MASTER

ACNP-6009

INVESTIGATION OF THE CORROSION ASPECTS OF SELECTED ALUMINUM ALLOYS

Final Report

By
Karlis Riskevics

January 31, 1961

Atomic Energy Division
Allis-Chalmers Manufacturing Company
Milwaukee, Wisconsin

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.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report 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 report.

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

This report has been reproduced directly from the best available copy.

Printed in USA. Price \$2.50. Available from the Office of Technical Services, Department of Commerce, Washington 25, D. C.

**PATHFINDER ATOMIC POWER PLANT
INVESTIGATION OF THE CORROSION ASPECTS
OF SELECTED ALUMINUM ALLOYS**

Final Report

by

Karlis Riskevics

Submitted to

**U. S. ATOMIC ENERGY COMMISSION
NORTHERN STATES POWER COMPANY**

and

CENTRAL UTILITIES ATOMIC POWER ASSOCIATES

by

ALLIS-CHALMERS MANUFACTURING COMPANY

Under

Agreement dated 2nd Day of May 1957, as Amended
between

Allis-Chalmers Mfg. Co. & Northern States Power Co.
under

AEC Contract No. AT (11-1)-589

January 31, 1961

Approved: C. B. Graham

C. B. Graham
Chief Engineer
Nuclear Power Dept.-Greendale

Approved: Hibbert Hill

Hibbert Hill
Chief Engineer

Approved: C. R. Braun

C. R. Braun
Manager
Nuclear Power Dept.-Greendale

NORTHERN STATES POWER COMPANY

15 SOUTH FIFTH STREET

MINNEAPOLIS 2, MINNESOTA

ALLIS-CHALMERS MANUFACTURING COMPANY

ATOMIC ENERGY DIVISION

MILWAUKEE 1, WISCONSIN

ACKNOWLEDGMENTS

The author wishes to acknowledge the support of these corrosion investigations by the U.S. Atomic Energy Commission. His heartfelt thanks go to Mr. George E. Panter, formerly engaged by the Nuclear Power Department-Greendale, and to the various other members of AEC's Aluminum Alloy Task Group for their helpful suggestions and advice in the organization of the test program and evaluation of the results.

His sincere thanks also go to Mr. R.B. Jerman and his staff for their operation of the test equipment and for their fine cooperation throughout the program - as well as to the many other individuals in this department who took part in these investigations.

Karlis Riskivics

Nuclear Power Dept.-Greendale
Allis-Chalmers Mfg. Company

TABLE OF CONTENTS

	Page
Acknowledgments.....	II
List of Illustrations.....	V
Abstract.....	I
1. Introduction.....	3
2. Literature Survey.....	7
2.1. General.....	7
2.2. Effects of Various Test Parameters on Corrosion of Aluminum.....	7
2.3. Summary of Literature Survey.....	14
3. Static Corrosion Tests at Greendale Labs....	17
3.1. General.....	17
3.2. Tests on 8001 Aluminum Alloy.....	20
3.3. Tests on 8001 Aluminum +2.5% Magnesium Alloy.....	38
3.4. Tests on X2219 Alloy Clad with M400...	42
3.5. Summary of Static Test Results.....	56
4. Dynamic Corrosion Tests at Greendale Labs...	59
4.1. General.....	59
4.2. Plain Aluminum Tests.....	61
4.3. Increased A/V Tests.....	92
4.4. Prefilmed Sample Tests.....	114
4.5. Summary of Dynamic Test Results.....	126
5. Conclusions.....	129
6. Bibliography.....	131

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

LIST OF ILLUSTRATIONS

<u>Figure Number</u>	<u>Title</u>	<u>Page</u>
3.1.1.	Autoclave - its closure assembly and sample holder with samples.....	19
3.1.2.	View of autoclave showing samples and control.....	19
3.2.1.1.	Sample coupon.....	21
3.2.1.2.	Corrosion sample dimensions - Test 3.....	25
3.2.3.1.	Static corrosion test #1 - 8001 aluminum.....	29
3.2.3.2.	Static corrosion test #2 - 8001 aluminum.....	30
3.2.3.3.	Static corrosion test #3 - 8001 aluminum.....	31
3.2.3.4.	Comparison graph - average corrosion rates, tests 1, 2, 3...8001 aluminum.....	33
3.2.3.5.	Plate after 21.7 days of exposure.....	35
3.2.3.6.	Same plate - machined and polished face.....	35
3.2.3.7.	Welded configuration after 7.85 days of exposure.....	35
3.2.3.8.	Tubes #1 and #2 after 21.7 days exposure.....	37
3.2.3.9.	Extruded tube assembly after 21.7 days of exposure.....	37
3.2.3.10.	Flat portion of extruded tube.....	37
3.3.3.1.	Static corrosion test - test 2 - 8001 AL and 2.5% MG.....	43
3.3.3.2.	Sample 1051 after 14.7 days exposure.....	44
3.3.3.3.	Sample 1052 after 14.7 days exposure.....	44
3.3.3.4.	Sample 1053 after 14.7 days exposure.....	44
3.3.3.5.	Samples after three days exposure.....	44
3.3.3.6.	Cross section of samples after 14.7 days.....	44

