄OH	2.0*
3	Zircaloy-4	Parallel	NH₄OH	0.2*
		face	-	~ ~
14	Zircaloy-2	VEE	LiOH	5.2
15	Zircaloy-4	VEE	LiOH	5 . 9**
13	Zircaloy-4	Parallel	LiOH	2.9 ^{**}
		face		
*Meas	urement of pi	lt depth fro	om extended s	ur-

TABLE 21. MAXIMUM CORROSION PENETRATION FOUND ON MSAR SPECIMENS

face of metal.
**Calculated pit depth from measured thickness
of oxide layer assuming 100-percent density
of ZrO₂.

and, in terms of calculated penetration rates, the lithium-hydroxidecontrolled rate becomes at least an order of magnitude higher than the rate for the ammonium-hydroxide-controlled case.

In both cases, the parallel-faced crevice showed lower penetrations than did the VEE crevices. Whether this can be ascribed to the more open crevice structure, or to the fact that the parallel-faced crevices were precrudded prior to insertion, must remain an open question in the light of existing data. There is, however, an important consideration that should be discussed at this point. The principal reason for testing these precrudded specimens was the frequently expressed fear that the presence of crud, per se, would cause an accelerated attack. The data indicate that such accelerated attack did not occur.

The case for the comparison of Zircaloy-2 and Zircaloy-4 is not quite so clearly defined. In the ammonium-hydroxide-controlled case, a comparison of specimens 2 and 5 on the basis of their comparable geometry, shows that the Zircaloy-2 apparently suffered less penetration. The worst case of metal loss noted in this ammoniated-water, pH-controlled study was observed near the closed edge of the VEE on the Zircaloy-4 specimen (no. 5). In the case of the lithiated-water test, the two values in Table 21 are quite close and therefore might be thought not to indicate a real difference. However, when the data on hydrogen pickup given earlier are considered, it becomes apparent that the Zircaloy-4 suffered the greater attack. If the assumption is made that the two zirconium alloys absorbed locally the same percentage of total corrosion-produced hydrogen, then the fact that the Zircaloy-4 specimen was shown to contain 3100 ppm of hydrogen against 1200 ppm for Zircaloy-2 definitely indicates that the slightly greater depth of penetration recorded for Zircaloy-4 in Table 21 is a real effect.

This discussion can be terminated by summarizing the more significant results that have been presented in the body of this report.

In the 1000-hr ammoniated-water test, crevices were filled with deposits of hydrated aluminum oxide (boehmite), believed to have been transported into the loop from ceramic parts in a coolant charging pump. Underneath the alumina deposits, much of the metal was unharmed. In certain areas, however, particularly near closed edges of VEE-shaped crevices and under some heavily crudded regions in the parallel-faced specimen, pitting and loss of metal occurred. The maximum pit depth found was ~0.002 in. and occurred near the closed edge of a Zircaloy-4 VEE. Normal white oxide formation underneath the boehmite deposits accompanied the pitting on these specimens. In no case, even with the added probability of metal-ion concentration cells introduced by the presence of aluminum, was corrosion really serious in this test.

Rapid corrosion ensued from almost the beginning of the 211-hr test in lithiated water. Such corrosion was detected by a relatively continuous and quite rapid increase in the resistance of the electrically heated specimens and by an accompanying increase in hydrogen concentration in the loop water. The specimens were highly embrittled by hydrogen pickup. The Zircaloy-4, VEE-crevice specimen was so brittle that it was fractured during removal from the loop. Deep pitting was observed on all three specimens, with as high as six to eight mils of accumulated white oxide in some pits.

No significant hydrogen pickup in these boiling crevice specimens was observed in the ammoniated-water test. For the much shorter lithiatedwater test, however, extreme hydrogen pickup was found both by chemical analysis and by metallographic examination. Based on chemical analysis, the Zircaloy-4 specimen picked up 3100 ppm of hydrogen in 211-hr exposure to lithiated water; Zircaloy-2 had accumulated only 1200 ppm under identical circumstances.

It becomes apparent that, over the longer period of time in which a reactor core would operate, some sort of crud deposit or stagnant area

corrosion mechanism might function in one way or another to cause pitting in crevices exposed to boiling water. A design is suggested in which all essential crevices be protected by excluding them from flux regions where boiling may occur.

