EURAEC-2016
BAW-3765-7
Joint U.S. - Euratom
R&D Program
January 1969

CORROSION AND HYDRIDING OF ZIRCALLOY

— Task 1 Final Report —

Corrosion and Hydriding of Zircaloy
Under Heat Transfer Conditions

by

M. M. Rubright
D. W. Koch
K. M. Ferguson

B. W. Whitaker
Project Manager

C. R. Johnson
Technical Manager

AEC Contract No. AT(30-1)-3765
B&W Contract No. 859-3101

Performed for
THE UNITED STATES ATOMIC ENERGY COMMISSION
by

BABCOCK & WILCOX
Research & Development Division
Research Center
Alliance, Ohio

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Babcock & Wilcox

[Handwritten signature]

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

**THIS PAGE
WAS INTENTIONALLY
LEFT BLANK**

ACKNOWLEDGMENT

The water chemistry analyses and the hydrogen analyses were performed under the direction of F. J. Pocock and J. W. Fox, respectively, of the Chemical Section. The end-of-life specimens were prepared by L. B. Gross of B&W's Nuclear Development Center.

LEGAL NOTICE

This document was prepared under the sponsorship of the United States Atomic Energy Commission pursuant to the Joint Research and Development Program established by the Agreement for Cooperation signed November 8, 1958 between the Government of the United States of America and the European Atomic Energy Community (Euratom). Neither the United States, the U. S. Atomic Energy Commission, the European Atomic Energy Community, the Euratom Commission, nor any person acting on behalf of either Commission:

- A. Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this document, or that the use of any information, apparatus, method, or process disclosed in this document may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method or process disclosed in this document.

As used in the above, "person acting on behalf of either Commission" includes any employee or contractor of either Commission or employee of such contractor to the extent that such employee or contractor or employee of such contractor prepares, handles, disseminates, or provides access to, any information pursuant to his employment or contract with either Commission or his employment with such contractor.

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

SUMMARY

The favorable nuclear properties, strength, and corrosion resistance of the zirconium alloys have led to their widespread use as fuel element cladding in water-cooled power reactors. There has been a steady increase in reactor operating temperatures and a lengthening of service life, however, over the conditions prevailing at the time the alloys were first placed in service. It is important that the ultimate performance limits of these alloys be established early enough in the development of reactor technology to permit the initiation of alternate technology if this is found necessary.

During service in water cooled reactors, Zircaloy cladding corrodes and absorbs some of the hydrogen released by the corrosion reaction. The corrosion rate of Zircaloy in high purity water at the temperatures of pressurized and boiling water reactors is not the limiting criterion in the application of this material. However, hydrogen does adversely affect certain mechanical properties of Zircaloy, and excessive hydrogen absorption during service could degrade those properties to the extent that either the operational conditions or the cladding life would have to be limited.

The program reported here was undertaken to determine the corrosion and hydriding characteristics of Zircaloy-4 under operating conditions simulating those expected in advanced water reactors. A number of 0.420-inch-diameter tubular Zircaloy-4 and Zircaloy-2 specimens were exposed to 640 F water in a high pressure dynamic loop. The coolant pressure was 2250 psi and the velocity past the specimen was about 13 fps. Special heaters inserted in the specimens gave surface heat fluxes of 600,000 Btu/hr-ft² over a 6-inch section. Isothermal specimens exposed to the loop coolant and isothermal specimens exposed in an autoclave maintained at 650 F - 2950 psi provided comparative data.

The program was divided into two test phases. In the first, specimens were exposed to high purity water for periods of 15 to 180 days. In the second phase, the effect of chemical shim control practices on the corrosion and the hydrogen absorption rates was evaluated; specimens were exposed for 51 days to a coolant containing 13,000 ppm boric acid, 4 to 6 ppm potassium hydroxide, and 0.5 ppm lithium hydroxide. Both coolants contained 20 to 40 cc per liter of added hydrogen. Two types of pre-exposure surface treatments were tested: standard pre-filming with 750 F - 1500 psi steam for 72 hours, and a simulated end-of-life condition obtained by artificially gas-hydriding and air-oxidizing specimens to an oxide thickness of 250 mg/dm² and 250 ppm of hydrogen.

The results of an earlier program conducted by B&W on similar specimens at a heat flux of 450,000 Btu/hr-ft² indicated that the corrosion of Zircaloy-4 under heat transfer conditions was equivalent to that measured under isothermal conditions if the metal surface temperatures were the same. However, the heat transfer specimens absorbed about 2-1/2 times more hydrogen than the isothermal specimens did. Experimental conditions were thought to be responsible for the discrepancy, and some of the experimental techniques were changed in this program to eliminate such uncertainties.

Results from the current test program are as follows:

1. The corrosion rates of Zircaloy under heat transfer and isothermal conditions are essentially the same.
2. More hydrogen is absorbed under heat transfer conditions than under isothermal conditions.
3. The presence of dissolved hydrogen in the coolant in concentrations of 20 to 40 cc per liter does not affect the hydrogen absorption rate.
4. The presence of chemical shim control solids did not affect the corrosion rate or the hydrogen absorption rate under the short-term conditions of the test.
5. Shim control chemicals did not concentrate on the cladding under the short-term conditions of the test.

CONTENTS

	Page
1. INTRODUCTION	1
1.1. Background	1
1.2. Previous Work	3
1.3. Test Objective	5
2. TEST EQUIPMENT	6
2.1. General Arrangement	6
2.2. Heat Transfer Tests	7
2.3. Loop Control Tests	9
2.4. Isothermal Autoclave Tests	10
3. TEST PROCEDURE	17
3.1. Loop Operation	17
3.2. General Specimen Details	17
3.3. Heat Transfer Tests	19
3.4. Loop Control Tests	22
3.5. Isothermal Autoclave Tests	23
3.6. Post-Test Examination	24
3.7. History of Test Operation	25
4. RESULTS	46
4.1. General	46
4.2. Oxide Measurements	48
4.3. Hydrogen Content	50
4.4. Hydrogen Gradient Analysis	51
4.5. Hydride Distribution	52
5. DISCUSSION	128
6. CONCLUSIONS	130
7. REFERENCES	132

List of Tables

Table	Page
3-1. Test Conditions	28
3-2. Certified Mill Report for Specimen Stock — Zircaloy-4 . . .	29
3-3. Certified Mill Report for Specimen Stock — Zircaloy-2 . . .	30
3-4. Certified Mill Report for Zircaloy-4 Material Used for Heat Transfer Flanges	31
3-5. Certified Mill Report for Zircaloy-4 Material Used for Heat Transfer End Plugs	31
3-6. Specimen Exposure Data	32
4-1. Metallographic Measurement of Oxide Thickness — Prefilmed Specimens	60
4-2. Metallographic Measurement of Oxide Thickness — End-of-Life Specimens	61
4-3. Corrosion Data for Heat Transfer Specimens	62
4-4. Corrosion Data for Loop Control Specimens	62
4-5. Corrosion Data for Isothermal Specimens	63
4-6. Hydrogen Absorption Data for Heat Transfer Specimens . .	64
4-7. Hydrogen Absorption Data for Loop Control Specimens . . .	64
4-8. Hydrogen Absorption Data for Isothermal Specimens	64
4-9. Hydrogen Absorption Under Different Conditions	65
4-10. Hydrogen Absorption Data for Heat Transfer End Plugs . . .	65

List of Figures

Figure	
2-1. Loop Flow Diagram	11
2-2. Test Loop and Control Panels	12
2-3. Heat Transfer Test Sections	12
2-4. Heat Transfer Specimen in Operation	13
2-5. Heat Transfer Test Section Diagram	14
2-6. Heat Transfer Specimen With Flange and Heater	15
2-7. Heat Transfer and Loop Control Specimens in Exposure Configuration	16
2-8. Junction Between Heat Transfer and Loop Control Specimens	16
3-1. Layout of Specimens as Cut From Tubing	33
3-2. Complete Array of Samples After Pickling	33
3-3. Gas Hydriding Apparatus — Photograph	34
3-4. Gas Hydriding Apparatus — Diagram	34
3-5. Assembly for Prefilming Specimens — Heat Transfer Specimens	35
3-6. Assembly for Prefilming Specimens — Heat Transfer and Loop Control Specimens	35
3-7. Assembly for Prefilming Specimens — Flat Isothermal Autoclave Specimens	36

Figures (Cont'd)

Figure	Page
3-8. Assembly for Prefilming Specimens — Isothermal Autoclave Tube and Comparison Specimens	36
3-9. Assembly for Prefilming Specimens — Loading Completed.	37
3-10. Specimens With Spacer Grid Ferrules Attached	38
3-11. Closeup View of Ferrule on Specimen	39
3-12. End View of Ferrule on Specimen	39
3-13. Hot Spot on Heat Transfer Specimen	40
3-14. Sectioning Diagram for Heat Transfer Specimens	41
3-15. Sectioning Diagram for Heat Transfer Specimen 2-1	41
3-16. Sectioning Diagram for Loop Control Specimens	42
3-17. Sectioning Diagram for Isothermal Autoclave Specimens	43
3-18. Heat Transfer Corrosion Test Schedule	44
3-19. Photograph of Specimen DD-1 Failure	45
3-20. Enlargement of Specimen DD-1 Failure	45
4-1. Pre-Exposure Appearance of Typical Prefilmed Specimen	66
4-2. Pre-Exposure Appearance of EOL Specimen 4-16	67
4-3. Pre-Exposure Appearance of EOL Specimen 4-17	68
4-4. Pre-Exposure Appearance of EOL Specimen 4-18	69
4-5. Pre-Exposure Appearance of EOL Specimen 2-8	70
4-6. Pre-Exposure Appearance of EOL Specimen 2-9	71
4-7. Pre-Exposure Appearance of EOL Specimen 4-19	72
4-8. Pre-Exposure Appearance of EOL Specimen 2-12	73
4-9. Post-Exposure Appearance of Prefilmed Specimens — High Purity Water Environment, Heat Transfer Specimens	74
4-10. Post-Exposure Appearance of Prefilmed Specimens — High Purity Water Environment, Loop Control Specimens	75
4-11. Post-Exposure Appearance of Prefilmed Specimens — High Purity Water Environment, Isothermal Specimens	76
4-12. Post-Exposure Appearance of Prefilmed Specimens — Chemical Shim Environment, Heat Transfer Specimens	77
4-13. Post-Exposure Appearance of Prefilmed Specimens — Chemical Shim Environment, Loop Control Specimens	78
4-14. Post-Exposure Appearance of Prefilmed Specimens — Chemical Shim Environment, Isothermal Specimens	79
4-15. Post-Exposure Appearance of EOL Specimens — High Purity Water Environment, Heat Transfer Specimens	80
4-16. Post-Exposure Appearance of EOL Specimens — High Purity Water Environment, Loop Control Specimens	81
4-17. Post-Exposure Appearance of EOL Specimens — High Purity Water Environment, Isothermal Specimens	82
4-18. Post-Exposure Appearance of EOL Specimens — Chemical Shim Environment, Heat Transfer Specimens	83
4-19. Post-Exposure Appearance of EOL Specimens — Chemical Shim Environment, Loop Control Specimens	84

Figures (Cont'd)

Figure		Page
4-20.	Post-Exposure Appearance of EOL Specimens — Chemical Shim Environment, Isothermal Specimens	85
4-21.	Corrosion of Heat Transfer Specimens	86
4-22.	Corrosion of Loop Control Specimens	86
4-23.	Corrosion of Isothermal Specimens	86
4-24.	Hydrogen Assay Summary Sheet — Specimen 4-5	87
4-25.	Hydrogen Assay Summary Sheet — Specimen 4-13.	88
4-26.	Hydrogen Assay Summary Sheet — Specimen 4-4	89
4-27.	Hydrogen Assay Summary Sheet — Specimen 4-1	90
4-28.	Hydrogen Assay Summary Sheet — Specimen 4-3	91
4-29.	Hydrogen Assay Summary Sheet — Specimen 4-2	92
4-30.	Hydrogen Assay Summary Sheet — Specimen 2-1	93
4-31.	Hydrogen Assay Summary Sheet — Specimen 4-16.	94
4-32.	Hydrogen Assay Summary Sheet — Specimen 4-17.	95
4-33.	Hydrogen Assay Summary Sheet — Specimen 4-18.	96
4-34.	Hydrogen Assay Summary Sheet — Specimen 2-8	97
4-35.	Hydrogen Assay Summary Sheet — Specimen 2-9	98
4-36.	Hydrogen Assay Summary Sheet — Specimen 2-12.	99
4-37.	Hydrogen Assay Summary Sheet — Specimen 4-19.	100
4-38.	Comparison of Corrosion and Hydrogen Absorption for Heat Transfer and Isothermal Conditions.	101
4-39.	Hydrogen Gradient of Specimen 4-5	102
4-40.	Hydrogen Gradient of Specimen 4-13.	102
4-41.	Hydrogen Gradient of Specimen 4-4	103
4-42.	Hydrogen Gradient of Specimen 4-1	103
4-43.	Hydrogen Gradient of Specimen 4-3	104
4-44.	Hydrogen Gradient of Specimen 4-2	104
4-45.	Hydrogen Gradient of Specimen 2-1	105
4-46.	Metallographic Examination of Specimen 4-5	106
4-47.	Metallographic Examination of Specimen 4-13	107
4-48.	Metallographic Examination of Specimen 4-4	108
4-49.	Metallographic Examination of Specimen 4-1	109
4-50.	Metallographic Examination of Specimen 4-5, Various Conditions	110
4-51.	Metallographic Examination of Specimen 4-16	111
4-52.	Metallographic Examination of Specimen 4-17	112
4-53.	Metallographic Examination of Specimen 4-18	113
4-54.	Metallographic Examination of Specimen 2-8	114
4-55.	Metallographic Examination of Specimen 2-9	115
4-56.	Metallographic Comparison of EOL Heat Transfer Specimens	116
4-57.	Directional Effects in Hydride Formation, EOL Specimens	117
4-58.	Metallographic Examination of Specimen 4-3	118
4-59.	Metallographic Examination of Specimen 4-2	119
4-60.	Metallographic Examination of Specimen 2-1	120
4-61.	Metallographic Examination of Specimen 4-19	121
4-62.	Metallographic Examination of Specimen 2-12	122

Figures (Cont'd)

Figure	Page
4-63. Metallographic Examination of End Cap Area, Specimen 4-1	123
4-64. Metallographic Examination of End Cap Area, Specimens 4-16 and 2-8	124
4-65. Metallographic Examination of End Cap Area, Specimens 4-2 and 4-3	125
4-66. Metallographic Examination of End Cap Area, Specimen 4-19	126
4-67. Metallographic Examination of End Cap Area, Specimens 2-1 and 2-12	127

1. INTRODUCTION

1.1. Background

The fuel cladding for pressurized and boiling water reactors is usually one of the zirconium-tin alloys, Zircaloy-2 or Zircaloy-4. These alloys have sufficient strength and corrosion resistance to withstand the rigors of reactor service, and they have low neutron absorption characteristics which permit a reduction in the fuel enrichment and increase the neutron efficiency of a reactor. However, the continuing effort to improve the thermal performance of water reactors by increasing the temperatures and pressures and extending the time between refueling operations places additional stress on the fuel cladding. In addition, the periodic shuffling of fuel elements in the reactor core introduces a potential high-stress-fatigue over and above the cyclic thermal stresses occurring during normal service. Operational experience has shown that Zircaloy fuel cladding performs satisfactorily under present service conditions.¹ However, failures of experimental Zircaloy-clad fuel elements indicate that operational limitations need further definition before a Zircaloy-clad core is committed to the demanding conditions of some of the more advanced reactor designs.

The excellent corrosion resistance of Zircaloy in pressurized water at temperatures up to 680 F has been well established by long-term isothermal tests in static autoclaves. Based on reactor operating experience, even where moderate local boiling occurred, and on postirradiation examination of the oxide thickness on Zircaloy cladding, it appears that the isothermal corrosion data are suitable for predicting the corrosion of fuel element cladding. The corrosion of cladding under peak service conditions of 650 F surface temperature and 450,000 Btu/hr-ft² flux will produce a calculated oxide thickness of 0.7 mil (equivalent to ≈ 280 mg/dm²) after 1000 days in service.