<u>Figure Number</u>	<u>Title</u>	<u>Page</u>
3.4.3.1.	Static corrosion test #1 - X2219 aluminum clad with M400.....	47
3.4.3.2.	Static corrosion test #2.....	49
3.4.3.3.	Static corrosion test #3.....	51
3.4.3.4.	Sample coupon after 18.44 days exposure.....	53
3.4.3.5.	Reverse side of sample coupon.....	53
3.4.3.6.	Comparison graph for static tests on X2219 alloy clad with M400.....	55
3.5.1.	Comparison graph of static tests on 8001 aluminum and X2219 alloy clad with M400.....	57
4.2.2.1.	Dynamic corrosion loop flow diagram.....	63
4.2.2.2.	General view of corrosion test loops.....	64
4.2.2.3.	Corrosion loop showing circulating pump, heat exchangers and ion exchanger.....	64
4.2.2.4.	Test section of corrosion test loop.....	64
4.2.2.5.	Sample holder assembly.....	64
4.2.3.1.	Loop 1, test 1...water conditions.....	66
4.2.3.2.	Loop 2, test 1...water conditions.....	67
4.2.3.3.	Loop 3, test 1...water conditions.....	68
4.2.3.4.	Loop 2, test 2...water conditions.....	70
4.2.3.5.	Loop 3, test 2...water conditions.....	72
4.2.4.1.	Dynamic corrosion tests 1, 8001 aluminum.....	79
4.2.4.2.	Dynamic corrosion tests 2, 8001 aluminum.....	80
4.2.4.3.	Turbidity and corrosion test.....	81
4.2.4.4.	Corrosion test graph.....	83

<u>Figure Number</u>	<u>Title</u>	<u>Page</u>
4.2.4.5.	Corrosion test, loop 2, test 2...samples after 17.9 days of exposure.....	84
4.2.4.6.	Closeup of leading sample.....	84
4.2.4.7.	Closeup of trailing sample.....	84
4.2.4.8.	Loop 2, test 2...samples after 33.0 days.....	85
4.2.4.9.	Closeup of leading sample.....	85
4.2.4.10.	Closeup of middle sample.....	85
4.2.4.11.	Loop 3, test 2...samples after 36.3 days.....	86
4.2.4.12.	Closeup of leading sample.....	86
4.2.4.13.	Closeup of right-center sample.....	86
4.2.4.14.	Loop 2, test 2...samples after 69.7 days.....	88
4.2.4.15.	Closeup of leading sample.....	88
4.2.4.16.	Closeup of middle sample.....	88
4.2.4.17.	Loop 3, test 2...samples after 73.1 days.....	89
4.2.4.18.	Closeup of leading sample.....	89
4.2.4.19.	Closeup of right-center sample.....	89
4.2.4.20.	Loop 2, test 1...samples after 77.9 days.....	90
4.2.4.21.	Closeup of top-center sample.....	90
4.2.4.22.	Closeup of bottom-left sample.....	90
4.3.2.1.	Aluminum rack used in loop 2.....	95
4.3.3.1.	Loop 2, test 4...water conditions.....	98
4.3.3.2.	Loop 2, test 5...water conditions.....	99
4.3.4.1.	Dynamic corrosion tests graph - increased area to volume.....	103

<u>Figure Number</u>	<u>Title</u>	<u>Page</u>
4.3.4.2.	Aluminum tubing used as the excess area in loop 2, test 4.....	107
4.3.4.3.	Closeup of section of aluminum tubing.....	108
4.3.4.4.	Loop 2, test 4...samples after 22.8 days.....	109
4.3.4.5.	Closeup of leading sample.....	109
4.3.4.6.	Closeup of trailing sample.....	109
4.3.4.7.	Loop 2, test 4...samples after 35.7 days.....	110
4.3.4.8.	Closeup of leading sample.....	110
4.3.4.9.	Closeup of trailing sample.....	110
4.3.4.10.	Loop 2, test 4...samples after 79.5 days.....	112
4.3.4.11.	Closeup of leading sample.....	112
4.3.4.12.	Closeup of right-center sample.....	112
4.3.4.13.	Loop 2, test 4...samples after 107.0 days.....	113
4.3.4.14.	Closeup of leading sample.....	113
4.3.4.15.	Closeup of right-center sample.....	113
4.4.4.1.	Loop 3, test 3...water conditions.....	117
4.4.4.2.	Loop 3, test 4...water conditions.....	119
4.4.5.1.	Dynamic corrosion tests graph - prefilmed sample tests.....	121
4.4.5.2.	Loop 3, test 4...samples after 35.6 days.....	125
4.4.5.3.	Closeup of leading sample.....	125
4.4.5.4.	Closeup of right-center sample.....	125
4.5.1.	Comparison graph of dynamic tests on 8001 aluminum alloy.....	127

ABSTRACT

Aluminum alloy 8001 has been considered as fuel element cladding material in the Allis-Chalmers built Pathfinder reactor. This report contains a literature survey and experimental results from investigations of aluminum corrosion under both static and dynamic test conditions.