On bus bars that were in contact with Teflon insulating seals in the loop, nonadherent white corrosion product was found after the test. (In lithiated water, coverage of surface was total, and the deposit was quite thick; in ammoniated water, only partial coverage with thin deposits was observed.) This product resembled that known to occur in poorly rinsed Zircaloy specimens that retained residual fluoride from the pickling bath. No definite proof was found that this oxide was caused by hydrogen fluoride released by pyrolysis of Teflon. A reasonable probability exists that such was the case. It seems doubtful, however, that this factor contributed to the pitting and white oxide formation within the crevices. This view is given added strength by the difference in appearance and structure of the two oxide layers, together with the failure to find any fluoride in the oxide material in the crevices.

Certain work on Zircaloy corrosion, under way at present at the Bettis Atomic Power Laboratory, may be of help in the interpretation of results for the lithiated-water experiment. Chirigos reports⁸ that lithium hydroxide in higher concentrations rapidly attacks Zircaloy. His data show that when Zircaloy is immersed in lithium hydroxide solution in concentrations between 0.5 and 1.0 molar at a temperature of 680F, weight gains as high as 10,000 mg/dm² may be produced in 10 days' exposure. Such weight gains would be equivalent to very deep penetrations. For instance, weight gains in the neighborhood of 3000 mg/dm² would be equivalent to metal penetrations close to those found in the lithiatedwater test for specimens 14 and 15. This information tends to lend weight to the opinion that the increased corrosion observed in the lithiated-water test may be due to concentration of lithium hydroxide in these closed channels by a distillation column effect.

The use of copper or nickel bus bars fastened to Zircaloy test sections by eutectic diffusion bonding has been proposed frequently for use in electrically heated high-heat flux tests. A trial of this proposal during early stages of the experiment led to expensive failures of the specimens. The second design proposal consisted of cladding copper bus bars with Zircaloy. Such proposals in the past had been rejected because of the undesirable ratio of thermal-expansion coefficients of the two materials. However, since no alternate combination occurred to the designers of this experiment, this presumably radical design was adopted and has, for the duration of this test, performed beautifully. The following conclusions can be presented as being applicable under nucleate boiling conditions, in systems where upward-directed vertical flow occurs and, in particular, where crevices or stagnant flow regions exist.

- 1. Either Zircaloy-2 or Zircaloy-4 will undergo crevice corrosion in closed vertical channels under boiling heat transfer conditions at temperatures near 587F.
- 2. Much more drastic attack occurs in lithiated water than in ammoniated water. In pH 10.5 ammoniated water, even in the presence of deposited boehmite crud, pitting and white corrosion product formation were relatively minor. Such effects might not occur where no ionic or soluble materials are available in loop water, since these materials may concentrate in crevices and form metal ion or other types of concentration cells. Extensive whiteproduct formation and pitting will take place on reactorgrade Zircaloy surfaces that are in contact with high pH lithiated water under boiling conditions.
- 3. Hydrogen pickup and embrittlement will not occur in ammoniated water. In lithiated water, on the contrary, drastic embrittlement will occur. Hydrogen pickup can become extreme, as evidenced in this test by metallographic analyses, mechanical property tests, and chemical analyses.
- 4. Zircaloy-2 appears to be somewhat superior to Zircaloy-4 in its corrosion performance under boiling conditions, even with ammoniated water. With lithiated water under boiling conditions, Zircaloy-4 appears to lose its superiority even in resistance to hydrogen pickup and embrittlement, when exposed to boiling under crevice conditions in vertical channels.
- 5. The presence of crud deposits in Zircaloy crevices did not increase the rate of attack by coolant within such crevices.

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APPENDIX A. SAMPLE CALCULATIONS

Several types of engineering calculations were essential to design and operation of the crevice-corrosion test. Samples of some of these calculations, as used in carrying out the test, are included below.