During corrosion, Zircaloy absorbs some of the hydrogen released by the corrosion reaction. The effects of absorbed hydrogen on the mechanical properties and corrosion characteristics of Zircaloy are major factors in establishing the limitations on service to be imposed on Zircaloy fuel cladding. Experimental results show that Zircaloy-4 absorbs a smaller quantity of the corrosion-released hydrogen than does Zircaloy-2.² Although experimental data vary, most of the results available indicate that Zircaloy-2 can be expected to absorb up to 50% of the hydrogen released during corrosion, and that Zircaloy-4 absorbs up to two-thirds as much as does Zircaloy-2.

The hydrogen absorbed in Zircaloy during exposure to high-temperature water will either form an interstitial solid solution with zirconium or precipitate as zirconium hydride. The solubility of hydrogen in zirconium increases with an increase in temperature. At 650 F the solid solubility limit is about 150 ppm. If the solubility limit of hydrogen in zirconium is exceeded, then a solid (the delta form of zirconium hydride) will form and precipitate.

The hydrogen in zirconium tends to migrate through a thermal gradient (from the high-temperature to the low-temperature zone) so that a hydrogen concentration gradient will usually exist in the fuel cladding.³ Hydrogen entering the Zircaloy on the outside surface during corrosion will tend to remain at the surface as long as there is no change in the thermal gradient. When the solubility limit of hydrogen in zirconium is exceeded, the hydrogen will precipitate with zirconium, and a layer of zirconium hydride will form beneath the corrosion-produced oxide film. During reactor cooldown or hot standby, the temperature gradient across the cladding wall will disappear; some of the precipitated hydride "case" will dissolve, and the hydrogen will redistribute toward a generally uniform concentration.

As the temperature is decreased, the hydride will precipitate in the matrix as platelets. These hard, brittle hydrides form along specific crystallographic planes and affect the ductility of Zircaloy.⁴⁻⁶ The presence of such precipitates and their orientation with respect to the direction of stress affect the useful properties of the cladding. Hydrogen tends to precipitate in Zircaloy as platelets oriented in a direction that depends on the strain history of the material and the stress pattern at

the time of precipitation. There is evidence that differing modes of tube fabrication (currently, extrusion, drawing, reducing, or combinations of the three) produce textures which vary in their susceptibility to adverse orientation of the hydride. Material produced by the tube-reducing method appears to be least susceptible to hydride orientation that would be undesirable in fuel cladding. Hydrogen in solution does not significantly affect the mechanical properties of Zircaloy.⁷⁻⁹ In general, hydride platelets oriented in the circumferential direction are not as detrimental to cladding performance as those oriented in the radial direction. Precipitated hydrides oriented parallel to the direction of tensile strain do not affect the mechanical properties until the hydrogen concentration exceeds 500 ppm. However, if the hydrides are oriented perpendicular to the direction of tensile strain, the reduction of area values can be reduced to below 5% of that originally present.

Under the heat transfer conditions required for current and advanced water reactor designs, fuel cladding surface temperatures can exceed 650 F, and the temperature gradient through the cladding can be as high as 150 F, giving temperatures on the inside surface of the cladding in excess of 800 F. Corrosion of the cladding having such a temperature gradient could be hypothesized to proceed faster than that predicted from isothermal tests at the bulk water temperature. In a similar manner, absorption of the hydrogen produced by the corrosion reaction should increase with the increased corrosion rate. However, as mentioned above, hydrogen migrates down a temperature gradient in zirconium and concentrates in the lower temperature region. In the case of fuel cladding under high heat flux conditions, the region of lower temperature is at the corrosion surface where the hydrogen is being produced. This activity tends to promote concentration of the hydrogen at the outside surface of the cladding, and zirconium hydride will precipitate when the solubility limit is reached. The high concentration of hydrogen at the cladding surface may inhibit further absorption of hydrogen, and the precipitated zirconium hydride should not affect the mechanical properties of the cladding.

1.2. Previous Work

B&W was among the first to recognize the advantages of using Zircaloy in water-moderated power reactors. Since 1960 the Company

has sponsored continuing experimental programs to qualify the Zircalloys for service in advanced designs. A program similar in scope to that now being reported was conducted from 1964 to 1966. The corrosion and hydrogen absorption rates of Zircaloy-4 fuel cladding during pre- and post-transition periods were determined under isothermal and non-isothermal conditions simulating the environment of a pressurized water reactor system. These rates were determined by exposing internally heated specimens in flowing high-purity water at 2250 psi. Surface heat fluxes of 450,000 Btu/hr-ft² and surface temperatures of approximately 650 F were used. Local boiling prevailed under these operating conditions. The velocity of the bulk water past the specimen was 13 fps. Isothermal loop control specimens on the upstream end of each heat transfer specimen were exposed at the loop bulk water temperature of 630 F, and isothermal autoclave specimens were exposed at 655 F, the surface temperature of the heat transfer specimens. Total exposures ranged up to 440 days for the autoclave specimens and up to 246 days for the heat transfer and unheated bulk water specimens. The results were as follows:

1. Isothermal specimens exposed at 655 F exhibited a post-transition corrosion rate of 0.24 mg/dm²-day. The post-transition hydrogen absorption rate for these specimens was 0.009 mg/dm²-day.

2. The corrosion of Zircaloy-4 under the heat transfer conditions was equivalent to that found under the isothermal conditions when the metal temperature condition was the same. The heat transfer specimens absorbed approximately 2-1/2 times more hydrogen than did the isothermal specimens at the same metal temperature.

The appreciably higher absorption of hydrogen under heat transfer conditions was thought to be due to one or more of these reasons:

1. Zircaloy-4 absorbs much more hydrogen under local boiling test conditions than under isothermal or nonboiling conditions.
2. The presence of a hydride layer or zone of high hydrogen concentration enhanced rather than inhibited hydriding.
3. An extraneous source of contaminated hydrogen exists in the helium cover gas used inside the tubular specimen.

The program reported herein was initiated partially to resolve these matters.

1.3. Test Objective

The test was performed to provide quantitative data on the corrosion and hydriding rates of Zircaloy alloy fuel cladding under conditions simulating those expected in advanced water reactor service. Zircaloy-2 and Zircaloy-4 hydriding characteristics were compared, and a short test in borated water (simulating operation under chemical shim practice) was performed to determine whether a chemical shim environment has gross effects on corrosion and hydriding.

2. TEST EQUIPMENT

2.1. General Arrangement

The tests were conducted in a stainless steel utility loop. The main components were a pump, gas-fired furnace, individual heat transfer test stations, cooler, pressurizer, and cleanup systems for the loop water and the specimen's annular gas. A diagram of the loop is shown in Figure 2-1, and its actual appearance is shown in Figure 2-2.

The main system, fabricated from 3-inch stainless steel pipe (sch-160, type-304), was qualified for service at 2500 psi and 650 F. Coolant circulation was provided by a canned-motor centrifugal pump rated for service at 258 feet total head, 150 gpm flow, 2500 psi pressure, and 640 F inlet temperature. The test fluid circulated through the furnace, to the test stations, and then through the pump. A gas-fired furnace maintained the loop water at the required temperature. A carbon steel, electrically-heated pressurizer maintained constant loop pressure.

The five individual heat transfer test sections were fabricated from 1-inch schedule-80 pipe and were manifolded into a 3-inch schedule-80 pipe. Each section had valving to permit isolation of individual sections and installation and removal of specimens without halting the overall operation of the loop. The test sections are discussed further in another section.

Since the loop water absorbed heat while flowing over the test specimens, it had to be cooled to prevent flashing during its passage through the pump. The cooler was a double-pipe, U-bend configuration with an expansion joint at one end; the inner pipe was 2-1/2-inch, schedule-80, type-304 stainless steel, and the jacket was 3-inch, schedule-40 carbon steel. Plant cooling water circulating through the outer jacket provided the degree of cooling required.

A water-purification system, consisting of a regenerative heat exchanger, cooler, micrometallic filters, and ion-exchange resin beds,

maintained the high purity of the test fluid. Conductivity cells and sampling stations for pH and water chemistry analysis were installed at the inlet and outlet of the purification system. The inlet was connected to the main pump discharge and the outlet to the pump suction side, so that the main loop pump overcame the pressure drop in the purification system. High-purity water for initial filling and makeup was obtained by condensing, deaerating, and de-ionizing plant steam. Two air-operated positive displacement pumps were used for water makeup additions to the loop. An auxiliary connection to the loop downstream of the ion-exchange resin columns was used to add hydrogen to the loop. Similarly, the boric acid and the other chemicals needed for makeup during the chemical shim tests were added downstream of the resin columns. The ion exchange columns were filled with borated resins during the chemical shim test.

The isothermal corrosion test autoclave was connected into the test loop as shown in Figure 2-1. This system is described in another section of the report.

2.2. Heat Transfer Tests

The heat transfer tests were conducted in five test stations as shown in Figures 2-3 and 2-4. Each test section was constructed as shown in Figure 2-5. The test sections were made from 1-inch stainless steel pipe (sch-80, type-304) with a straight length of approximately 20 inches. Each test section was equipped with a pair of 1-inch type-316 stainless steel flanges. The configuration of the Zircaloy test specimens included a 2-inch-diameter, 1/4-inch-thick flange. The test specimens were sealed in the loop by inserting the specimen flanges between the test section flanges and making a seal between the flange surfaces with two silver-plated Inconel-X O-rings. The temperature of the coolant at the test section's inlet and outlet was measured and recorded by well thermocouples. The coolant flow was downward through the test section.

A quenching system permitted rapid cooling of the specimens to prevent hydrogen redistribution before specimens were removed. This system consisted of two air-operated, positive-displacement pumps, an expansion tank, a cooler, and solenoid valves. Test sections 1, 3, and 5 were connected to one pump, and test sections 2 and 4 to the other.

pump. The position of the quenching water connection is indicated in Figure 2-5. In addition, shutoff valves, which were normally in the open position, were in the quenching system's lines. Each test station system was instrumented so that the operation of one switch would simultaneously open both solenoid valves and start the pump operating. A sheath thermocouple was installed in the quenching water outlet line to measure the temperature of the effluent test fluid. A 5-to-10 psig atmosphere of nitrogen was maintained over the quenching water expansion tank.

Each test station had duplicate globe valves for flow control and shutoff, an orifice for flow measurement, and a vent for use during the installation of specimens.

The specimens were heated internally by electrical heaters providing surface heat fluxes of 600,000 Btu/hr-ft². The heaters were 0.370 inch in diameter and 18-5/8 inches in overall length, and had a 6-inch-long zone of high heating. A central chromel-alumel sheathed thermocouple was placed in the high-heat flux zone of the heater. The heaters were provided with cooling jackets at the lower end, and thermocouples were attached to the cooling water outlet lines. A layer of magnesium oxide deposited on the heaters insulated them from the specimens. Figure 2-6 shows a specimen, heater, and flange assembly.

The 0.001-inch annulus between the heater and the inner wall of the specimen was filled with a 40-psig static layer of specially-purified helium to improve heat transfer and to protect the inner surface of the specimen from oxidation. The helium supply system comprised a helium gas cylinder, two purifying columns, a stainless steel gas storage cylinder of 5-gallon capacity, and a manifold with supply lines to each test station. The gas from the cylinders was passed through a purification column filled with hafnium chips maintained at 900 F to remove any hydrogen and oxygen present, and then through a column filled with freshly regenerated molecular sieve to remove traces of water. (Zirconium or titanium could be substituted for the hafnium.) The gas reservoir was valved at both ends and was ordinarily shut off from both the gas manifold and the cylinder. Gages on each test station indicated individual specimen pressures, and helium makeup was added as necessary. The reservoir

valving ensured that there was no direct connection between the gas cylinder and the test station.

The electrical connections to the heaters were made as shown in Figure 2-3. The "hot" lead was connected to the heater, and the ground wire was connected to the adjacent loop piping. The heaters were instrumented so that an alarm would sound and power to the heaters would automatically shut off under any of these conditions:

1. High heater temperature.
2. High heater current.
3. High electrode temperature.
4. Low test section flow.

A 20-station annunciator was used to identify the source of the alarm and indicate the area of operational difficulty.

Each heater had a separate power supply consisting of a saturable reactor-transformer combination rated at a maximum of 15 kVA with a maximum of 700 amperes and 25 volt output. The heater panelboard, shown in the center of Figure 2-2, contained all the instruments necessary for the control of the heaters.

2.3. Loop Control Tests

Control specimens were attached to the upstream end of the heat transfer specimens to provide comparative data on loop conditions without heat transfer. The 6-inch-long specimens were attached by a Zircaloy holder threaded at both ends. The holders screwed into corresponding female threaded plugs welded into the ends of the heat transfer and the loop control specimens. The threaded portions of the 1-inch holder were each 3/8-inch long, leaving a 1/4-inch spacing between the specimens. A corresponding single-threaded plug fit into the upstream end of the loop control specimen. The diameters of the two end plugs were the same size as the specimen's OD, and a smooth surface was thus formed at the joint between the specimens. Both sections of the holders had three Zircaloy spacer rods 120 degrees apart, which served to center the specimen in the test section.

Figure 2-7 shows the heat transfer and loop control specimens in the assembled configuration as they were placed in the loop. Figure 2-8 is a close-up view of the area around the junction of the two specimens

showing the holder, with its spacer rods, and sections of the heat transfer and the loop control specimens.

2.4. Isothermal Autoclave Tests

The isothermal corrosion tests were conducted in a 316 stainless steel autoclave having a 5-inch inside diameter and a 3.3-foot inside length. The autoclave was heated by 12 strip heaters (totalling 7 kW) arranged around the outer periphery and length of the autoclave to provide uniform heating. Four of the heaters were positioned around the bottom of the autoclave and were controlled manually by the adjustment of a Variac. The other eight heaters were connected for automatic operation, and their output was controlled by another Variac. The autoclave could be shifted to automatic operation after having been manually brought to the test conditions.

The autoclave had the necessary controls, recorders, and safety devices. The entire system, including tubing, fittings, and valves, was constructed of stainless steel. The autoclave was connected into the test loop with 3/8-inch stainless steel tubing. A positive displacement pump and pressure let-down system permitted autoclave operation at 655 F and 3000 psi. A portion of the coolant from the main test loop passed through the pump and into the autoclave through a preheater coil wrapped around the top of the autoclave. The fluid left the autoclave at the bottom, passed through an air-operated diaphragm valve, and re-entered the loop. The specimens were held in a 304 stainless steel holder.

The temperature of the autoclave was controlled by a thermocouple in a well extending 29 inches from the top cover of the autoclave. Surface thermocouples measured the vertical temperature gradient of the autoclave, which was nominally maintained to within ± 5 F. A sampling line was near the bottom of the autoclave.

Figure 2-1. Loop Flow Diagram

Figure 2-2. Test Loop and Control Panels

Figure 2-3. Heat Transfer Test Sections

Figure 2-4. Heat Transfer Specimen in Operation

Figure 2-5. Heat Transfer Test Section Diagram

Figure 2-6. Heat Transfer Specimen With Flange and Heater

Figure 2-7. Heat Transfer and Loop Control Specimens
in Exposure Configuration

Figure 2-8. Junction Between Heat Transfer and Loop Control Specimens

3. TEST PROCEDURE

3.1. Loop Operation

The test loop had been stored in a dry condition since the completion of a similar test program in 1966. However, considerable work was done on the loop in preparation for this test, so it was assumed that the interior surface was contaminated. Therefore, the loop was filled with deaerated, demineralized water from the plant supply and rinsed and vented until the effluent reached operating specifications.

The test conditions for the two environmental phases of the program are listed in Table 3-1. The loop water was analyzed once a week for suspended solids, chloride, and fluoride concentration. It was analyzed daily for hydrogen content during both test phases, and for boric acid, potassium hydroxide, and lithium hydroxide during the second phase of the program. Makeup additions were made daily during Phase II, and hydrogen makeup was added as necessary during both phases. Flow through the bypass purification system was maintained at about 0.7 gpm, which was sufficient to maintain the loop water conditions within the specifications.

3.2. General Specimen Details

The tests included an evaluation of both Zircaloy-2 and Zircaloy-4 for corrosion and hydrogen absorption characteristics. Tables 3-2 and 3-3 show the certified mill test reports for the tubing used to prepare the specimens. Tables 3-4 and 3-5 show the certified mill analyses of the Zircaloy-4 stock used to fabricate the flanges and end caps for the heat transfer specimens.