Tests Conducted:

Static corrosion tests were made on 8001, 8001 + 2.5% Mg and X2219 clad with M400 aluminum alloys.

Dynamic corrosion tests were made only on the 8001 alloy. These tests were performed in three identical dynamic corrosion test loops and consisted of:

1. Initial tests in each loop to investigate corrosion behavior in high purity water at high temperatures and high flow velocities.
2. Reproducibility tests.
3. An evaluation of aluminum-surface-area-to-water-volume-ratio effects on corrosion resistance.
4. Prefilmed sample tests...in which test specimens were prefilmed at two different temperatures in a static autoclave prior to the dynamic tests.

Conclusions Reached:

Experimental test results indicated that the corrosion rates of the 8001 aluminum alloy were too high for an economical design of the reactor core.

A considerable amount of uncertainty was found to exist in the corrosion literature, as well as in the experimental data, regarding effects of various test parameters on corrosion behavior of this alloy.

Time limitations for application to the Pathfinder reactor prohibited further investigation of this material. Consequently, a recommendation of the 8001 aluminum alloy as the boiling water reactor core cladding material, operating at Pathfinder conditions, could not be made.

Further investigations in the corrosion behavior of the 8001 alloy, particularly under heat flux and in conjunction with corrosion inhibitors, are necessary in order to explore and evaluate more fully the possibilities of this material for boiling water reactors operating at Pathfinder conditions.

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

1. INTRODUCTION

In recent years aluminum has received considerable attention as a nuclear reactor fuel element cladding material. Consideration of aluminum is based on its low thermal neutron absorption cross-section, light weight, ease of fabrication and low cost. Extensive aluminum corrosion testing programs have been carried on at government and civilian laboratories during the past eight years. Consequently, there is a great wealth of information available relative to corrosion behavior of aluminum in various environments. However, as reactor design temperatures increased, it was discovered that aluminum as a cladding material had unproved corrosion resistance in high purity, high temperature water. Nevertheless, interest in aluminum has continued because it held out the promise of an inexpensive cladding material for fuel elements when compared to zirconium alloys or stainless steel for the same application.

In the temperature range of 500-600°F there have been questionable results under various corrosion testing conditions. Many laboratories have concentrated efforts on developing a satisfactory high temperature aluminum alloy. As a result of the extensive corrosion research programs conducted at Hanford Atomic Operations and Argonne National Laboratories an aluminum alloy containing essentially 1% nickel and 1/2% iron was developed. This alloy is known as 8001 and has held the most promise from the corrosion standpoint as a material which can be used as reactor fuel cladding material in boiling water reactors.

The 8001 alloy has been extensively tested in dynamic corrosion loops simulating reactor water conditions and has demonstrated resistance to high temperature corrosion in boiling water environments. Much of the corrosion testing work has been done in corrosion testing loops which essentially are pressurized hot water loops, but very little corrosion testing information has been developed by in-pile reactor experiments. The tests in-pile and out-of-pile have yielded much information relative to the corrosion behavior of aluminum alloys. Unfortunately, the mass of information is exceedingly difficult to interpret in terms of proper application of aluminum in boiling water environments.

Investigations into the corrosion mechanism of aluminum in high temperature water have led to the understanding of several phenomena which possibly control the corrosion of aluminum alloys. Such factors as alloy composition, pH of the water environment, and temperature of the water are fairly well understood. It has been well established that increased temperatures produce increased corrosion rates. Low pH environments, particularly around a value of 4.5, have been found to produce a corrosion film on most aluminum alloys which exhibits protection and reduced corrosion rates. However, there are other phenomena influencing the corrosion of aluminum, which are not well understood or have not been thoroughly investigated at this time; for instance, the aluminum - surface-area-to-water-volume-ratio, radiation effects, alloy composition variations, et.al.

The greatest bulk of aluminum corrosion information originated at various government laboratories. However, civilian laboratories, including Allis-Chalmers Mfg. Co, have also contributed pertinent data. Shortly after the development of the 8001 aluminum alloy at government laboratories, Allis-Chalmers undertook the design of the Pathfinder reactor in which the 8001 alloy was chosen as the fuel element cladding material. Despite the fact that the 8001 aluminum alloy was developed for high temperature applications and had been used as cladding material in several boiling water reactors there was insufficient information available on the corrosion behavior of this alloy at the proposed Pathfinder reactor conditions.