HEAT BALANCE ACROSS TEST SECTION

Temperature, Flow, and Electrical Measurement Data at Subcooled Conditions

```
Water temperature
                                          580F
     Pressure
                                          1400 psia
     Specific heat, liquid (cp)
                                          1.31 Btu/16F
     Flow rate (w)
                                          1470 lb/hr (one test section)
     Temperature difference (\Delta T)
                                          4.8F
     q = w \times cp \times \Delta T = 1470(1.31)(4.8) = 9240 Btu/hr
     Estimated heat loss by electrical power input to maintain outlet
     temperature equal to inlet temperature, or \Delta T = 0.
     Temperature: inlet = 580F; outlet = 580F
     Amps = 1.9 \times 160 = 300
     Volts = 5.6
     Power (P) = amps \times volts = 300 \times 5.6 = 1700 watts
     Heat loss (q_{I}) = 1700 watts x 3.415 Btu/watt = 5800 Btu/hr
     Total heat dissipated (q_T) = q + q_L = 9240 + 5800 = 15,040 Btu/hr
Electrical Measurement Data at Operating Conditions
     Amps = 600
     Volts = 9.9
     P = amps \times volts = 600 \times 9.9 = 5940 watts
     Total heat dissipated (q_T) equals
              5940 watts x 3.415 Btu/watt-hr = 20,300 Btu/hr
```

ESTIMATED PERCENT OF SPECIMEN SUBJECTED TO NUCLEATE BOILING CONDITIONS

$\Delta T(subcooled)$	=	4.8F	(average	value)
$\Delta T(nucleate boiling)$	Ξ	2.6F	(average	value)
Percent subjected to boiling	2	<u>4.8 -</u> 4.8	$\frac{2.6}{3} \times 100$) = 46%

QUALITY STEAM GENERATED

Pressure (P)	1400 psia
Temperature (T)	587F

Specific heat, liquid (cp) 1.31 Btu/16F Enthalpy, saturated steam (h) 1173 Btu/16 lb Flow rate (w) 1470 lb/hr Superheat (dt) 4.8 - 2.6 = 2.2FSuperheat available for vapor $(q_{sh}) = wc_p dt$ $q_{sh} = 1470 (1.31)(2.2) = 4240 Btu/hr$. Pound steam generated (w_s) = q_{sh}/h $w_s = 4240/1173 = 3.16 lb/hr$.

Percent quality = $3.6/1470 \times 100 = 0.25\%$ quality stream.

SPECIMEN OUTSIDE WALL TEMPERATURE

Jens	s and Lottis Equation	for Wall Supe	rheat in Local Boiling
∆T _s =	$\frac{60(Q/10^6)^{0.25}}{e^{P/900}},$	where:	Q = 500,000 Btu/hr-ft ² P = 1400 psia e = 2.718 .
$\Delta T_s =$	60(500,000/10 ⁸) ^{0.25} e ^{1400/900}	<u>60(0.5)^{0.25} e^{1.555}</u>	$\frac{60(0.842)}{4.73}$,
where	$\Delta T_{s} = 10.7F$ $\Delta T_{s} = t_{w} - t_{s}$ $t_{w} = \Delta T_{s} + t_{s}$ $t_{w} = 10.7 + 587$	t _w t _s t _w	= 597.7F = saturation temp. = 587F = wall temperature .

SPECIMEN RESISTANCE CHANGE

Ammoniated-Water Run				
Specimen No. 5 (Test Section 1)	$\frac{0.0161 \text{ ohms} - 0.0157 \text{ ohms}}{0.0157 \text{ ohms}} \times 100 = 2.54\%$			
Specimen No. 2 (Test Section 2)	$\frac{0.0167 - 0.0163}{0.0163} \times 100 = 2.39\%$			
Specimen No. 3 (Test Section 3)	$\frac{0.0156 - 0.0155}{0.0155} \times 100 = \frac{0.65\%}{5.58\%}$			
Average = $\frac{5.58\%}{3}$ = 1.9	% change in electrical resistance.			

Specimen No. 14 (Test Section 1)	$\frac{0.0181 - 0.0162}{0.0162} \times 100 = 11.72\%$
Specimen No. 15 (Test Section 2)	$\frac{0.0192 - 0.0167}{0.0167} \times 100 = 14.95\%$
Specimen No. 13 (Test Section 3)	$\frac{0.0182 - 0.0165}{0.0165} \times 100 = \frac{10.30\%}{36.97\%}$
36.97%	

Average = $\frac{36.97\%}{3}$ = 12.3% change in electrical resistance.