Figure 3-1 shows the scheme used in cutting the tubing stock and indicates the pretest condition and identity of each length of tubing. The specimens were pickled in an aqueous solution of 39 vol % nitric acid (sp gr 1.42) and 3.6 vol % hydrofluoric acid (52%) at 80 F until the desired

amount of metal was removed from the OD and ID of the specimen. The specific procedures used in preparing the various specimens are listed in Appendix A.

The test program utilized three types of corrosion specimens—heat transfer, loop control, and isothermal autoclave—and two types of comparison specimens. One type of control specimen was treated on its OD, either by prefilming or by appropriate end-of-life treatment, to represent the condition of the heat transfer and the loop control specimens before exposure. The other type of control specimen was treated on both the OD and the ID to give the pre-exposure condition of the isothermal autoclave specimens. Each group of specimens included both types of control specimens. Figure 3-2 shows the appearance of such an array of specimens after pickling and welding of the appropriate flanges and end caps to the heat transfer and loop comparison specimens.

3.2.1. Specimen Pretest Surface Conditioning

Two types of pretest surface conditions were used. One type, the "prefilmed," had a surface oxide coating equivalent to 14 mg/dm². The second type, designated "end-of-life" (EOL), simulated the projected cladding condition at the end of 1000 days of reactor operation; it contained about 250 ppm of hydrogen with an oxide thickness equivalent to 250 mg/dm².

The EOL condition was created by gas-hydridding the specimens to the required hydrogen content and then air-oxidizing them to the proper oxide thickness. Previous hydridding experience indicated that conventional gas hydridding to the high hydrogen levels required would take as long as 72 hours if temperatures were kept low enough to prevent reducing the strength of the cold-worked cladding. Winton has reported a method for gas-hydridding zirconium alloys in which a low partial pressure of carbon tetrachloride is added to the furnace before the hydrogen is added.¹⁰ The carbon tetrachloride disrupts the semi-impervious oxide film on the metal and permits the hydrogen to react more rapidly with the zirconium. This procedure reduced the total time cycle for hydridding a batch of material and did not require excessive temperatures. Exposures at 750 F varied from 40 to 150 minutes, depending on the amount of hydrogen to be introduced.

Figures 3-3 and 3-4 show the gas hydriding apparatus. The furnace is a heated 4-inch Inconel tube connected directly to a 4-inch vacuum diffusion pump. The specimens were loaded into the furnace section by removing a blind flange. The hydrogen was passed directly from the gas bottle into the evacuated furnace without additional purification. The argon used for purging the furnace before and after the hydriding operation was purified by passing it over hot zirconium chips before it entered the furnace.

The EOL conditioning technique was performed at B&W's Nuclear Development Center, Lynchburg, Virginia, in conjunction with another phase of this program. Several hydriding cycles were run to standardize the procedure and to determine the variability of the hydrogen concentration over the length of the specimen. This work, described in BAW-3765-6,⁹ demonstrated that the hydrogen content was uniform over the gage area of the specimen. The hydrided specimens were then oxidized by heating in air at 900 F. The proper oxidation time was determined by heating small samples of the materials at 900 F, withdrawing them at intervals, and measuring the oxide buildup. The required time varied, but was generally about 300 hours for an oxide buildup of the required 250 mg/dm².

The prefilm condition was achieved by exposing the test specimens and controls to 750 F - 1500 psig high-purity steam for 72 hours in an autoclave. They were loaded in a sequentially assembled rack, shown in Figures 3-5 through 3-9. The rack contained four sub-assemblies consisting of the following units in ascending order: a unit holding heat transfer and loop control specimens, suspended from a series of threaded studs; a unit holding a number of flat isothermal autoclave specimens, suspended from stainless steel wires; another array of suspended heat transfer specimens; and a unit containing tubular isothermal autoclave and comparison specimens.

3.3. Heat Transfer Tests

The heat transfer specimens were Zircaloy tubes (12-5/16 inches long, 0.420-inch OD, 0.370-inch ID) with an end cap welded on one end and a Zircaloy flange on the other. The threaded end cap was attached to the threaded spacer which was also attached to the loop control specimen. The flange sealed the heat transfer specimen in the test section. Specimens were identified on the end caps.

The heat transfer section, as shown in Figure 3-1 and described in Appendix A, was formed from a piece of tubing originally 15 inches long. After the tubing had been pickled to the appropriate size, the end caps and flanges were Heliarc-welded in place, and the sealed tube was given the desired pre-exposure treatment either by prefilming or EOL formation. The inside of the specimen remained in the as-pickled state because it was sealed off from the environment. The "C" end was then cut off at the flange interface, and the end was saved for comparison. In this manner, the interior of the heat transfer specimens was available for heater insertion without being hydrided or oxidized before or during the test.

Three of the specimens used in the second phase of the program, which involved exposure to a chemical shim environment, had representative spacer grid ferrules attached in the hot zone to check for possible effects from solids concentration. Figures 3-10, 3-11, and 3-12 show these ferrules attached to the specimens.

The heat transfer specimens and heaters were designed so that each specimen had a 6-inch-long section to which the heat flux was applied. The upstream end of this section was approximately 1 inch from the end of the specimen. The heated section contained "hot spots" at each end to provide a thermal barrier against the diffusion of hydrogen to the cooler ends of the specimen. These hot spots were raised positions of the tube (1 mil thick and 1/16 inch wide) which were obtained by masking the tubing during the pickling process. A closeup view of such a hot spot is shown in Figure 3-13 (can also be seen on the left side of the specimen in Figure 2-8).

Each heater was fitted individually to its specimen to minimize the size of the annulus between the heater and the specimen. By doing this, good thermal contact was maintained, and the heater was cooled efficiently. This permitted operation at high power levels without exceeding the operating temperature limits of the heaters. The annulus was typically on the order of 1 mil, and, as mentioned earlier, was filled with helium. The central rod temperatures of the heaters were limited to 1700 F maximum to ensure heater life. This limitation was not exceeded when prefilmed specimens operated at surface heat fluxes of 600,000 Btu/hr-ft². Specimen surface temperatures were calculated

to be 655 F during operation. The heater power to produce this heat flux was about 13 kW.

The heavy oxide coatings of the end-of-life specimens added an additional thermal barrier by virtue of their low thermal conductivity. When attempts were made to increase the heater output to the design rating, excessive heater temperatures resulted. Therefore, lower power ratings were used during the startup of all EOL specimens. After a period of operation it was noted that heater temperatures decreased in most of the EOL specimens. For these specimens, heater power could be raised to the design level of 13 kW; however, heater temperatures in a few specimens remained high, and heater power had to be reduced to as low as 9.1 kW for these specimens.

Detailed procedures for preparing the heat transfer specimens are listed in Appendix A. These procedures were followed for all specimens. A rigorous cleaning procedure ensured that hydrogen-containing contaminants on the interior of the specimen were removed during the insertion process. The procedure was as follows:

1. Assemble the heat transfer specimen.
2. Assemble the bulk water specimen and holder and attach to the heat transfer specimen.
3. Isolate and quench the test section to about 100 F.
4. Install the specimen (without the heater) in the test section. Keep the vent in the quenching system open. Use an old heater to align the specimen in the test section. Keep the interior of the specimen as dry as possible.
5. Rinse the interior of the specimen thoroughly with anhydrous reagent-grade methanol.
6. Purge the interior of the specimen with dry purified helium. Use the gas from the annular gas purification train. Continue the purge for 10 minutes.
7. Heat the test section flange with a torch to approximately 400 F to evaporate any moisture. Continue the helium purging throughout this step.
8. Allow the flange to cool to about 100 F. Continue purging with helium throughout this step.

9. Install the heater and make the necessary connections for cooling water, annular helium supply, and vacuum.
10. Start the cooling water flowing through the jacket on the heater.
11. Helium-pressurize the interior of the specimen to 40 psig.
12. Turn off the helium supply, and evacuate the annular section between the heater and the specimen. Evacuate to about 10 microns pressure.
13. Repeat steps 11 and 12 at least four times.
14. Helium-pressurize the annulus to 40 psig.
15. Check the flow meter for proper low flow alarm calibration.
16. Make the necessary electrical connections.
17. Establish flow through the test section.
18. Proceed with normal electrical startup.

The shutdown procedure was as follows:

1. Gradually decrease the power to the heater, taking about 5 minutes to turn off the power.
2. Isolate the test section.
3. Immediately start quenching the test station by injecting cold deionized water through the quenching circuit to the specimen to prevent redistribution of the hydrogen gradient.
4. When the test section and heater temperature are about 100 F, remove the heater and specimen assembly from the test section.
5. Remove the heater from the specimen.

3.4. Loop Control Tests

The loop control specimens were exposed to the bulk water conditions in the loop. The test conditions were 640 F-2250 psig water, and pH 7 high-purity water in Test Phase I and a chemical shim environment

in Test Phase II. The water chemistry conditions are listed in Table 4-1. The flow past the specimens was in a downward direction at 13 fps. The specimens were 6-inch pieces of tubing which were sealed at both ends with threaded end-plugs. The loop control specimen was mounted upstream of the heat transfer specimen, as described previously, and the spacer connecting the two specimens was threaded into one of the end plugs. A spacer with a squared-off end was threaded into the other end plug of the loop control specimen. Three 1/16-inch Zircaloy rods were positioned 120 degrees apart to center the specimens.

The bulk water samples were exposed for about 30 minutes longer than were the corresponding heat transfer specimens because it took that long to bring the heater power to full rating.

3.5. Isothermal Autoclave Tests

The isothermal autoclave tests were conducted in a AISI-type 316 stainless steel autoclave as described previously. The test conditions were:

Temperature, F	655 $\pm$ 5
Pressure, psig	3000 $\pm$ 100
Flow rate, gph	22

The test temperature corresponds to the calculated oxide surface temperature (655 F) of the heat transfer specimens under the test heat flux. The autoclave was connected into the test loop through stainless steel fittings and tubing. The flow through the tubing was rapid enough to maintain the water chemistry in the autoclaves similar to that in the main test loop. The autoclave water was analyzed at least once per month for pH, resistivity (where appropriate), dissolved oxygen, chloride, fluoride, and suspended solids.

Two specimen configurations were used: 4-inch tubular specimens and 2-inch flat specimens. The flat specimens were made by splitting a 2-inch tubular specimen and then flattening the split halves. There were one tubular and two flat specimens exposed for each heat transfer and loop control sample. The specimens were exposed in a stainless

steel holder made from the top part of a prefilming rack (Figure 3-8). The tubular specimens were held in a vertical position, and the flat specimens were suspended from stainless steel wires in a manner similar to that shown in Figure 3-7. There were usually 5 tubular specimens and 10 flat specimens undergoing exposure at any one time (these were equivalent to the five heat transfer samples in the main test loop).

3.6. Post-Test Examination

The post-test evaluation was as follows:

1. Visual examination and photographs.
2. Metallographic examination and photographs.
3. Weight change determinations.
4. Analysis for bulk hydrogen across the specimen wall.
5. Analysis for hydrogen concentration across the specimen wall (for heat transfer specimens only).

The specimens were sectioned in accordance with the diagrams shown in Figures 3-14 through 3-17. The sectioning-arrangement of heat transfer specimen 2-1 had to be altered because of a failed area requiring metallurgical examination. A jeweler's saw with an 0.010-inch-thick blade was used for all sectioning.

The end caps of selected specimens were examined metallographically to determine whether the colder regions were acting as hydrogen sinks. Longitudinal sections of the end caps were metallographically examined in both the as-quenched and the heat-treated conditions, and the specimens were analyzed for hydrogen content. The end caps were sectioned as shown in Figure 3-14. One-half of each end cap, and the accompanying tube, was heat treated to precipitate the hydride as follows:

1. The specimens were placed in a furnace preheated to 660 F and held for 23 minutes until they had reached a temperature of 643 F.
2. The specimens were maintained at a temperature from 640 to 643 F for about 7 minutes.
3. The furnace was turned off and allowed to cool overnight (about 13 hours). The temperature at the end of 13 hours was 150 F.

The specimens were loaded into a capped stainless steel pipe for the foregoing test treatment. The loading and sealing were performed in a helium-filled welding dry-box, and the heat treatment was performed in a helium atmosphere. The specimens receiving the heat-treatment were the three long-exposure specimens (4-1, 4-2, and 2-1) and the other samples exposed to the chemical shim environment (specimens 4-3, 4-19, and 2-12).

The specimens were prepared for hydrogen analysis as described in Appendix B. The hydrogen content was determined with a Serfass vacuum fusion apparatus. Material for the bulk hydrogen analysis was appropriately sized pieces from the specimen segments assigned for such analysis. In addition, segments of both the heat transfer comparison specimens ("C" specimens) and the isothermal comparison specimen ("H" specimens) were analyzed. Material for the analysis of the hydrogen gradient segments was machined turnings from the outside of the specimens. The samples (about 1-3/8 inches long) from the three segments of the heated zone were fitted over a mandrel and rotated at the lowest feasible speed, and successive circumferential cuts were made on them as follows:

<u>Cut No.</u>	<u>Depth of cut</u>
A	1 mil off radius
B	1-1/2 mils off radius
C	3-1/2 mils off radius
D	6 mils off radius
E	13 mils (remainder)

The stringent precautions taken in the machining and the subsequent preparation work are outlined in Appendix B. An analysis of turnings from the individual cuts provided an indication of the gradient through the thickness of the specimens.

3.7. History of Test Operation

Operation of the loop began on February 22, 1967; insertion of the first set of specimens began on March 3, 1967, and was completed on

March 9, 1967. The loop operated from that time until the scheduled operation was completed on November 21, 1967. There were two scheduled outages and one unscheduled one. The loop was shut down from May 3 through 9, 1967, to perform urgently-required maintenance operations on the main loop control valves. The loop was unavailable for the exposure of specimens from September 21 through 28, 1967, so that a new plant fuel supply line could be installed and the high-purity water environment could be changed to the simulated chemical shim environment. There was another outage from October 18 to 21, 1967, to repair damage to the annulus gas supply system due to a specimen failure (no specimens were exposed during this outage, but the loop continued to operate). The scheduled operation was completed on November 21, 1967. The isothermal autoclave exposures were interrupted by the first two outages, but remained operating during the heat transfer specimen outage of October 18 to 21 since the loop continued to operate. Figure 3-18 and Table 3-6 show the chronology of the individual specimen exposures.

3.7.1. Heat Transfer Specimen Failure

There was one specimen failure: On October 18, 1967, the station holding heat transfer specimen DD-1 gave an alarm indicating high current through the specimen heater, and the power to the heater was automatically stopped. This Zircaloy-2 specimen had accumulated an exposure of 6 months to the high-purity water environment in Test Phase I and 475 hours to the representative chemical shim environment (13,000 ppm boric acid, 4 to 6 ppm potassium hydroxide, 0.5 ppm lithium hydroxide, and 20 to 40 cc per liter dissolved hydrogen). It was originally thought that the alarm had been triggered by a surge in the plant power (since there was a history of such surges at the approximate time of failure) or some other anomalous signal. The alarm was therefore cancelled, and the power was reapplied after the specimen had cooled. The alarm re-sounded almost immediately, and it became apparent that the wall of the specimen had perforated and that loop water had entered the interior of the specimen. Arrangements were made to remove the specimen from the loop after isolating the test station and quenching the specimen to prevent redistribution of its hydrogen. At the same time, an increase in

the pressure of the annular helium supply signified that the gas supply to the other four specimens in the loop had become contaminated with water. Action was taken to isolate all the stations from the loop, and the five specimens were rinsed and examined.

The loop assembly supplying helium to the interior of the specimens was modified to prevent cross-contamination in the event of future failures. The four sound specimens were reinstalled in the loop, and exposure was resumed on October 21, 1967.

The interiors of the four specimens were carefully examined with a borescope and no damage from the brief encounter with steam was apparent. Figure 3-19 shows the appearance of the failed specimen. The two penetrations of the specimen's wall seen in the photograph evidently correspond to the initiation of the two alarms. The appearance of the penetrations indicates that the Zircaloy-2 wall material had melted as the result of the high temperature accompanying the formation of short circuits from the heater power (about 13 kW) arcing across the highly conductive loop water to the wall. The arrangement for sectioning the specimen for post-test examination was altered to that shown in Figure 3-15 to permit metallurgical examination of the failed area without any loss of material for subsequent chemical analysis.