The Pathfinder fuel element cladding material would be subjected to the following boiling water conditions:

Pressure	600 psi
Temperature	489°F
Water Composition	High Purity
Water pH	6 - 7
Water Velocity	14 - 30 fps
Heat Flux	130,000 - 462,000 Btu/ft ² hr.
Cladding Temperature	~ 614°F (323°C)
Aluminum-Surface-Area-To-Water-Volume-Ratio	134 cm ² /liter

Consequently, a corrosion testing program was conceived at Allis-Chalmers and test equipment was designed and fabricated. Corrosion tests of the 8001 aluminum alloy were made both under static and dynamic test conditions. Static tests were also made on the 8001 + 2.5% Mg and X2219 clad with M400 alloys. The dynamic tests were performed both without and with attempts at corrosion rate reduction.

This report consists essentially of three parts: Section 2 presents a literature survey, section 3 describes the static corrosion tests made at Allis-Chalmers, and section 4 describes the dynamic corrosion tests made at Allis-Chalmers.

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

2. LITERATURE SURVEY

2.1. GENERAL

The material presented in section 2. of this report resulted from thorough literature searches made in order to accumulate sufficient positive evidence relative to applicability of the 8001 aluminum alloy as the fuel cladding material in Pathfinder. The Extensive corrosion testing programs conducted on aluminum have led to many technical reports which illustrate various factors contributing to the corrosion behavior of aluminum under various testing conditions. Collection and interpretation of the information on aluminum corrosion becomes very difficult when it is understood that each test is primarily designed for testing one variable under a certain set of fixed conditions of temperature, pressure, water velocity, etc. Previously, attempts have been made to evaluate and condense in usable form the corrosion information developed on aluminum alloys over the past few years. Each of these attempts has been complicated by the fact that there exists between many test facilities very few constant factors. Consequently, the inter-relationships of variables within the tests themselves, as well as the variables that exist between testing facilities, result in considerable confusion and cause the evaluation of numerous test results to be somewhat questionable.

It is the intent of the presentation in this section to consider chiefly the corrosion behavior of 8001 aluminum alloy under test conditions which most closely simulate the boiling water conditions expected in the Pathfinder reactor. Many of the same difficulties involved in interpreting test information, as pointed out above, enter into the problems of relating corrosion information from test facilities to what would be applicable to the Pathfinder reactor. Factors such as mechanical strength, fabrication problems and special operational problems related to aluminum are not discussed here.

2.2. EFFECTS OF VARIOUS TEST PARAMETERS ON THE CORROSION OF ALUMINUM

Research and development work performed at various laboratories, including Greendale, has shown that a considerable number of variables determine the corrosion characteristics of aluminum alloys. Some of the most important variables have been found to be:

- 1) Alloy composition
- 2) Temperature
- 3) Water velocity
- 4) pH
- 5) Water composition
- 6) Heat transfer effects
- 7) Radiation

These and other parameters, such as: specimen surface preparation, replacement effects, inhibitors, etc., act either separately or in combination to yield a complex of variables, the effects of which are not completely understood and investigated at this time. However, as described in the following text, many observations and conclusions have been made relative to the effects of these parameters on the corrosion behavior of aluminum.

1. Alloy Composition

Commercial grades of aluminum are corrosion resistant to water at temperatures up to 400°F. Pure aluminum has been used in several water cooled reactors where temperatures of less than 400 degrees were employed. The corrosion of pure aluminum in water above 400°F results in a bulky, flaky, oxide film that is easily removed from the aluminum and eventually reduced to a fine, powdery corrosion product which is carried away in the water. Poor corrosion resistance of pure aluminum in high temperature water was taken under study by Draley and Ruther at Argonne National Laboratory who developed an alloy resistant to corrosion at higher temperatures through the addition of 1% nickel and approximately 1/2% iron. This alloy demonstrated satisfactory resistance to intergranular attack in numerous dynamic tests and suggested that the material could be employed as fuel cladding for boiling water reactors. The designation of 8001 was assigned to this alloy. This alloy under dynamic conditions exhibited essentially the same low corrosion characteristics as other alloys tested in semi-static or static autoclave tests

Numerous other alloy compositions have been investigated. Recent experiments have revealed that high purity powder metallurgy products of very low silicon content in the 8001 alloy base produce a more corrosion resistant material than the commercial 8001 alloy described in this report.

2. Temperature

Aluminum corrodes fairly slowly and in a uniform manner in low temperature deionized water. However, as the temperature increases, the corrosion rate increases correspondingly. In fact, it has been demonstrated that at higher temperatures, the corrosion mechanism changes and the uniform corrosion rate gives way to an accelerated corrosion which has been termed "intergranular". 8001 does not undergo intergranular corrosion at temperatures in the neighborhood of 500-600 degrees F. Nevertheless, at or above these temperatures this alloy suffers considerable corrosion attack in high purity water. The effect of increased temperature in increasing corrosion rates of aluminum has been studied between temperatures of 500-600°F. However, there exists considerable confusion in the information resulting from many of these tests. It can be stated that increased temperature increases the corrosion rate of aluminum in the above temperature range under dynamic conditions.