Table 3-1. Test Conditions

	<u>Dynamic loop</u>	<u>Static loop</u>
Type of specimen	Heat transfer, loop control	Isothermal
Fluid temperature, F	640 ± 10	655 ± 10
Pressure, psig	2250 ± 50	3000 ± 100
Velocity, fps	13 ± 1	Nil
Environment		
<u>Phase I</u>		High purity water
pH		7 ± 1
Min resistivity, ohms		10 ⁶
Max oxygen content, ppm		0.01
Max chloride content, ppm		0.10
Max fluoride content, ppm		0.10
Max total solids, ppm		1.0
Dissolved hydrogen, STP, cc/t		20-40
<u>Phase II</u>		Simulated chemical shim
pH		8-10
Boric acid, ppm		13,000
Potassium hydroxide, ppm		5 ± 1
Lithium hydroxide, ppm		0.5 ± 0.1
Dissolved hydrogen, STP, cc/t		20-40
Max oxygen content, ppm		0.01
Max chloride content, ppm		0.10
Max fluoride content, ppm		0.10

Table 3-2. Certified Mill Report for Specimen
Stock — Zircaloy-4(a)

Ingot Chemistry (Ingot M-930) (ppm except as noted)						
	Top	2	3	4	Bottom	Average
Sn, %	1.40	1.41	1.39	1.41	1.37	1.40
Fe, %	0.21	0.23	0.21	0.20	0.21	0.21
Cr, %	0.09	0.11	0.10	0.10	0.10	0.10
Fe+Cr, %	0.30	0.34	0.31	0.30	0.31	0.31
Al	<20	<20	<20	<20	<20	<20
B	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
C	80	--	--	--	115	--
Cd	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Co	<10	<10	<10	<10	<10	<10
Cu	<20	<20	<20	<20	<20	<20
Ca	<20	<20	<20	<20	<20	<20
H	10	--	--	--	11	--
Hf	<100	<100	<100	<100	<100	<100
Mg	<10	<10	<10	<10	<10	<10
Mn	<20	<20	<20	<20	<20	<20
Mo	<20	<20	<20	<20	<20	<20
N	25	25	25	30	30	27
Ni	<35	<35	<35	<35	<35	<35
Na	<10	<10	<10	<10	<10	<10
Pb	<20	<20	<20	<20	<20	<20
Si	<30	<30	<30	<30	<30	<30
Cl	<10	<10	<10	<10	<10	<10
Ti	<20	<20	<20	<20	<20	<20
V	<20	<20	<20	<20	<20	<20
W	<50	<50	<50	<50	<50	<50
O	1320	--	--	--	1160	--

Finished Product Chemical Analysis, ppm

<u>Position</u>	<u>Ni</u>	<u>H₂</u>	<u>N₂</u>	<u>O₂</u>
Random	12	10	65	1460

Mechanical Properties

Ultimate tensile strength, kpsi	101.5	103.9
Yield strength, 2% offset	79.8	80.3
Elongation in 2 inches, %	21.0	21.0

(a) Material supplied by Wolverine Tube Company.

Table 3-3. Certified Mill Report for Specimen
Stock — Zircaloy-2(a)

Ingot Chemistry (Ingot K-958) (ppm except as noted)						
	Top	2	3	4	Bottom	Average
Sn, %	1.63	1.58	1.62	1.59	1.43	1.57
Fe, %	0.13	0.13	0.12	0.11	0.12	0.12
Cr, %	0.11	0.11	0.12	0.11	0.09	0.11
Ni, %	0.06	0.05	0.05	0.05	0.04	0.05
Fe+Cr+Ni, %	0.30	0.29	0.29	0.27	0.25	0.28
Al	20	<20	<20	25	<20	<21
B	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
C	118	--	--	--	120	--
Cd	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Co	<10	<10	<10	<10	<10	<10
Cl	<10	<10	<10	<10	<10	<10
Cu	<20	<20	<20	<20	<20	<20
Ca	<20	<20	<20	<20	<20	<20
H	23	--	--	--	16	--
Hf	<100	<100	<100	<100	<100	<100
Mg	<10	<10	<10	<10	<10	<10
Mn	<20	<20	<20	<20	<20	<20
Mo	<20	<20	<20	<20	<20	<20
N	30	30	30	35	35	32
Na	<10	<10	<10	<10	<10	<10
Pb	<20	<20	<20	<20	<20	<20
Si	65	55	55	60	30	53
Ti	<20	<20	<20	<20	<20	<20
U	1.0	--	--	--	<1	--
V	<20	<20	<20	<20	<20	<20
W	<50	<50	<50	<50	<50	<50
O	1400	--	--	--	1540	--

Finished Product Chemical Analysis, ppm

Position	Ni	H ₂	N ₂	O ₂
Random	37	10	27	1330

Mechanical Properties

Ultimate tensile strength, kpsi	101.9	102.6
Yield strength, 2% offset	78.5	78.5
Elongation in 2 inches, %	21.5	21.0

(a) Material supplied by Wolverine Tube Company.

Table 3-4. Certified Mill Report for Zircaloy-4 Material
Used for Heat Transfer Flanges^(a)

Ingot Chemistry (Ingot M-926) (ppm except as noted)			
	Top	Middle	Bottom
Sn, %	1.44	1.49	1.35
Fe, %	0.20	0.22	0.19
Cr, %	0.09	0.11	0.10
Fe+Cr, %	0.29	0.32	0.29
Al	<20	<20	<20
B	<0.2	<0.2	<0.2
C	90	100	110
Cd	<0.2	<0.2	<0.2
Co	<10	<10	<10
Cu	<20	<20	<20
H	16	--	10
Hf	<100	<100	<100
Mn	<20	<20	<20
N	30	--	25
Ni	<35	<35	<35
Si	40	35	30
Ti	<20	<20	<20
U	<1	--	<1
W	<50	<50	<50

(a) Material supplied by Carborundum Metals Climax, Inc.

Table 3-5. Certified Mill Report for Zircaloy-4 Material
Used for Heat Transfer End Plugs^(a)

Ingot Chemistry (Ingot M-942) (ppm except as noted)			
	Top	Middle	Bottom
Sn, %	1.44	1.61	1.50
Fe, %	0.19	0.22	0.21
Cr, %	0.10	0.12	0.12
Fe+Cr, %	0.29	0.34	0.33
Al	<20	<20	<20
B	<0.2	<0.2	<0.2
C	120	<80	96
Cd	<0.2	<0.2	<0.2
Co	<10	<10	<10
Cu	<20	<20	<20
H	15	--	5
Hf	100	90	100
Mn	<20	<20	<20
N	19	--	18
Ni	20	32	28
Si	<35	<35	<35
Ti	<20	<20	<20
U	<1	--	<1
W	<50	<50	<50

(a) Material supplied by Carborundum Metals Climax, Inc.

Table 3-6. Specimen Exposure Data

<u>Specimen No.</u>	<u>Specimen type</u>	<u>Insertion date</u>	<u>Removal date</u>	<u>Accumulated exposure, hr</u>
4-13	Heat transfer	3-3-67	5-3-67	1450
	Isothermal autoclave	3-9-67	5-3-67	1315
4-5	Heat transfer	5-10-67	6-12-67	785
	Isothermal autoclave	5-12-67	6-12-67	763
4-16	Heat transfer	6-12-67	7-27-67	1072
	Isothermal autoclave	6-13-67	7-30-67	1081
4-4	Heat transfer	3-7-67	7-12-67	2846
	Isothermal autoclave	3-9-67	7-12-67	2745
2-8	Heat transfer	7-12-67	8-29-67	1144
	Isothermal autoclave	7-14-67	8-30-67	1103
4-17	Heat transfer	7-12-67	8-28-67	1144
	Isothermal autoclave	7-31-67	8-30-67	719
2-9	Heat transfer	8-28-67	9-12-67	360
	Isothermal autoclave	8-31-67	9-15-67	360
4-18	Heat transfer	8-29-67	9-13-67	360
	Isothermal autoclave	8-31-67	9-15-67	360
4-1	Heat transfer	3-9-67	9-13-67	4330
	Isothermal autoclave	3-9-67	9-20-67	4321
2-1	Heat transfer	3-8-67	10-18-67	4332 + 475
	Isothermal autoclave	3-9-67	11-20-67	4321 + 1225
4-2	Heat transfer	3-8-67	11-21-67	4326 + 1160
	Isothermal autoclave	3-9-67	11-20-67	4321 + 1225
4-3	Heat transfer	9-28-67	11-21-67	1160
	Isothermal autoclave	9-28-67	11-20-67	1225
2-12	Heat transfer	9-28-67	11-21-67	1160
	Isothermal autoclave	9-28-67	11-20-67	1225
4-19	Heat transfer	9-28-67	11-21-67	1160
	Isothermal autoclave	9-28-67	11-20-67	1225

Figure 3-1. Layout of Specimens as Cut From Tubing

- A. ARCHIVE SPECIMEN, AS RECEIVED
- B. LOOP CONTROL SPECIMEN
- C. PRE-TREATMENT CONTROL (REMOVED AFTER PREFILMING)
- D. HEAT TRANSFER SPECIMEN
- E. ISOTHERMAL AUTOCLAVE SPECIMEN-TUBE
- F, G. ISOTHERMAL AUTOCLAVE SPECIMEN-FLATTENED STRIPS
- H. PRE-TREATMENT CONTROL

Figure 3-2. Complete Array of Samples After Pickling

Figure 3-3. Gas Hydriding Apparatus — Photograph

Figure 3-4. Gas Hydriding Apparatus — Diagram

Figure 3-5. Assembly for Pre-filming Specimens — Heat Transfer Specimens

Figure 3-6. Assembly for Pre-filming Specimens — Heat Transfer and Loop Control Specimens

Figure 3-7. Assembly for Pre-filming Specimens
— Flat Isothermal
Autoclave Specimens

Figure 3-8. Assembly for Pre-filming Specimens
— Isothermal
Autoclave Tube and
Comparison Specimens

Figure 3-9. Assembly for Prefilming Specimens —
Loading Completed

Figure 3-10. Specimens With Spacer Grid Ferrules Attached

Figure 3-11. Closeup View of Ferrule on Specimen

Figure 3-12. End View of Ferrule on Specimen

Figure 3-13. Hot Spot on Heat Transfer Specimen

Figure 3-14. Sectioning Diagram for Heat Transfer Specimens

Figure 3-15. Sectioning Diagram for Heat Transfer Specimen 2-1

Figure 3-16. Sectioning Diagram for Loop Control Specimens

1. NOT ANALYZED
2. BULK HYDROGEN ANALYSIS
3. LONGITUDINAL METALLOGRAPHY FOR HYDRIDE
4. TRANSVERSE METALLOGRAPHY FOR OXIDE AND HYDRIDE
5. BULK HYDROGEN ANALYSIS (DUPLICATE SAMPLE)
6. NOT ANALYZED

Figure 3-17. Sectioning Diagram for Isothermal Autoclave Specimens

1. NOT ANALYZED
2. NOT ANALYZED
3. BULK HYDROGEN ANALYSIS
4. NOT ANALYZED
5. NOT ANALYZED

TUBE SECTIONS

1. TRANSVERSE METALLOGRAPHY FOR HYDRIDE AND OXIDE
2. BULK HYDROGEN ANALYSIS
3. LONGITUDINAL METALLOGRAPHY FOR HYDRIDE
4. NOT ANALYZED

FLAT SECTIONS

SECTIONING DIAGRAMS FOR ISOTHERMAL AUTOCLAVE SPECIMENS

Figure 3-18. Heat Transfer Corrosion Test Schedule

Figure 3-19. Photograph of Specimen DD-1 Failure

Figure 3-20. Enlargement of Specimen DD-1 Failure

4. RESULTS

4.1. General

Each specimen was photographed before and after exposure. The prefilmed specimens were essentially uniform in appearance before exposure (Figure 4-1 shows a segment array of one such specimen). The end-of-life (EOL) specimens were not as uniform in appearance as the prefilmed specimens (Figures 4-2 through 4-8 show the pre-exposure appearance of each of the EOL specimens exposed in this program).

Figures 4-9 through 4-14 show the post-exposure appearance of the prefilmed specimens. The DD-2 specimen in Figure 4-9 and the corresponding BB-2, EE-2, FF-2, and GG-2 in Figures 4-10 and 4-11 are unexposed prefilmed specimens included for comparison. The "C" specimen in Figure 4-9 and the "H" specimen in Figures 4-10 and 4-11 show individual unexposed specimens for additional comparison.

The prefilmed specimens displayed a darkening in the heat-transfer segments over the area of the end plugs. Only one specimen demonstrated additional alteration after exposure. This was specimen 4-2, which had been exposed to high purity water for 180 days (Test Phase I) and to a representative chemical shim environment for 51 days (Test Phase II). The specimen developed a mottled appearance on its heat transfer and loop control segments during Test Phase II. The extent of the mottling was not as severe in the heated zone of the heat transfer segment. Specimen 2-1, which was also exposed during both test phases, did not show mottling. However, it was not exposed as long in Test Phase II (20 days versus 51 days for specimen 4-1) and was composed of Zircaloy-2 alloy rather than Zircaloy-4.

Figures 4-12 through 4-14 show specimens that were exposed to the chemical shim environment and include comparison specimens. Specimens DD-1 and D-2 were exposed to high-purity water for 180 days and for an additional time to the chemical shim environment (51 days for

specimen D-2 and 20 days for DD-1). Specimen D-1 was exposed to the high-purity water for 180 days and thus gives an idea of the appearance of DD-1 and D-2 before exposure to the chemical shim environment. The various arrays of specimen DD-2 serve as comparisons for specimen D-3, which had only a chemical shim exposure history.

Figures 4-15 through 4-20 show the appearance of the EOL specimens after exposure. There is a distinct change in the appearance of these specimens with exposure, particularly in the heat transfer specimens. Figure 4-15 contains the heat transfer specimens exposed to the high purity water environment, and shows the color change that occurred in the area in which the high heat flux was applied. Specimen D-20 was not exposed and can be used for comparison. Comparison of the appearance of specimens D-16 (45-day exposure), D-17 (30-day exposure), and D-18 (15-day exposure) shows that the amount of darkening increases with exposure time. The same effect is seen in specimens DD-8 (45-day) and DD-9 (15-day). The loop control specimens (Figure 4-16) and isothermal specimens (Figure 4-17) showed a general lightening in color with increasing exposure.

Figures 4-18 through 4-20 show the appearance of the EOL specimens exposed to the chemical shim environment. Specimen D-21 is included for comparison. The darkening of specimens under this environment is not as severe as that occurring in the high purity water environment and is almost unnoticeable in the specimen DD-12.

The general increase in darkening of the oxide coatings corresponds with an apparent increase in the thermal conductivity of the oxide surface coating with lengthening exposure. In general, full power could not be applied to the heaters contained in the EOL specimens at the beginning of exposure because the full-power heat could not be transferred rapidly enough to the loop water; consequently, the heater temperature increased to an unsafe level. A gradual increase to full power could be made after several days of loop exposure, however. The thermal conductivity of the coating on specimen DD-12 never improved enough to permit full power operation.

4. 2. Oxide Measurements

Under ordinary conditions, corrosion rates are calculated from changes in the specimen weights resulting from exposure. Such an approach could not be used in this project for several reasons: (1) the size and the weight of the heat transfer specimen, including flanges and end-plugs which are partially shielded from exposure; (2) the differing corrosion kinetics for the heated and unheated areas of the heat transfer specimen; (3) the metal-to-metal mechanical seal of the flange on the specimens; (4) the difficulty in removing particles of electrical insulation of the heater from the inside surface of the specimen; (5) the difficulty of removing residues of the silver-plated O-rings from the flange; and (6) the possibility of scratches resulting from insertion and removal of the heater from the interior of the specimen. In addition, the actual weight changes for the isothermal specimens are on the order of several milligrams, and the precision in measuring weight differences of such magnitude is poor because of experimental and statistical considerations.

Accordingly, the corrosion rates for the specimens were calculated from metallographic measurement of the oxide thickness. Extensive work performed during the previous program indicated that there is a reproducible correlation between the weight gain and the oxide thickness, and that the conversion factor is 1 micron oxide thickness = 15.6 mg/dm².

These measurements were made using a Filar Eyepiece at a magnification greater than 1000X; the specimens were nickel-plated to protect the oxide. Such determinations could have been made on silver-wrapped specimens, but nickel plating is more desirable when the specimens are to be etched as these were. The number of readings taken per sample varied according to the variation in oxide thickness. An average of 15 readings, for example, was taken for a specimen having a very uniform thickness. A greater number of readings was necessary if the oxide thickness was nonuniform. When changes were relatively extensive in the area covered, as viewed at both 100X and 1000X, the proportion covered by the various depths were approximated so that the average values could be representative. Although this method of obtaining values seems to depend a great deal on personal judgment, it is

believed that they are accurate enough to calculate corrosion rates and correlate with chemical analyses for hydrogen.