3. Water Velocity

The effect of water velocity on the corrosion rate of aluminum has been extensively studied at the relatively low velocities of 2-7 feet per second. In the range of 20-30 feet per second the corrosion rate of aluminum is considerably increased. This indicates that water velocity past the corrosion test specimens is one of the most important variables in corrosion of aluminum exposed to high temperature water. Velocities as high as 100 feet/second have been used in the study of the effect of velocity on aluminum corrosion. Under the conditions of these high velocities, corrosion rate exceeds 300 mils per year while under the same conditions a velocity of 20 fps produces a corrosion rate of 30-40 mils per year. Effect of velocity in increasing aluminum corrosion rate is not quite as pronounced when the tests are conducted in high temperature water with a pH of 4.5.

Investigations at Hanford have shown that corrosion of 8001 was independent of velocities from 23-35 feet per second when tests were performed in low pH water. Dynamic corrosion tests of aluminum conducted at Argonne, Oak Ridge, and by Dupont Company have satisfactorily demonstrated that increased velocity causes increased metal loss from aluminum test coupons. Experimental work performed at Oak Ridge under various temperatures in high purity water has indicated that effect of velocity on corrosion behavior of 8001 is very significant. Tests there, ranging in velocity

from 20-107 feet per second with temperatures from 350°F to over 600°F, yielded an average corrosion rate of 40 mils per year. This high corrosion rate is to be compared with approximately 8 mils for static tests on the same material.

It is unfortunate that most of the dynamic corrosion testing information available on aluminum has been obtained essentially in pressurized water loops. In many cases, these facilities have not been exposed to "in-reactor" conditions. Consequently, the specimens tested do not necessarily reveal corrosion rates which might be experienced with aluminum exposed to high purity, high velocity water under actual reactor conditions. The effect of velocity on corrosion rate of aluminum is partially explained by erosion of the protective corrosion film. The film developed in high purity neutral water tends to be somewhat soft and flaky and is easily removed by the high velocity water. Contrary to this, the protective film produced on aluminum under low pH conditions tends to be thin, adherent and quite protective. The difference in corrosion film compositions seem to explain why velocity effect is not as severe in low pH systems.

4. Effects of pH

Low corrosion rates for aluminum have been demonstrated at several laboratories during tests conducted at pH 4.5. Corrosion rates in dynamic systems are usually higher at pH above 7 than at pH between 3.5 and 7. Corrosion attack at the lower pH, especially when produced with H_3PO_4 , is smaller than at the same pH produced by either HNO_3 or H_2SO_4 .

Hanford has found the corrosion rate of 8001, when tested at pH 4.5 and velocities of 23-25 feet per second, to be .8 mils/year. This compares to tests conducted at Argonne and Greendale Laboratories at pH-7 which showed a corrosion rate for 8001 under similar conditions to be 12-26 mils/year. However, the use of low pH by means of H_3PO_4 introduces corrosion problems with stainless steel. Corrosion rate of stainless steel is accelerated at this lower pH and the production of crud, resulting from corrosion products circulating in the water, is increased when the loop is operated at a low pH. "In-reactor" systems suffer from the increased activity as a result of formation of P 32 and Si 31 which are beta and gamma emitters. Likewise, experiments conducted with pH control in the Borax reactor demonstrated increased water decomposition resulting from neutron flux reacting with low pH water. This gives rise to problems associated with increased quantities of hydrogen and oxygen produced

in reactors where the pH is maintained low by the addition of phosphoric acid.

Corrosion testing loops operated at Hanford, with phosphoric acid used as the corrosion inhibitor, exhibited increased crud quantities and activities. It is the belief of people who operate these "in-reactor" loops at Hanford, that special design consideration must be made to permit operation of reactors with relatively high levels of activity. Accommodations must be provided for frequent decontamination of the reactors operated at low pH. In order to understand more fully the problems associated with a reactor with water controlled at pH 4.5 with phosphoric acid, it may be necessary to conduct either more "in-pile" corrosion loop tests or to operate reactors under these conditions. Such experiments are required in order to determine effects of crud bursts, decontamination, and special shielding problems resulting from phosphoric acid addition to these reactors.

The results of aluminum corrosion testing, using low pH as an inhibitor for aluminum corrosion, have led the group at Hanford to express an opinion regarding use of aluminum at pH higher than 4.5. It is the belief of this group that no known aluminum alloy can be recommended for satisfactory service at the present time in boiling water reactors operating at a temperature greater than 350°F if used in pH 6-7 reactor water. On the other hand, this same group points to the complications of controlling pH by the use of phosphoric acid.

5. Water Composition

Experiments conducted on aluminum corrosion at Chalk River, Canada and Greendale Laboratories have adequately illustrated the fact that there is a relationship between quantity of aluminum corrosion products circulating in corrosion testing loops and corrosion rate of the coupons being tested. This relationship is frequently expressed as the "aluminum-surface-area-to-water-volume-ratio", usually referred to as A/V.

Corrosion rates of 8001 aluminum obtained at Chalk River under conditions approximating those expected in Pathfinder were 45 mils per year, when no consideration was given to the excess aluminum surface area. Tests conducted under conditions of excessive aluminum-surface-area-to-loop-water-volume resulted in

corrosion rates as low as 8 mils/year. In experiments performed at Greendale Laboratories in circulating water loops approaching Pathfinder conditions, corrosion rates of 6-22 mils/year were obtained. These corrosion rates resulted from an increase of aluminum surface area in relationship to loop water volume. The minimum corrosion rates of 6 mils/year were obtained with aluminum-surface-area-to-volume-ratios approximating those expected in the Pathfinder core. However, the relationship of surface-area-to-volume really is an expression of aluminum corrosion product concentration in the circulating water. The relationship that exists between concentrations and corrosion rates is not well understood at this time.

It is fairly well known that at low flow velocities the area-to-volume ratio does not have much effect. It is also known that at a lower pH the area-to-volume ratio is more effective than at pH7 or higher. However, it has been found that in order for the A/V ratio phenomenon to be effective the excess area should be properly located in the system and a by-pass purification stream should be operative. These two factors are opposite in nature since one tends to increase and the other to decrease concentration of corrosion products in the circulating water. No sound theoretical explanation has been derived to explain this apparent incongruity.

6. Heat Transfer Effects

The corrosion rate of aluminum cladding on fuel elements is higher than might be calculated from the water temperature. Corroding surfaces of the fuel element are at a higher temperature than the circulating bulk water. . . a result of temperature drop through the water and corrosion product films. The investigators at Hanford have for some time been trying to evaluate the heat transfer phenomenon across aluminum fuel element cladding in order to obtain a more realistic approach to the corroding nature of aluminum under reactor conditions.

Heat transfer corrosion tests have been conducted at San Jose for the purpose of measuring temperatures produced on the aluminum surfaces themselves, as well as the effects of this increased metal temperature. To date, the findings resulting from these heat transfer corrosion tests indicate that corrosion film produced on aluminum samples under the influence of heat flux may cause metal temperature to be 100-140°F higher than the circulating water temperature. The resulting corrosion rates are considerably higher than those experienced in corrosion tests without heat transfer.

Corrosion rates measured on some samples under the influence of heat transfer have been from 2 to 5 times greater than on samples tested at circulating water temperatures. Water adjacent to the corroding sample under heat flux is at a somewhat higher temperature than the bulk circulating water. Consequently, it is not saturated with aluminum corrosion products. Dissolution of aluminum corrosion products takes place at the surface of the metal causing excessive metal loss. Most favorable results of corrosion testing have been found when water was maintained at a pH of 4.5 with H_3PO_4 . Assuming the metal temperature to have increased approximately $100^\circ F$ above the circulating water temperature, corrosion rates could be as high as 50 mils/year for 8001 aluminum at Pathfinder reactor conditions. This would be based on the assumption that corrosion film buildup and crud deposition on the aluminum fuel elements was sufficiently great to cause at least $100^\circ F$ increase in metal temperature with resulting increase in corrosion rate of 2 to 5 times that experienced in circulating water tests conducted in dynamic corrosion testing loops at Greendale.

7. Irradiation

Contradictory results have been obtained at various laboratories of effects of irradiation on corrosion behavior of aluminum in high temperature, high purity water. The consensus of opinion among investigators is that effects of irradiation on corrosion of aluminum are relatively small.

The following tables 2.2.1., 2.2.2., and 2.2.3. are compilations of latest available corrosion information from tests performed at various laboratories on the 8001 alloy at conditions approximating those expected in the Pathfinder core.

Table 2.2.1. lists dynamic test results. The four items at the bottom of the table represent tests made at flow velocities of 2-7 fps. The other tests were run at 16 to 44 fps. From the table it is apparent that corrosion rates of aluminum cladding in Pathfinder may vary between 2.0 and 130 mils/year. At flow rates of 2 to 7 fps, rates may vary between 1.5 and 8.8 mils/year.

Table 2.2.2. is a compilation of data from static or semi-static (ANL) tests on the 8001 alloy. Corrosion rates are seen to vary between .35 and 39 mils/year. The last two items in this table illustrate the beneficial effects of H_3PO_4 additions to the test solutions.

Rates indicated for these tests are between .4 and .7 mils/year. The lower corrosion rates obtained in static or semi-static water may be due to higher concentration of corrosion products in water in contact with the test specimens. Increased flow reduces the concentration and increases the corrosion rate. Erosion effects are also not present in static tests.

Table 2.2.3. illustrates dynamic test results in which solution pH was controlled by H_3PO_4 additions. The corrosion rates obtained vary between .06 and 4.2 mils/year. Wide variety of test operating conditions and test equipment design are largely responsible for differences in the reported test results.