The results of the oxide measurements are listed in Tables 4-1 and 4-2. The extreme variability of the oxide thicknesses of the EOL specimens makes the appraisal of the actual amount of corrosion suffered during the exposure periods very difficult to perform, and only limited qualitative statements will be made for these specimens. In the same vein, the variability of the thickness from area to area means that an oxide measurement on one segment could not realistically be compared with the hydrogen content of another segment.

Tables 4-3, 4-4, and 4-5 are summaries of the corrosion data for the prefilmed specimens arranged according to specimen type. Figures 4-21 through 4-23 are plots of the corrosion data for the prefilmed specimens. All data have been corrected for the amount of oxide on the specimens before the start of the exposure period by subtracting 15 mg/dm² (the average oxide thickness of the prefilm coating) from the final oxide thickness. The specimens exposed during this test were essentially single specimens for each exposure period, and the lack of replicate samples does not permit drawing more definitive curves than those shown in the three figures. Isothermal test operating conditions in the present tests were the same as those in the previous B&W test except for the presence of dissolved hydrogen in the present test; therefore, the data from the previous test have been entered on the graph in Figure 4-23.

The agreement in the results for the isothermal rates indicates that the presence of dissolved hydrogen does not decrease the corrosion rate. The generally good fit of the values for the chemical shim environment indicates that its presence should not greatly increase the corrosion rate.

The corrosion rate values for the loop control specimens and the isothermal specimens show similar shaped curves, but with lower values for the loop control specimens. The general agreement in curve shape indicates that corrosion rates under isothermal conditions follow the same mechanism, whether under static or dynamic conditions. The lower rate for the loop control specimens can be explained by the difference in exposure temperature (640 F for loop control exposures and 650 F for the isothermal tests).

There is also generally good correlation between the corrosion rates under heat transfer and isothermal conditions, although there is some departure for the long-exposure specimens. The exact temperatures at the interface of the coolant and the heat transfer specimen are unknown and change with the location (the coolant temperature will increase as it travels over the heated surface) and may be higher than the 650 ± 5 F temperature used for comparison in the isothermal tests. The heat transfer corrosion curve cannot be drawn more definitely than is shown because of a lack of intermediate values and replicate determinations. Data from the previous test cannot be used in this case because of dissimilar test conditions. There is no drastic difference between the individual values on the heat transfer and the isothermal corrosion curves, and it appears that realistic corrosion data can be determined by testing under representative isothermal conditions.

4.3. Hydrogen Content

Tables 4-6, 4-7, 4-8, and 4-10 list the analytical values for hydrogen content for the prefilmed specimens. Figures 4-24 through 4-37 are summary sheets showing the analytical hydrogen values for all the specimens resulting from this program and include the values for both prefilmed and EOL specimens.

The results of the hydrogen assay for the EOL specimens were very erratic. The randomness is ascribed to the nonuniform nature of the oxide layer, as described in section 4.2, and the statistical variation expected in chemical analysis of specimens with this level of hydrogen. This randomness, together with the general analytical difficulty encountered in measuring relatively small differences in hydrogen content when the overall level was high, means that it is not possible to determine with any precision the amount of hydrogen absorbed by EOL specimens. Consequently, no quantitative interpretation of the EOL specimens is possible, although some qualitative information on the distribution of the hydrogen was determined in the metallographic examination and is discussed in sections 4.5.2 and 4.5.3.

Entries in Tables 4-6, 4-7, and 4-8 also compare the actual values of hydrogen found by assay with the hydrogen theoretically available from the corrosion reaction. The hydrogen pickup is calculated according to the equation

$$\text{hydrogen pickup (mg/dm}^2\text{)} = \frac{\text{original wt (g)} \times \Delta\text{H (ppm)} \times 10^{-3}}{\text{surface area (dm}^2\text{)}}$$

The ΔH is obtained by subtracting the hydrogen content of the as-received tubing (10 ppm) from the post-test hydrogen concentration in the specimen. The hydrogen value contains the amount of hydrogen absorbed during the prefilming step, since there is no "good figure" that can be used for this correction. This should give a constant "error," however. The theoretical hydrogen value from the corrosion reaction is calculated as follows:

$$\text{theoretical hydrogen} = \frac{\text{oxide thickness (mg/dm}^2\text{)}}{8}$$

Table 4-9 is a summary of the hydrogen absorption data found in Tables 4-6 through 4-8. Examination of the data indicates that in every case there is absorption of a greater fraction of the hydrogen set free by the corrosion reaction by the heat transfer specimens than by corresponding isothermal specimens. These results are in the same direction as those found in the previous B&W test (discussed in section 1.2, page 4). Figure 4-38, a plot of the hydrogen absorption under heat transfer and isothermal conditions, indicates that the two rates are approaching each other as the exposure period increases. The apparent narrowing of the gap is greatly dependent upon the value of one set of data, that of the long exposure specimen, and there is a possibility that this convergence is not real. Extrapolation of both curves to 1000 days' exposure indicates that there will be a difference in the two rates even after this time.

4.4. Hydrogen Gradient Analysis

Successive circumferential cuts were made on three segments of each heat transfer specimen as described in section 3.6. These cuts were taken as follows:

<u>Cut No.</u>	<u>Depth of cut</u>
A	1 mil off radius
B	1-1/2 mils off radius
C	3-1/2 mils off radius
D	6 mils off radius
E	13 mils (remainder)

The results of the hydrogen assay of each of these individual cuts are given in Figures 4-24 through 4-37. Figures 4-38 through 4-45 are plots of the hydrogen gradients of each of the prefilmed specimens. There is an axial gradient as well as a radial gradient for some of the specimens. The hydrogen content is somewhat higher on the downstream end of the specimens, which could be expected to be in contact with water of a slightly higher temperature, and thus would be at a higher temperature. The high hydrogen content in the outer few mils of the wall (which is the coolest zone) illustrates the concentrating effect of a thermal gradient on hydride distribution.

4.5. Hydride Distribution

The specimens were examined metallographically to determine the distribution, size, and relative content of the microscopically visible zirconium hydride. The examinations were made on nickel-plated specimens etched with a mixture containing 5 cc hydrofluoric acid, 2.5 cc nitric acid, 10 to 12 cc water, and 40 cc glycerine. The results are described in the following four subsections.

4.5.1. Prefilmed Specimens, High Purity Water Environment

Figures 4-46 through 4-50 illustrate the pertinent observations of the examination. The loop control specimen seems to offer the best baseline data, since it had no thermal gradient across the tube wall or along its length, and the cooling time was short enough to limit changes in the hydride form.

In the loop control specimens, the fine-grained hydride precipitate shows a tendency to grow larger by coalescence upon increased exposure, and the total amount visible shows a slight increase. Distribution of the hydride is fairly uniform throughout the wall. In the

heat transfer specimens, the hydride precipitate coalesces to form somewhat coarser particles than are seen in the loop control specimens. The downstream hot spot (position 8 on the figures) appears to perform satisfactorily its function of limiting hydride migration to the cooler zone of the specimen. There appears to be less hydride at this location than at the upstream location (position 6 on the figures). In the isothermal specimens, there is an increase of hydride upon exposure. The slow cooling inherent in shutting down the autoclave caused pronounced precipitation of the hydride from solution and coalescence into prominent particles. The amount of visible hydride is approximately 50% higher after 180 days than after 30 days. This agrees with the average oxide depth determined in the isothermal samples:

$$\frac{180 \text{ days}}{30 \text{ days}} = \frac{3}{2} \text{ hydride} = \frac{10.8 \times 10^{-5}}{7.1 \times 10^{-5}} \text{ inches oxide.}$$

Since the examined isothermal specimens were flattened tube sections, it was thought desirable to determine whether the associated cold deformation influenced hydride precipitation. Therefore, segments from specimen 4-5 with three different histories were examined. Significant features are shown in Figure 4-50. Specimen A-5 is a piece of the original tubing, as received, with no mechanical or chemical treatment. It shows small but well-defined particles of hydride (10 ppm hydrogen content) uniformly distributed. Specimen H-5, which had been prefilmed but not exposed, shows marked coalescence of the hydride precipitated during the slow cooling accompanying the autoclave shutdown. Section E-5 is a tubular isothermal specimen which had not been flattened. The transverse plane reveals a hydride condition similar to the prefilmed specimen and to the flattened isothermal specimens. Comparison with F-5-2 in Figure 4-46 shows a greater amount of precipitate in the flattened specimen, both in the radially directed particles at the outer surface and in the interior of the wall. On this basis it would appear that deformation promotes hydride precipitation and coalescence. The foregoing observations establish that the cooling rate after exposure determines the size of the hydride particles.

One word of caution should be added here. Apparent "edge effects" in the prefilmed specimens should not be misinterpreted, particularly in comparing these specimens with those of the EOL group. For example, the outer surfaces of specimens D-1-6, D-4-6, and B-5-4, and the inner surfaces of F-4-2, which appear a little dark, represent very slight differences in level rather than a change in hydride concentration. The exact cause of this "edge effect" is not known, but it may occur during polishing or etching.

4.5.2. End-of-Life Specimens, High Purity Water Environment

Figures 4-51 through 4-57 illustrate the structural features observed in the EOL specimens. The loop control specimen again serves as a baseline for comparison.

In the loop control specimens, there appears to be an increase in the amount of hydride visible as the time of exposure increases, and the hydride is most sharply defined in the specimens with the longest exposure time (B-16 and BB-8). The hydride distribution is uniform throughout.

All of the Zircaloy-4 heat transfer specimens contain a zone of relatively high hydride concentration at the outer surface, and the zone became more sharply defined and concentrated as the exposure time increased (see Figure 4-56^{*}). The distribution of the hydride did not seem to be affected by the downstream "hot spot." The total amount of visible hydride in the heat transfer specimens is judged to be less than in the loop control specimens, and it does not appear that the increased hydride in the outer zone is enough to make the total amount equal to that seen in the loop control specimens. For example, there is not a large difference between the hydride-enriched outside zone in

- - - - -

*It can be seen that specimen 2-8 has a pattern of hydride distribution identical to that of specimen 4-16. This substantiated a surmise that this specimen, which had been identified as having a Zircaloy-2 composition, was mislabeled. Preparatory work in etching the specimen for metallographic examination indicated that it was of Zircaloy-4 composition. This was confirmed when a chemical analysis of the archive specimen indicated almost complete absence of nickel and the proper concentration of iron.

D-18-6 and the uniform structure of the loop control section B-18-4 in Figure 4-54. The analytical chemical values do not show considerable difference between the segments at the two locations. This could mean that part of the hydride in the tube wall under the hydride-enriched outer zone is in solid solution.

In the isothermal specimens the general type of structure is similar to that of the loop specimens, but there is additional cross-growth of hydride in both the outside and the inside areas, which becomes more prominent with increased exposure time. The term cross-growth is applied to the patterns shown in Figure 4-57. In this figure, area B-16-4, a transverse plane through the loop control specimen, represents the hydride distribution throughout the specimen; area G-16-2, a transverse plane through the isothermal specimen, shows radially directed hydride immediately beneath the outside oxide layer; and area G-17-4, a longitudinal plane through the isothermal specimen, shows radially distributed hydride crossing the elongated grains at the inside diameter. Hydride of the form seen in G-16-2 could be mistaken for cracks at 100X, and the pattern represented by G-17-4 tends to give an impression of a higher hydride concentration than actually exists.

In the Zircaloy-2 specimen 2-9, the loop control specimen has uniformly distributed hydride. The heat transfer sample shows some indication of migration to a 5-mil-deep zone at its outside diameter, but it is much less than that of the Zircaloy-4 specimen having the same exposure. Hydride in the isothermal specimen is uniformly distributed, and more is visible than in the loop and the heat transfer specimens.

The depth of the surface in the Zircaloy-4 specimens seems to be related to both the structural features and the exposure times. Heat transfer specimens D-16 and D-17 (45 day and 30 day exposures) have similar oxide thicknesses and structures, which differ significantly from those of the 15-day exposure specimen D-18. The oxide on isothermal specimen 4-16, which was exposed for 45 days, is much thicker than that on the 30- and 15-day exposure specimens 4-17 and 4-18. Oxidation of the Zircaloy-2 specimen was quite erratic, as can be seen from the areas in Figure 4-55 and the values in Table 4-2.

4.5.3. Prefilmed and EOL Specimens, Chemical Shim Environment

Figures 4-58 through 6-62 illustrate significant features observed in the examination of these specimens. The hydrides in the loop control specimen are uniformly distributed, both in the prefilmed and the EOL specimens. The amount of visible hydride in the prefilmed specimens is roughly proportional to the length of the exposure. There were no clear cut relationships for the EOL loop control specimens. In the heat transfer specimens, the amount of hydride is a function of exposure time. There is evidence of some coalescence of hydride in the long-term exposure specimens (specimens 4-2 and 2-1), but no such evidence in the loop control specimens. The hot-spot (shoulder) area has no effect on hydride distribution, and there is no significant difference in the amount of hydride visible in the three specimens. In the EOL specimens, Zircaloy-2 specimen 2-12 shows a greater tendency for a hydride-concentrated zone near the outside diameter than does Zircaloy-4 specimen 4-19. This is a reversal of the trend for the specimens exposed to high purity water.

In the isothermal specimens, the slowly cooled prefilmed specimens reveal coarse hydride similar to that seen in the high purity water specimens (section 4.5.1). The 51-day exposure specimen 4-3 generally has a lower content of visible hydride than does the 231-day total exposure specimen 4-2. Specimen G-3 has a very erratic hydride distribution; the longitudinal area in specimen G-3-4 (Figure 4-58) is an unusually high hydride area and is not representative of the hydride content in this specimen. The Zircaloy-2 specimen has an apparently higher visible hydride content than specimen 4-2 does, and its distribution is more uniform. The EOL isothermal specimens are confusing, because Zircaloy-2 specimen 2-12 has more of the visible characteristics of the Zircaloy-4 group than it does of the other EOL Zircaloy-2 specimen, and EOL Zircaloy-4 specimen 4-19 lacks some of the characteristics associated with this alloy.

4.5.4. End Cap Specimens

Longitudinal planes through the end caps of selected heat transfer specimens were examined in the as-received and the heat-treated

conditions. The heat treatment was conducted as described in section 3.6 and essentially consists of heating the sample to 643 F, holding at temperature for 7 minutes, and allowing to cool slowly overnight.

Hydride in the weld structures joining the end cap and the tube is difficult to detect microscopically with the illuminating methods used in examining wrought structures. Under polarized light, however, the interfering details in the cast weld structure are darkened and thus subdued, and the hydride is brilliant white. Therefore all the areas in the tube at the end cap were photographed under suitably polarized conditions. The hydride particles appear somewhat larger under polarized light than under white illumination, but this presents no problem in determining relative size, concentration, and distribution.

Figures 4-63 through 4-67 show representative areas of the specimens examined. Some general observations are as follows:

1. The weld structures and the heat-affected (or grain-refined) zones in the specimen contain very little hydride in either the as-received or the heat-treated condition.
2. In the as-received condition, the portions of the tube unaffected by the heat of welding contain an amount and a distribution of hydride generally similar to that found at the hot spot areas. This is to be expected, since the upstream hot spot is immediately adjacent to the area examined.
3. Heat-treating the area produces coarse hydride particles through precipitation and coalescence during slow cooling in the prefilmed specimens. Heat-treatment of the EOL specimens, however, does not produce drastic changes.

Typical conditions in the heat transfer specimens at the end caps are shown in Figures 4-63 through 4-67 and discussed as follows:

1. Specimen 4-1 (Figure 4-63) — This specimen had the longest exposure to high purity water. The fine particles of hydride in

the normal* structure as it left the loop are converted to coarse, elongated particles in the heat treatment. The grain-refined zone and the weld structure in the tube contain only a few particles of visible hydride, both in the as-received and the heat-treated condition.

2. Specimens 4-16 and 2-8 (Figure 4-64) — The areas shown are from the normal tube positions, as received. They compare closely with the structures in areas away from the end cap, particularly in areas of relatively low hydride concentration. The difference between the effects of conventional and polarized light are also shown in this figure.