2.3 Summary of Literature Survey

As described in the preceeding section the following important factors are involved in the corrosion testing and, ultimately, the application of aluminum to boiling water reactor designs:

1. Alloy composition
2. Temperature
3. Water velocity
4. pH
5. Water composition
6. Heat transfer effects
7. Radiation

In addition to these factors, variables, such as: pre-filming, gas concentration, replacement and erosion effects are to be considered in fuel element cladding design.

Although much corrosion testing information is available, wide differences between test results obtained at various laboratories indicate that further research is needed. There is also a lack of in-pile corrosion test data at Pathfinder conditions. Further examination and evaluation of the corrosion factors is necessary to arrive at data which can be used with confidence in the design of boiling water reactors.

TABLE 2.2.1

DYNAMIC TEST RESULTS ON 8001 ALUMINUM

SOURCE	TEMPER- ATURE °F	pH RANGE	FLOW RATE (fps)	TEST TIME DAYS	A/V (cm ² /) Liter	PREFILM- ING CONDI- TIONS	CORROSION RATE (mils/yr)
ANL	475	7.1-7.5	16-22	----	71-73	----	8.7-17.4
HW	482	6-7	20	----	high	----	5.4
ANL	500	6.3-7.0	16-22	----	8-73	----	2.0-16.5
AECL	500	6.5-7.0	dyn	----	-----	----	130
AECL	500	6.5-7.0	dyn	----	170-567	----	25
AECL	500	6.5-7.0	20	----	-----	----	17-20
A-C	500	6.2-6.9	24	74	45	----	23
A-C	500	6.3-6.7	28	95	45	----	24
A-C	500	6.6-7.0	31	81	45	----	22
A-C	500	5.8	28	70	45	----	17
A-C	500	5.9-6.4	27	73	45	----	15
A-C	500	6.0	28	73	45	500°F 7 days	48
A-C	500	5.9-7.0	27	134	45	600°F 3 days	14.2
A-C	500	6.0	28	57	2620	----	23
A-C	500	5.9	28	107	134	----	7.2
A-C	500	5.3-6.6	27	126	134	----	6.1
Du Pont	500	6-7	37	65	-----	----	30.
Du Pont	500	6-7	27	65	-----	----	12.
Du Pont	500	6-7	18	65	-----	----	4.
ORNL	500	6-7	20-31	10	11	----	39-76
ORNL	500	6-7	31-44	10	11	----	40-79
ORNL	500	6-7	20-31	10	11	----	41
ORNL	500	6-7	31-44	10	11	----	43
AECL	500-500	6.5-7	20	----	high	----	8
AECL	500-550	6.5-7	20	----	low	----	45
AECL	500-550	6.5-7	20	----	----	570° Static	2
HW	572	6-7	19	30	----	----	18
HW	572	6-7	38	30	----	----	29
HW	572	6-7	20	----	----	----	24
ANL	600	6.8-7.4	16-22	----	16-84	----	8.5-16.6
WAPD	680	7.0	20	----	-----	----	5.0
ANL	475	7.1-7.5	6-7	----	71-73	----	2.7-4.5
HW	482	6-7	2-4	----	high	----	6-8
ANL	500	6.3-7.0	6-7	----	49-73	----	1.5-6.1
ANL	600	6.8-7.0	6-7	----	76	----	6.5-8.8

TABLE 2.2.2.

STATIC TEST RESULTS ON 8001 ALUMINUM

SOURCE	TEMPER- ATURE (°F)	pH RANGE	INHIBI- TOR	TEST TIME DAYS	CORROSION RATE (MILS/YR)
ANL	475	7.1-7.5	----	----	1.2-1.9
ANL	500	6.3-7.0	----	----	1.2-1.9
A-C	500	5.4-7.0	----	to 37	.35-4.0
HW	554	6-7	----	30	.59
AECL	572	6.5-7.0	----	----	1.3-2.1
ANL	600	6.8-7.0	----	----	5.5
WAPD	680	6.5-7.0	----	up to 238	39.0
ALCOA	680	6-7	----	77	8.0
HW	572	4.5	H ₃ PO ₄	----	.48
ANL	600	4.5-5.5	H ₃ PO ₄	----	.4-.7

TABLE 2.2.3.