3. Specimens 4-2 and 4-3 (Figure 4-65) — The normal tube structures before and after heat treatment show the pronounced change in the size and total content of hydrides produced in prefilmed specimens by slow cooling.

4. Specimen 4-19 (Figure 4-66) — The normal specimen structure (as received) in this EOL specimen compares well with the area around one of the hot spots. Slow cooling after heat-treating resulted in precipitation of more hydride, but the hydrides did not coalesce into long, coarse particles. No significant change in the weld structure occurred during the heat treatment.

5. Specimens 2-1 and 2-12 (Figure 4-67) — These are Zircaloy-2 specimens. In the long-term exposure, prefilmed specimen 2-1, there is coalescence of hydride with heat treating and slow cooling, but no additional precipitation of hydride. In EOL specimen 2-12 there seems to be no additional precipitation of hydride, and it is questionable whether coalescence of hydride occurred.

The foregoing results indicate that the end caps do not act as hydrogen sinks in the heat transfer specimens. The visible amounts of hydride precipitated and coalesced in the prefilmed Zircaloy-4 specimens during slow cooling could equal the amounts already present in solution.

- - - - -

* Normal refers to portions of specimens that were unaffected by the heat of welding.

The two surprising phenomena found in the study of the end caps are the lower degree of hydride coalescence in the EOL specimens and the very low hydride content in the weld structures and weld heat-affected zones in the heat transfer specimens. One explanation for the diminished coalescence in the EOL specimens and the Zircaloy-2 specimens is that this is associated with the chemistry of the matrix. Conversion of zirconium into zirconium hydride will change the overall composition of the Zircaloy matrix, and this change would be greater in the EOL specimens than in the prefilmed specimens. The change in the matrix, then, would reduce the extent of coalescence. The diminished extent of coalescence in Zircaloy-2 specimens might be influenced by the nickel in the alloy. It is likely that a longer time at the heat-treating temperature would promote coalescence during slow cooling, and reference to GG-1-4 (Figure 4-60) shows that this does occur in isothermal specimens. It appears that pronounced coalescence is not likely to occur in EOL-treated specimens regardless of the time spent at the heat-treating temperature, because coalescence did not occur in the isothermal specimens.

The only plausible explanation for the very low hydride content in the weld structures and weld heat-affected zones in the heat transfer specimens is that a surface condition exists which either prevents diffusion of nascent hydrogen into the metal or reacts with it to form nonabsorbed molecular hydrogen or some other nonabsorbed compound. The possibility exists that during the welding operation an oxide film could form on the metal and react differently from the oxide formed during the prefilming step. There is no reason to believe that the weld metal would not absorb hydrogen to form the hydride.

Table 4-1. Metallographic Measurement of Oxide Thickness —
Prefilmed Specimens

Specimen type	Specimen No.	Oxide depth, $\times 10^{-3}$ inches	Oxide depth, microns	Equivalent weight gain, mg/dm ²
Loop control	B-1-4	9.7	2.43	37.9
Heat transfer	D-1-3	15.7	3.99	62.2
Isothermal	F-1-2	12.0	3.05	47.5
Isothermal	G-1-2	11.9	3.02	47.2
Isothermal	F-1-4	10.1	2.57	40.0
Isothermal	G-1-4	9.1	2.31	36.1
Loop control	B-2-4	10.7	2.72	42.4
Heat transfer	D-2-3	15.9	4.04	63.0
Isothermal	F-2-2	13.1	3.33	51.9
Isothermal	G-2-2	11.7	2.97	46.4
Isothermal	F-2-4	9.7	2.43	37.9
Isothermal	G-2-4	9.1	2.31	36.1
Loop control	B-3-4	6.9	1.75	27.3
Heat transfer	D-3-3	8.1	2.06	32.1
Isothermal	F-3-2	6.4	1.63	25.4
Isothermal	G-3-2	5.8	1.50	23.4
Isothermal	F-3-4	7.1	1.80	28.1
Isothermal	G-3-4	6.7	1.70	26.5
Loop control	B-4-4	7.1	1.80	28.1
Heat transfer	D-4-3	12.4	3.15	49.1
Heat transfer	D-4-6	13.7	3.48	58.5
Isothermal	F-4-2	8.1	2.06	32.1
Isothermal	G-4-2	8.3	2.11	32.9
Isothermal	F-4-4	8.5	2.16	33.7
Isothermal	G-4-4	8.2	2.08	32.5
Loop control	B-5-4	6.7	1.70	26.5
Heat transfer	D-5-3	6.7	1.70	26.5
Heat transfer	D-5-6	7.9	2.01	31.3
Isothermal	F-5-2	7.1	2.06	32.1
Isothermal	G-5-2	7.5	1.91	29.7
Isothermal	F-5-4	7.1	2.06	32.1
Isothermal	G-5-4	6.7	1.70	26.5
Loop control	B-13-4	8.3	2.11	32.9
Heat transfer	D-13-3	8.0	2.03	31.6
Isothermal	F-13-2	7.5	1.91	29.7
Isothermal	G-13-2	7.6	1.93	30.1
Loop control	BB-1-4 ^(a)	8.9	2.26	35.3
Heat transfer	DD-1-6 ^(a)	19.4	4.93	76.9
Isothermal	FF-1-2 ^(a)	13.9	3.53	55.1
Isothermal	GG-1-2 ^(a)	13.1	3.33	51.9
Isothermal	FF-1-4 ^(a)	10.9	2.77	43.2
Isothermal	GG-1-4 ^(a)	11.3	2.87	44.8

(a) Zircaloy-2 composition.

Table 4-2. Metallographic Measurement of Oxide Thickness — End-of-Life Specimens

Specimen type	Specimen No.	Oxide depth, $\times 10^{-5}$ inches	Oxide depth, microns	Equivalent weight gain, mg/dm ²
Loop control	B-16-4	99.8	25.3	394.7
Heat transfer	D-16-3	68.7	17.4	271.8
Heat transfer	D-16-6	78.8	20.0	312.2
Isothermal	F-16-2	107.0	27.2	424.3
Isothermal	G-16-2	94.9	24.1	376.0
Isothermal	F-16-4	107.0	27.2	424.3
Isothermal	G-16-4	94.9	24.1	376.0
Loop control	B-17-4	78.2	19.9	310.4
Heat transfer	D-17-3	57.8	14.7	229.4
Heat transfer	D-17-6	82.8	21.0	327.6
Isothermal	F-17-2	57.8	14.7	229.4
Isothermal	G-17-2	48.5	12.3	191.9
Isothermal	F-17-4	64.6	16.4	255.8
Isothermal	G-17-4	60.0	15.2	237.1
Loop control	B-18-4	75.8	19.2	299.5
Heat transfer	D-18-3	42.5	10.8	168.5
Heat transfer	D-18-6	52.5	13.3	207.5
Isothermal	F-18-2	52.5	13.3	207.5
Isothermal	G-18-2	68.7	17.4	271.4
Isothermal	F-18-4	54.5	13.8	215.3
Isothermal	G-18-4	52.5	13.3	207.5
Loop control	B-19-4	105.0	26.7	416.5
Heat transfer	D-19-3	92.9	23.6	368.2
Isothermal	F-19-2	84.8	21.5	335.4
Isothermal	G-19-2	80.8	20.5	319.8
Isothermal	F-19-4	82.8	21.0	327.6
Isothermal	G-19-4	86.8	22.0	343.2
Loop control	BB-8-4	96 (70-130) ^(b)	24.4	380.6
Heat transfer	DD-8-3	65	16.5	257.4
Heat transfer	DD-8-6	91 (60-120) ^(b)	23.1	360.4
Isothermal	FF-8-2	80	20.3	316.7
Isothermal	GG-8-2	79	20.1	313.6
Isothermal	FF-8-4	97	24.6	383.8
Isothermal	GG-8-4	79	20.1	313.6
Loop control	BB-9-4 ^(a)	86 (60-140) ^(b)	21.8	340.1
Heat transfer	DD-9-4 ^(a)	122 (70-175) ^(b)	31.0	483.6
Heat transfer	DD-9-6 ^(a)	91 (50-110) ^(b)	23.1	360.4
Isothermal	FF-9-2 ^(a)	77 (55-120) ^(b)	19.6	305.8
Isothermal	GG-9-2 ^(a)	98 (60-150) ^(b)	24.9	388.4
Isothermal	FF-9-4 ^(a)	87 (50-125) ^(b)	22.1	344.8
Isothermal	GG-9-4 ^(a)	130 (55-175) ^(b)	33.0	514.8
Loop control	BB-12-4 ^(a)	84.8	21.5	335.4
Heat transfer	DD-12-3 ^(a)	70.7	18.0	280.8
Isothermal	FF-12-2 ^(a)	72.7	18.5	288.6
Isothermal	GG-12-2 ^(a)	72.7	18.5	288.6
Isothermal	FF-12-4 ^(a)	64.6	16.4	255.8
Isothermal	GG-12-4 ^(a)	66.7	16.9	263.6

(a) Zircaloy-2 composition.

(b) Figure in parentheses is range of depths measured.

Table 4-3. Corrosion Data for Heat Transfer Specimens
(Corrected for Pre-Exposure Surface
Contribution)

Specimen No.	Exposure period, days	Corrosion, mg/dm ²
D-5-3	30, H ₂ O	11.5
D-5-6	30, H ₂ O	16.5
D-13-3	60, H ₂ O	16.6
D-4-3	120, H ₂ O	34.1
D-4-6	120, H ₂ O	43.5
D-1-3	180, H ₂ O	47.2
D-3-3	51, C-S ^(b)	17.2
D-2-3	180, H ₂ O 51, C-S ^(b)	48.0
DD-1-6 ^(a)	180, H ₂ O 20, C-S ^(b)	61.9

(a) Zircaloy-2 composition.

(b) Chemical shim environment.

Table 4-4. Corrosion Data for Loop Control Specimens
(Corrected for Pre-Exposure Surface
Contribution)

Specimen No.	Exposure period, days	Corrosion, mg/dm ²
B-5-4	30, H ₂ O	11.5
B-13-4	60, H ₂ O	17.9
B-4-4	120, H ₂ O	13.1
B-1-4	180, H ₂ O	22.9
B-3-4	51, C-S ^(b)	12.3
B-2-4	180, H ₂ O 51, C-S ^(b)	27.4
BB-1-4 ^(a)	180, H ₂ O 20, C-S ^(b)	20.3

(a) Zircaloy-2 composition.

(b) Chemical shim environment.

Table 4-5. Corrosion Data for Isothermal Specimens
(Corrected for Pre-exposure Surface
Contribution)

Specimen No.	Exposure period, days	Corrosion, mg/dm ²
F-5-2	30, H ₂ O	17.1
G-5-2	30, H ₂ O	14.7
F-13-2	60, H ₂ O	14.7
G-13-2	60, H ₂ O	15.1
F-4-2	120, H ₂ O	17.1
G-4-2	120, H ₂ O	17.9
F-4-4	120, H ₂ O	18.7
G-4-4	120, H ₂ O	17.5
F-1-2	180, H ₂ O	32.5
G-1-2	180, H ₂ O	32.2
F-1-4	180, H ₂ O	25.0
G-1-4	180, H ₂ O	21.1
F-3-2	51, C-S(b)	10.4
G-3-2	51, C-S(b)	8.4
F-3-4	51, C-S(b)	13.1
G-3-4	51, C-S(b)	11.5
F-2-2	180, H ₂ O +	36.9
G-2-2	51, C-S(b)	31.4
F-2-4	51, C-S(b)	22.9
G-2-4	51, C-S(b)	21.1
FF-1-2(a)	180, H ₂ O +	40.1
GG-1-2(a)	20, C-S(b)	35.9
FF-1-4(a)	20, C-S(b)	28.2
GG-1-4(a)	20, C-S(b)	29.8

(a) Zircaloy-2 composition.

(b) Chemical shim environment.

Table 4-6. Hydrogen Absorption Data for Heat Transfer Specimens

Specimen No.	Exposure period, days	Hydrogen pickup, ppm	Hydrogen pickup, $\mu\text{g}/\text{dm}^2$	Theoretical hydrogen, mg/dm^2	Hydrogen absorbed, %
D-5-2	30, H_2O	42.3	1.63	3.31	49.2
D-5-5	30, H_2O	39.3	1.52	3.91	38.9
D-13-2	60, H_2O	42.2	1.63	3.95	41.3
D-13-5	60, H_2O	44.0	1.70	3.95	43.0
D-4-2	120, H_2O	48.4	1.83	6.14	29.8
D-4-5	120, H_2O	43.2	1.65	7.31	23.0
D-1-2	180, H_2O	52.9	2.02	7.78	26.0
D-1-5	180, H_2O	54.2	2.07	7.78	26.6
D-3-2	51, C-S(b)	53.1	2.03	4.01	50.6
D-3-5	51, C-S(b)	46.6	1.85	4.01	46.6
D-2-2	180, H_2O	60.3	2.42	7.87	33.3
D-2-5	51, C-S(b)	101.3	3.91	7.87	49.7
DD-1-2(a)	180, H_2O	75.9	2.97	9.61	30.9
DD-1-5(a)	21, C-S(b)	85.6	3.35	9.61	34.9

Table 4-7. Hydrogen Absorption Data for Loop Control Specimens

B-5-2	30, H_2O	22.4	0.87	3.31	26.3
B-5-5	30, H_2O	24.8	0.97	3.31	29.3
B-13-2	60, H_2O	18.9	0.74	4.11	18.0
B-13-5	60, H_2O	18.1	0.71	4.11	17.3
B-4-2	120, H_2O	20.9	0.81	3.51	23.1
B-4-5	120, H_2O	20.8	0.81	3.51	23.1
B-1-2	180, H_2O	22.2	0.85	4.74	17.9
B-1-5	180, H_2O	15.8	0.61	4.74	12.9
B-3-2	51, C-S(b)	24.0	0.94	3.41	27.6
B-3-5	51, C-S(b)	22.3	0.87	3.41	25.5
B-2-2	180, H_2O	26.9	1.05	5.36	19.6
B-2-5	51, C-S(b)	22.1	0.86	5.36	16.0
BB-1-2(a)	180, H_2O	19.4	0.76	4.41	17.2
BB-1-5(a)	21, C-S(b)	20.7	0.82	4.41	18.6

Table 4-8. Hydrogen Absorption Data for Isothermal Specimens

F-5-3	30, H_2O	39.4	0.80	4.01	20.0
G-5-3	30, H_2O	40.5	0.88	3.71	23.7
F-13-3	60, H_2O	29.6	0.61	3.71	16.7
G-13-3	60, H_2O	37.3	0.77	3.76	20.5
F-4-3	120, H_2O	34.2	0.73	4.0	18.3
G-4-3	120, H_2O	31.8	0.68	4.1	16.6
F-1-3	180, H_2O	48.6	1.01	5.94	17.0
G-1-3	180, H_2O	46.1	0.99	5.90	16.8
F-3-3	51, C-S(b)	26.4	0.57	3.51	16.3
G-3-3	51, C-S(b)	24.8	0.52	3.31	15.7
F-2-3	180, H_2O	43.1	0.90	6.49	13.9
G-2-3	51, C-S(b)	56.7	1.19	5.80	20.5
FF-1-3(a)	180, H_2O (b)	71.1	1.46	6.09	21.2
GG-1-3(a)	20, C-S(b)	76.0	1.51	6.09	21.9

(a) Zircaloy-2 composition.

(b) Chemical steam environment.

Table 4-9. Hydrogen Absorption Under Different Conditions

Specimen type	Exposure to H ₂ O, days				Exposure to chemical shim, days		
	30	60	120	180	51	51 + 180 in H ₂ O	20 + 180 in H ₂ O ^(a)
Heat transfer	49.2	41.3	29.8	26.0	50.6	33.3	30.9
	38.9	43.0	23.0	26.6	63.6	49.7	30.9
Isothermal	20.0	16.7	18.3	17.0	16.3	13.9	21.2
	23.7	20.5	16.6	16.8	15.7	20.5	21.9
Loop control	26.3	18.0	23.1	17.9	27.6	19.6	17.2
	29.3	17.3	23.1	12.9	25.5	16.0	18.6

(a) Zircaloy-2 composition.

Table 4-10. Hydrogen Absorption Data for Heat Transfer End Plugs

Specimen No.	Exposure period, days	Hydrogen content, ppm			
		Wall, downstream	Wall, upstream	Plug, downstream	Plug, upstream
D-5	30, H ₂ O	46.8	40.0	66.6	34.3
D-13	60, H ₂ O	41.5	53.7	40.8	44.5
D-4	120, H ₂ O	58.5	50.6	70.9	52.2
D-1	180, H ₂ O	77.3	74.0	69.7	62.0
D-3	51, C-S ^(b)	50.8	43.5	48.8	44.0
D-2	180, H ₂ O	100	61.1	52.6	60.3
	51, C-S ^(b)				
DD-1 ^(a)	180, H ₂ O	93.4	99.3	70.8	70.4
	20, C-S ^(b)				

(a) Zircaloy-2 composition.

(b) Chemical shim environment.

Figure 4-1. Pre-Exposure Appearance of Typical Prefilmed Specimen

Figure 4-2. Pre-Exposure Appearance of EOL Specimen 4-16

Figure 4-3. Pre-Exposure Appearance of EOL Specimen 4-17

Figure 4-4. Pre-Exposure Appearance of EOL Specimen 4-18

Figure 4-5. Pre-Exposure Appearance of EOL Specimen 2-8

Figure 4-6. Pre-Exposure Appearance of EOL Specimen 2-9

Figure 4-7. Pre-Exposure Appearance of EOL Specimen 4-19

Figure 4-8. Pre-Exposure Appearance of EOL Specimen 2-12

Figure 4-9. Post-Exposure Appearance of Prefilmed Specimens — High Purity Water Environment, Heat Transfer Specimens

Figure 4-10. Post-Exposure Appearance of Prefilmed Specimens — High Purity Water Environment, Loop Control Specimens

Figure 4-11. Post-Exposure Appearance of Prefilmed Specimens — High Purity Water Environment, Isothermal Specimens

Figure 4-12. Post-Exposure Appearance of Prefilmed Specimens — Chemical Shim Environment, Heat Transfer Specimens

Figure 4-13. Post-Exposure Appearance of Prefilmed Specimens — Chemical Shim Environment, Loop Control Specimens

Figure 4-14. Post-Exposure Appearance of Prefilmed Specimens — Chemical Shim Environment, Isothermal Specimens

Figure 4-15. Post-Exposure Appearance of EOL Specimens
— High Purity Water Environment, Heat
Transfer Specimens

Figure 4-16. Post-Exposure Appearance of EOL Specimens
 — High Purity Water Environment, Loop
 Control Specimens

Figure 4-17. Post-Exposure Appearance of EOL Specimens
— High Purity Water Environment, Isothermal
Specimens

Figure 4-18. Post-Exposure Appearance of EOL Specimens
— Chemical Shim Environment, Heat Transfer
Specimens

Figure 4-19. Post-Exposure Appearance of EOL Specimens
— Chemical Shim Environment, Loop Control
Specimens

Figure 4-20. Post-Exposure Appearance of EOL Specimens
— Chemical Shim Environment, Isothermal
Specimens

Figure 4-22. Corrosion of Loop Control Specimens

Figure 4-23. Corrosion of Isothermal Specimens

Figure 4-24. Hydrogen Assay Summary Sheet —
Specimen 4-5

Figure 4-25. Hydrogen Assay Summary Sheet —
Specimen 4-13

Figure 4-26. Hydrogen Assay Summary Sheet — Specimen 4-4

Figure 4-27. Hydrogen Assay Summary Sheet — Specimen 4-1

Figure 4-28. Hydrogen Assay Summary Sheet —
Specimen 4-3

Figure 4-29. Hydrogen Assay Summary Sheet —
Specimen 4-2

Alloy
Pre-exposure Condition
Exposure Environment

Exposure Duration

Zircaloy-4
Pre-filmed
Water +
Chemical Shim

180 ± 51 Days

Figure 4-30. Hydrogen Assay Summary Sheet —
Specimen 2-1

Alloy	Zircaloy-2
Pre-exposure Condition	Pre-filmed
Exposure Environment	Water
Exposure Duration	Chemical Shim 180 ± 20 Days

Figure 4-31. Hydrogen Assay Summary Sheet —
Specimen 4-16

Alloy
Pre-exposure Condition
Exposure Environment
Exposure Duration

Zircaloy-4
EOL
Water
45 Days

Figure 4-32. Hydrogen Assay Summary Sheet —
Specimen 4-17

Figure 4-33. Hydrogen Assay Summary Sheet —
Specimen 4-18

Figure 4-34. Hydrogen Assay Summary Sheet — Specimen 2-8

Alloy	Zircaloy-4
Pre-exposure Condition	EOL
Exposure Environment	Water
Exposure Duration	45 Days

Figure 4-35. Hydrogen Assay Summary Sheet —
Specimen 2-9

Alloy	Zircaloy-2
Pre-exposure Condition	EOL
Exposure Environment	Water
Exposure Duration	15 Days

Figure 4-36. Hydrogen Assay Summary Sheet —
Specimen 2-12

Alloy
Pre-exposure Condition
Exposure Environment
Exposure Duration

Zircaloy-2
EOL
Chemical Shim
51 Days

Figure 4-37. Hydrogen Assay Summary Sheet —
Specimen 4-19

Figure 4-38. Comparison of Corrosion and Hydrogen Absorption for Heat Transfer and Isothermal Conditions

Figure 4-39. Hydrogen Gradient of Specimen 4-5

Figure 4-40. Hydrogen Gradient of Specimen 4-13

Figure 4-41. Hydrogen Gradient of Specimen 4-4

Figure 4-42. Hydrogen Gradient of Specimen 4-1

Figure 4-43. Hydrogen Gradient of Specimen 4-3

Figure 4-44. Hydrogen Gradient of Specimen 4-2

Figure 4-45. Hydrogen Gradient of Specimen 2-1

HYDROGEN GRADIENT FOR SPECIMEN 2-1

Figure 4-46. Metallographic Examination of Specimen 4-5

Figure 4-47. Metallographic Examination of Specimen 4-13

Figure 4-48. Metallographic Examination of Specimen 4-4

Figure 4-49. Metallographic Examination of Specimen 4-1

Figure 4-50. Metallographic Examination of Specimen 4-5,
Various Conditions

Figure 4-51. Metallographic Examination of Specimen 4-16

Figure 4-52. Metallographic Examination of Specimen 4-17

Figure 4-53. Metallographic Examination of Specimen 4-18

Figure 4-54. Metallographic Examination of Specimen 2-8

Figure 4-55. Metallographic Examination of Specimen 2-9

Figure 4-56. Metallographic Comparison of EOL Heat Transfer Specimens

Figure 4-57. Directional Effects in Hydride Formation,
EOL Specimens

Figure 4-58. Metallographic Examination of Specimen 4-3

Figure 4-59. Metallographic Examination of Specimen 4-2

Figure 4-60. Metallographic Examination of Specimen 2-1

Figure 4-61. Metallographic Examination of Specimen 4-19

Figure 4-62. Metallographic Examination of Specimen 2-12

Figure 4-63. Metallographic Examination of End Cap Area,
Specimen 4-1

Figure 4-64. Metallographic Examination of End Cap Area,
Specimens 4-16 and 2-8

Figure 4-65. Metallographic Examination of End Cap Area,
Specimens 4-2 and 4-3

Figure 4-66. Metallographic Examination of End Cap Area,
Specimen 4-19

Upper left: Normal tube structure, after exposure
Upper right: Normal tube structure, heat treated
Lower left: Weld structure, after exposure
Lower right: Weld structure, heat treated

Zircaloy 4 Specimen No. 19 At End Cap

Figure 4-67. Metallographic Examination of End Cap Area,
Specimens 2-1 and 2-12

5. DISCUSSION

The most significant finding from this program is that the Zircalloys absorb more corrosion-produced hydrogen under heat transfer conditions than under isothermal conditions. This difference in the absorption rates is much greater than that in the corrosion rates under the same two conditions. These findings confirm those from B&W's previous program on the subject. In the recent program, two potential sources of hydrogen contamination were considered: (1) contamination of the inside wall of a specimen by water or hydrogen-containing compounds; (2) contamination by traces of water in the helium gas used in the annulus between the heater and the interior wall of a specimen. Since great pains were taken to prevent contamination by both sources, the difference in hydrogen absorption values must be due to other factors.

The major difference in the operating conditions of the two types of specimens is the nature of the microenvironment next to the specimen's wall. The environment adjacent to the isothermal test specimen is a layer of liquid coolant. Under the high heat fluxes used in this test, local boiling occurs on the heat-transfer specimen, and the microenvironment in the area of the specimen's wall is a mixture of steam and water. This environment of steam-water of low oxygen content is apparently the cause of the enhanced hydrogen absorption. An alternate possibility is that hydrogen absorption is autocatalytic; that is, material of high hydrogen content absorbs more hydrogen than does material of low hydrogen content.

Evaluation of the hydriding rate in the past has usually involved either isothermal testing or the use of low heat flux conditions where local boiling has not been present. This phenomenon of increased hydrogen absorption under heat transfer conditions has become apparent only recently with the development of reliable, long-lived, high-heat-flux equipment.

The general reproducibility of the isothermal absorption rates between this test and the previous test indicates that the presence of dissolved hydrogen does not increase the hydrogen absorption rate. This suggests that Zircaloy does not absorb hydrogen in the molecular form, and that the hydrogen resulting from the corrosion reaction is absorbed at the time of liberation while it is in the atomic or "nascent" form.

The technique used to simulate end-of-life cladding conditions did not yield completely satisfactory specimens. The major drawbacks to the technique were that the oxide coatings were not of the same physical form as the actual cladding coatings, and they had poor uniformity. A better technique should be developed to obtain such coatings. If enough preparation time exists, the best way now available is exposure to steam at elevated temperatures, but the time required is long, and careful replenishment practices must be followed to prevent the buildup of hydrogen to such an extent that the reaction kinetics change.

6. CONCLUSIONS AND RECOMMENDATIONS

The results of the tests described in this report led to the following conclusions:

1. The corrosion rates of Zircaloy under heat transfer and isothermal conditions are essentially the same. Fuel cladding operating at a 650 F surface temperature for a 1000-day core life will experience a metal wastage of about 0.7 mil. Additionally, the corrosion film formed will have an insulating effect to the transfer of heat from the cladding to the coolant that will result in an increase in average cladding temperature of as much as 35 F toward the end of core life. This loss of metal combined with the reduced strength associated with the increased cladding temperature should be considered during the design of the fuel element so that additional wall thickness is incorporated in the fuel cladding or other action is taken as necessary to ensure the mechanical integrity of the fuel element during service.

2. Zircaloy absorbs more corrosion-released hydrogen under heat transfer conditions than under isothermal conditions, indicating that realistic testing of this phenomenon should be performed under representative heat transfer conditions. Cladding in a pressurized water reactor will absorb about 225 ppm hydrogen in a 1000-day core life. Under operating conditions the hydrogen will be concentrated in a layer on the outer (coolant) side of the cladding beneath the corrosion film and will have a negligible effect on the cladding behavior. However, after slow cooling from operating conditions, the hydrogen will be uniformly distributed through the cladding thickness and will cause a significant reduction in ductility. Therefore, care must be exercised in handling spent fuel elements to preclude mechanical damage, since even slight plastic deformation of the cladding could result in rupture.

3. The presence of dissolved hydrogen in the coolant in concentrations of 20 to 40 cc per liter does not affect the hydrogen absorption rate, indicating that hydrogen is not absorbed in the dissolved gas form.

4. The presence of chemical shim control solids did not affect the corrosion rate or the hydrogen absorption rate during the 51-day test period. There is an uncertainty as to the effect of shim control and pH adjusting chemicals on longer term corrosion and hydriding of Zircaloy, particularly under the local boiling conditions (a possible localized concentrating mechanism) prevalent in current pressurized water reactors. An investigation by Hilner and Chirigos¹¹ demonstrated an acceleration of corrosion and hydriding of Zircaloy in lithium hydroxide solutions of concentrations greater than 0.005 molar. The present test used potassium hydroxide as the pH adjusting agent; however, lithium hydroxide is being seriously considered as a pH adjusting chemical, and in view of the Hilner and Chirigos results, the effect of lithium hydroxide on Zircaloy corrosion under heat transfer conditions should be investigated.

5. There was no evidence of concentration of the shim control chemicals on the cladding during the 51-day test period.

7. REFERENCES

- ¹ Lyman, L. R., Metallurgical Examination of PWR Core 1 Blanket Fuel Rods at End of Third Seed Life, Westinghouse Atomic Power Division, WAPD-TM-433, August 1964.
- ² Kass, S., The Development of the Zircalloys, Westinghouse Atomic Power Division, WAPD-T-1549, September 1963.
- ³ Sawatzky, A., "The Diffusion and Solubility of Hydrogen in the Alpha-Phase of Zr-2," J. Nucl. Materials, 2, 62-68 (1960).
- ⁴ Louthan, M. R., Jr., and Marshall, R. P., Directional Hydriding of Zircaloy Cladding, "Savannah River Laboratories, presented to the 11th Annual AEC Corrosion Symposium, May 23, 1962.
- ⁵ Whitwham, D., Metallographic Study of the System ZrH_x (Mem. Scient. Rev. Metall. LVII, 1, 1960), APEX-614, April 1961.
- ⁶ Rundle, R. E., Shull, C. G., and Wollan, E. O., "The Crystal Structure of Thorium and Zirconium Dihydrides by X-Ray and Neutron Diffraction," Acta Crystallographica, 5, 22 (1952).
- ⁷ Burton, H. H., Hydrogen Effects on Zircaloy-2 Tensile Properties, HW-61077, July 10, 1959.
- ⁸ Mudge, W. L., Jr., "Effect of Hydrogen on the Embrittlement of Zirconium and Zirconium-Tin Alloys," Zirconium and Zirconium Alloys, ASM Symposium 146 (1953).
- ⁹ Lowe, A. L., Jr. and Johnson, C. R., Effects of Hydrogen and Precipitated Hydrides on Mechanical Properties of Zircaloy-4, Task 2 Final Report - Corrosion and Hydriding of Zircaloy, The Babcock & Wilcox Company, BAW-3765-6, Lynchburg, Virginia, March 1968 (EURAE-1954).
- ¹⁰ Winton, J., A Method for Gas Hydriding Zirconium Alloys at 400 C, TRG Report 1255 (1966).

- ¹¹ Hilner, E. and Chirigos, J. N., The Effect of Lithium Hydroxide and Related Solutions on the Corrosion Rate of Zircaloy in 680 F Water, WAPD-TM-307, August 1962.

APPENDIX A
Specimen Preparation Procedure

1. Measure and lay off the tube (approximately 30 inches) as shown in Figure 3-1. Begin the measurements on the "A" end, and make up for any deviations in the length of the tube from 30 inches total by altering the length of the "H" segment.
2. Identify all the segments by scribing the appropriate label on the left end of all segments except the "D" end of the C-D segment, which is marked on the right end.
3. Make cuts at the junction between the A and B and B and C segments. Deburr the cut ends of the tubing.
4. Reserve the "A" segment as an archive specimen. Store in a desiccator for possible future use. Reserve the "B" segment for additional treatment later and store in a desiccator.
5. Deburr ends of tubing.
6. Degrease in acetone.
7. Measure the inside diameter of the tubing. Obtain maximum and minimum readings in the middle and 1-inch from each end.
8. Rinse in acetone.
9. Pickle approximately 0.0015 inch off the ID of the 23-inch-long C-H segment by circulating the pickling solution through it with a peristaltic pump.
10. Circulate 800 ml of fresh warm tap water through the ID for 1 to 2 minutes.
11. Remove from the circulating system and soak in warm running tap water for 5 to 10 minutes.
12. Rinse in running demineralized water for 2 to 5 minutes.
13. Immerse and rinse in methyl alcohol.
14. Dry.
15. Measure the ID as in step 7.
16. Reverse the specimen end-for-end in the circulating line and pickle about 0.0015 inch off the ID.
17. Repeat steps 9 through 15 until the ID has reached 0.370 inch.
18. Soak the specimen in warm running tap water for at least 1/2 hour.
19. Rinse in running demineralized water for 5 to 10 minutes.
20. Rinse in methyl alcohol.
21. Dry.
22. Take final dimensional measurements of the ID.
23. Store in desiccator until next step.
24. Make cuts at the junctions of D and E, E and F-G, and F-G and H. This will give four segments. Save segments E, F-G, and H for the preparational procedure outlined in steps 121 through 132. Save segment B for the preparational procedure outlined in steps 81 through 120.

Heat Transfer Specimen Preparation

25. Take C-D segment and measure OD. Obtain maximum and minimum readings at 1-3/8 inches and 8 inches from the "D" end and 1-1/8 inches from the "C" end.
26. Install a tight-fitting, 1/16-inch-wide Neoprene rubber ring at locations 7/8-inch from the "D" end of the specimen and at 6 inches from the first ring (6-7/8 inches).
27. Plug both ends of the specimen with appropriately sized rubber stoppers.
28. Pickle about 0.0015 inch off the OD by immersing the specimen in the pickling solution and rotating the segment 180 degrees around its axis.
29. While still wet from the pickling solution, immerse the specimen in warm running tap water and rinse thoroughly for 5 to 10 minutes.
30. Immerse and rinse in running demineralized water for 2 to 5 minutes.
31. Rinse in methyl alcohol.
32. Dry.
33. Measure the OD as in step 25.
34. Install the specimen 90 degrees from its previous rotational location and pickle about 0.0015 inch off the OD, rotating it 180 degrees around its axis.
35. Repeat steps 28 through 32.
36. Remove the Neoprene rings.
37. Install the specimen 90 degrees from its previous rotational location and pickle about 0.0005 inch off the OD.
38. Repeat steps 29 through 32.
39. Install specimen at 90 degrees from its previous rotational location and pickle about 0.0005 inch off the OD.
40. Repeat steps 29 through 32.
41. Remove end plugs.
42. Soak the specimen in warm running tap water for at least 1/2 hour.
43. Immerse and rinse in running demineralized water for 5 to 10 minutes.
44. Rinse in methyl alcohol.
45. Dry.
46. Measure OD as in step 25.
47. Store in desiccator until the next step.
48. Heliarc-weld the end caps and flanges in place in a dry box. Handle with clean, white gloves during welding. Weld end cap with threads on the "D"-labeled end and weld end cap without threads at the other

end. Weld the flange 12-1/16 inches from the "D" end of the specimen.

49. Rinse in acetone.
50. Measure OD.
51. Plug the threaded end cap with suitable rubber stopper.
52. Pickle about 0.0005 inch off the OD.
53. Immerse in warm running tap water and rinse for 5 to 10 minutes.
54. Immerse in running demineralized water and rinse for 2 to 5 minutes.
55. Rinse in methyl alcohol.
56. Dry.
57. Measure OD.
58. Install the specimen 90 degrees from its previous rotational direction and pickle about 0.0005 inch off the OD.
59. Soak specimen in warm running tap water for at least 1/2 hour.
60. Immerse in running demineralized water for 5 to 10 minutes.
61. Dry.
62. Take final dimensional measurements of the OD (final dimension is specified as 0.420 ± 0.0005 inch).
63. Rinse in acetone.
64. Rinse in demineralized water.
65. Rinse in acetone.
66. Weigh.
67. Perform the appropriate prefilming or hydriding operation.
68. Reweigh.
69. Make at least two 35 mm slides for two referenced, diametrically opposite surfaces.
70. Rinse in acetone.
71. Store in desiccator until the next step.
72. Machine-cut the "C" portion off the specimen at the bottom of the flange. Retain "C" specimen for future analysis and reference.
73. Chase threads in end cap.
74. Rinse in acetone.
75. Leak-check with helium mass spectrometer.
76. Rinse in acetone.
77. Rinse in demineralized water.
78. Rinse in acetone.
79. Reweigh.

80. Store in desiccator until time for insertion in loop.

Loop Control Specimen Preparation

81. Plug both ends of the "B" segment with appropriately sized rubber stoppers.
82. Pickle about 0.0015 inch off OD by immersing the specimen into the pickling solution and rotating the segment 180 degrees around its axis.
83. While still wet from the pickling solution, immerse the specimen in warm running tap water and rinse thoroughly for 5 to 10 minutes.
84. Immerse and rinse in running demineralized water for 2 to 5 minutes.
85. Rinse in methyl alcohol.
86. Dry.
87. Measure the OD.
88. Install the specimen 90 degrees from its previous rotational location and pickle about 0.0015 inch off the OD, rotating it 180 degrees around its axis.
89. Repeat steps 83 through 86.
90. Remove end plug.
91. Soak the specimen in warm running tap water for at least 1/2 hour.
92. Immerse in running demineralized water for 5 to 10 minutes.
93. Rinse in methyl alcohol.
94. Dry.
95. Measure OD and ID.
96. Store in desiccator until next step.
97. Heliarc-weld end plugs into place in a dry box. Both end caps are to be threaded.
98. Rinse in acetone.
99. Plug the threaded ends with suitable rubber stoppers.
100. Pickle about 0.0005 inch off the OD.
101. Immerse in warm running tap water and rinse for 5 to 10 minutes.
102. Immerse in running demineralized water and rinse for 2 to 5 minutes.
103. Rinse in methyl alcohol.
104. Dry.
105. Measure OD.

106. Install specimen 90 degrees from its previous rotational direction and pickle about 0.0005 inch off the OD.
107. Soak specimen in warm running tap water.
108. Immerse in running demineralized water for 5 to 10 minutes.
109. Rinse in methyl alcohol.
110. Dry.
111. Take final dimensional measurement of the OD (specified as 0.420 ± 0.005 inch) and length.
112. Rinse in acetone.
113. Rinse in demineralized water.
114. Rinse in acetone.
115. Weigh.
116. Perform the appropriate prefilming or hydriding operation.
117. Reweigh.
118. Make at least two 35 mm slides for two referenced, diametrically opposite surfaces.
119. Rinse in acetone.
120. Store in desiccator until time for insertion in loop.

Isothermal Autoclave Specimens Preparation

121. Plug both ends of the "E," "F-G," and "H" segments with appropriately sized rubber stoppers.
122. Follow steps 82 through 95 as outlined in the Loop Control Specimen Preparation.
123. Store in desiccator until next step.
124. Split the F-G segment into two strips. Flatten slowly to prevent work-hardening.
125. Make the final dimensional measurement of the specimens (OD, ID, thickness, and length).
126. Rinse in acetone.
127. Perform the appropriate prefilming or hydriding operation.
128. Reweigh.
129. Make at least two 35 mm slides for two referenced, diametrically opposite surfaces.
130. Rinse in acetone.
131. Store in desiccator until time for insertion in loop. Reserve the "H" specimen for reference and analysis.

APPENDIX B
Specimen Preparation Procedure for Hydrogen Analyses

1. Bulk Hydrogen Analyses (Rings)

1. Cut rings from tubular test specimens at the required locations (generally about 1/16-inch long, depending on the expected hydrogen concentration).
2. Deburr rings, maintaining sharp corners to provide representative cross sections.
3. Rinse in methyl alcohol.
4. Dry in air.
5. Rinse in ether (first rinse).
6. Dry in air.
7. Rinse in ether (second rinse). Use three 50 cc beakers covered with proper sized watch glasses for the foregoing three rinses. Use fresh solutions for every three specimens.
8. Dry in air.
9. Vacuum desiccate for a minimum of 1 hour.
10. Weigh. About 0.25 gram is required for a sample of medium concentration.
11. Wrap with a 4-inch length of clean wire, and tie the ends of the wire together. The wire is to be precleaned as in steps 3 through 8.
12. Clean the wire-wrapped specimen as in steps 3 through 8.
13. Place in a clean glass vial (precleaned as in steps 3 through 8).
14. Place new, clean aluminum foil in the vial caps.
15. Make label for the vial and put specimen identification number on the label.
16. Vacuum desiccate for a minimum of 1 hour.
17. Submit to chemistry laboratory for analysis.

2. Hydrogen Gradient Analyses

2.1. Turnings

1. Clean lathe and all tools with acetone and methyl alcohol.
2. Cover machine with clean aluminum foil to catch all chips and turnings. If a long turning is made, cut it before it breaks off and becomes lost.
3. Machine gradient samples—machine the required thickness off with one cut, if possible. DO NOT OVERHEAT THE SPECIMENS OR CHIPS; DO NOT USE OIL, GREASE, OR COOLANT.

<u>Cut No.</u>	<u>Depth of cut</u>
A	1 mil off radius
B	1-1/2 mils off radius
C	3-1/2 mils off radius
D	6 mils off radius
E	13 mils off radius (remainder)

4. Place turnings from each cut into a clean 50 ml beaker (prepared as in B-1-3 through B-1-8.
5. Rinse turnings with methyl alcohol.
6. Dry in air.
7. Rinse with ether (first rinse).
8. Dry in air.
9. Rinse with ether (second rinse).
10. Dry in air.
11. Transfer to a clean glass vial and vacuum desiccate for 1 hour.
12. Clean tin capsules (individually) as in steps A5 to A10.
13. Make a ball from a 4-inch length of clean iron wire.
14. Rinse the iron wire ball as in steps A8 to A10 above, and place in the bottom of the tin capsule.
15. Vacuum desiccate for a minimum of 1 hour.
16. Weigh the tin capsule and iron wire ball.
17. Fill the tin capsule almost to the top with the specimen turnings.
18. Crimp the capsule.
19. Compact the capsule to make it smaller.
20. Pierce holes in the capsule with a clean needle to aid in subsequent evacuation.
21. Vacuum desiccate for a minimum of 1 hour.
22. Weigh the filled capsule.
23. Place capsule in a clean glass vial, prepared as in steps A5 through A10.
24. Submit to chemistry laboratory for analysis.

2.2. Remainder Sample

1. Cut rings from the specimen. The ring will have to be longer than that used in the bulk samples and should weigh not less than 0.30 gram.
2. Rinse in methyl alcohol.

3. Dry in air.
4. Rinse in ether (first rinse).
5. Dry in air.
6. Rinse in ether (second rinse).
7. Dry in air.
8. Vacuum desiccate for a minimum of 1 hour.
9. Weigh.
10. Wrap with a 4-inch length of clean iron wire precleaned as in steps B2 through B7.
11. Clean as in steps B2 through B7.
12. Place in a clean glass vial, prepared as in steps B2 through B7.
13. Vacuum desiccate for a minimum of 1 hour.
14. Submit to chemistry laboratory for analysis.

3. Preparation of Standards for Bulk Hydrogen Analysis Samples

1. Rinse in methyl alcohol.
2. Dry in air.
3. Rinse in ether (first rinse).
4. Dry in air.
5. Rinse in ether (second rinse).
6. Dry in air.
7. Vacuum desiccate for at least 1 hour.
8. Weigh.
9. Wrap with a 4-inch length of clean iron wire (precleaned as in steps 1 through 6, above).
10. Rinse as in steps 1 through 6, above.
11. Place in a clean glass vial prepared and cleaned as in steps 1 through 6, above.
12. Vacuum desiccate for a minimum of 1 hour.
13. Submit to chemistry laboratory for analysis.

4. Standards for Hydrogen Gradient Analysis Samples

1. Rinse with methyl alcohol.
2. Dry in air.
3. Rinse in ether (first rinse).
4. Dry in air.

5. Rinse in ether.
6. Dry in air.
7. Vacuum desiccate for a minimum of 1 hour.
8. Weigh.
9. Rinse tin capsules, individually, as in steps 1 through 6, above.
10. Make a ball from a 4-inch length of clean iron wire.
11. Rinse the iron wire ball as in steps 1 through 6, above, and place in the bottom of the tin capsule.
12. Flatten the tin capsule and roll it over the standard sample.
13. Pierce holes in the capsule with a clean needle to aid in subsequent evacuation.
14. Vacuum desiccate for a minimum of 1 hour.
15. Weigh.
16. Vacuum desiccate for a minimum of 1 hour.
17. Submit to chemistry laboratory for analysis.

DISTRIBUTION

1. U. S. Atomic Energy Commission (21)
Brussels Office
APO, New York 09667
Attn: Senior AEC Representative
2. U. S. Atomic Energy Commission (2)
New York Operations Office
376 Hudson Street
New York, New York 10014
Attn: Leo Graup
Reports Library
3. U. S. Atomic Energy Commission
Brookhaven Area Office
New York Patents Group
Upton, New York 11973
Attn: Harmon S. Potter
4. U. S. Atomic Energy Commission
Office of Foreign Activities, GM
Washington, D. C. 20545
5. U. S. Atomic Energy Commission
General Counsel for Patents
Washington, D. C. 20545
Attn: Roland A. Anderson
6. U. S. Atomic Energy Commission
Division of Technical Information Extension
P.O. Box 62
Oak Ridge, Tennessee 37830
7. U. S. Atomic Energy Commission (6)
Division of Reactor Development & Technology
Washington, D. C. 20545
Attn: J. M. Simmons
F. Kerze, Jr.
W. H. Layman
M. A. Rosen
A. J. Pressesky
E. E. Kintner

8. U.S. Atomic Energy Commission (2)
Division of Naval Reactors
Washington, D.C.
Attn: Robert H. Steele
9. U.S. Atomic Energy Commission
Oak Ridge Operations Office
P.O. Box E
Oak Ridge, Tennessee 37830
Attn: C. Matthews
10. U.S. Atomic Energy Commission
Savannah River Laboratory
P.O. Box A
Aiken, South Carolina 29802
Attn: S. Rideout
11. U.S. Atomic Energy Commission
c/o Atomic Energy of Canada, Limited
Chalk River, Ontario, Canada
Attn: G. W. Perry
12. U.S. Atomic Energy Commission
c/o Whiteshell Nuclear Research
Establishment AECL
Pinawa, Manitoba, Canada
Attn: A. Sawatzky
13. Oak Ridge National Laboratory (3)
Union Carbide Corporation
AEC Operations
P.O. Box X
Oak Ridge, Tennessee 37830
Attn: P. Patriarca
J. E. Cunningham
P. L. Rittenhouse
14. Battelle Memorial Institute (5)
Pacific Northwest Laboratory
P.O. Box 999
Richland, Washington 99352
Attn: J. J. Cadwell
R. L. Dillon
A. L. Berment
R. G. Wheeler
D. R. de Halas

15. Argonne National Laboratory (2)
9700 South Cass Avenue
Argonne, Illinois 60439
Attn: S. Greenberg
J. E. Draley

16. Atomics International
P.O. Box 309
Canoga Park, California 91304
Attn: H. Pearlman

17. Battelle Memorial Institute (2)
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201
Attn: S. Paprocki
W. Berry

18. Westinghouse Electric Corporation (4)
Bettis Atomic Power Laboratory
P.O. Box 79
West Mifflin, Pennsylvania 15122
Attn: B. Lustman (2)
W. J. Babyak (2)

19. Combustion Engineering, Inc. (2)
Nuclear Division
Prospect Hill Road
Windsor, Connecticut 06095
Attn: S. S. Christopher
W. P. Chernock

20. General Electric Company (4)
Vallecitos Atomic Laboratory
P.O. Box 846
Pleasanton, California 94566
Attn: H. H. Klepfer (2)
K. Cohen (2)

21. Knolls Atomic Power Laboratory
P.O. Box 1072
Schenectady, New York 12301
Attn: A. E. Bibb

22. General Electric Company (2)
Nuclear Materials & Propulsion Operation
P.O. Box 15132
Cincinnati, Ohio 45215
Attn: F. White
D. H. Ahmann

23. General Electric Company
Atomic Power Equipment Department
P.O. Box 254
San Jose, California 95125
Attn: D. H. Imhoff
24. Superior Tube Company
Morristown, Pennsylvania
Attn: C. Matthews
25. United Nuclear Corporation
5 New Street
White Plains, New York 10601
Attn: W. S. Mott
26. Westinghouse Electric Corporation (3)
Atomic Power Division
P.O. Box 355
Pittsburgh, Pennsylvania 15230
Attn: R. Allio (2)
P. G. DeHuff
27. Wah Chang Corporation
P.O. Box 460
Albany, Oregon 97321
Attn: S. Worchester
28. The Babcock & Wilcox Company (37)
Allen, RK/Alliance	Library (2)
Barringer, HS	Littrell, LW (2)
Boyer, RL	Lowe, AL, Jr. (2)
Breazeale, WM	Lynch, ED
Central Files (6)	Poor, HH/Alliance
Deuster, RW	Probert, PB/Barberton
Esleeck, SH	Rubright, MM/Alliance (2)
Ferguson, KM	Schmitt, DH
Grant, SP	Swenson, HS/Alliance
Holt, CD	Travis, CC/TRG
Johnson, CR (2)	Trent, CR
Jones, CE/Alliance	Webb, RA, Jr.
Koch, DW/Alliance (2)	Whitaker, BW
Leirvik, RM	