DYNAMIC TEST RESULTS ON 8001 ALUMINUM WITH pH CONTROL

SOURCE	TEMPER- ATURE (°F)	pH RANGE	INHIBI- TOR	FLOW RATE (fps)	TEST TIME DAYS	A/V (cm ² / Liter)	CORROSION RATE (mils/year)
HW	482	4-4.5	H ₃ PO ₄	20	----	----	0.3
ANL	500	5.3-6.3	H ₃ PO ₄	16-22	----	----	5.1
HW	554	4.5	H ₃ PO ₄	20	----	high	0.06
HW	572	4.5	H ₃ PO ₄	20	----	----	1.3
HW	572	4.5	H ₃ PO ₄	25-35	----	----	0.72
ANL	599	3.5	H ₃ PO ₄	18	188	----	0.25
ANL	600	4.5-5.5	H ₃ PO ₄	16-22	----	----	.77-4.2
ANL	500	5.5	H ₃ PO ₄	6-7	----	----	.7-1.9

3. STATIC CORROSION TESTS MADE AT GREENDALE LABS

3.1. General

A number of static corrosion tests were made at the Greendale Laboratories. The purposes of these tests were:

- 1) to screen materials for possible application as fuel element cladding in the Pathfinder reactor,
- 2) to help in selecting an aluminum alloy that would withstand the high temperature corrosive conditions expected in Pathfinder,
- 3) to confirm and compare static corrosion test data obtained at other civilian and government laboratories.

Only the materials exhibiting good static corrosion characteristics at high temperatures were expected to withstand the dynamic corrosion tests at the Pathfinder conditions.

A total of eight tests were performed on several aluminum alloys as follows:

- 1) 8001 Al alloy - 3 tests
- 2) 8001 Al + 2.5% Mg - 2 tests
- 3) X2219 clad with M400 - 3 tests

The tests were operated at 500°F and 681 psia. The maximum test time for a single test extended to 47.5 days.

The test equipment consisted of a 316 stainless steel autoclave made by Autoclave Engineers, Erie, Pa., and associated controls for automatic operation. The reactor specifications were as follows:

Capacity	- 1 liter
Inside diameter	- 3 inches
Inside length	- 9-3/8 inches
Working Pressure	- 5,000 psi @ 650°F 3,000 psi @ 900°F
Hydrostatic Test Pressure	- 8,000 psi @ 72°F (1 hour)

Figures 3.1.1. and 3.1.2. illustrate the autoclave, its closure and its controls. The photographs also show 3 aluminum samples held between sapphire rods in the sample holder.

The corrosion test results were evaluated visually by specimen appearance changes and, also, by weight change measurements. The following "Autoclave Sample Corrosion Rate Calculation Procedure" was derived in order to express the corrosion attack in meaningful terms.

It was assumed:

- 1) that the corroded aluminum was converted entirely into $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (Boehmite),
- 2) that the weight gains of the specimens consisted of $(-\text{O}_3 \cdot \text{H}_2\text{O})$,
- 3) that no aluminum or boehmite had departed off the samples.

The amount of metal corroded was calculated in the following manner:

- 1) weight of aluminum corroded = (weight gain)
(.818)
- 2) mils of penetration = (weight gain) (9.2)
- 3) corrosion or weight loss in mg/cm^2 = (weight gain)
(63.4)

These equations apply only to the standard size (2" x .5" x .125") samples used. The first formula is independent of area of the specimens. The second and third formulae are dependent on area and may be converted to another sample size or shape by multiplying the right hand side of the equations by $\frac{12.9}{\text{surface area}}$.

FIGURE 3.1.1. Autoclave . . . Its Closure Assembly and Sample Holder with Samples
(A-C 206460-A)

FIGURE 3.1.2 View
of Autoclave Showing
Samples and Control
(A-C 206460-D)

The 12.9 figure is the surface area of the standard sample, as shown in Figure 3.2.1.1. This area disregards the surface area of the edges of the samples, since the edges are positioned in the holder in such manner that the corrosion attack on them is negligible.

3.2. Tests on 8001 Aluminum Alloy

Three tests were performed on samples of 8001 aluminum alloy. The samples tested in the first two tests were of identical shape and size. The samples tested in the third test were of different sizes and shapes. The purpose of the first test was: 1) to initiate the static corrosion testing program, 2) to develop experience in using the autoclave, and 3) to study the corrosion characteristics of the 8001 Al alloy. The second test was performed in order to check reproducibility of the data obtained during the first test. The third test was made in order to investigate effects of size and shape as well as effects of different fabrication methods on corrosion behavior of this alloy.

3.2.1. Test Material Description

The sample material tested was 8001 aluminum alloy obtained from different suppliers. The material in Tests 1 and 2 was supplied by ALCOA Research Labs under the code number S-173677. The hardness of the material, as supplied, was H-18. The test coupons used in Tests 1 were annealed by Allis-Chalmers Research Labs at 650°F. The coupons used in Test 2 were heat treated at Greendale Labs for 360 hours at 500°F, after which the material was slowly cooled (4 hours) to room temperature.

Materials tested in Test 3 were in these shapes: a sheet specimen, drawn tube sections, extruded tube assembly, and a heliarc welded configuration. The exact metallurgical history of these test specimens was not available. The sample sheet material was supplied by Reynolds Metals Co. from Lot #4654. The test specimen was cut from a sheet of 10" x 33" x 1/8" size in the "as rolled" condition. The drawn tubes in the "as drawn" condition were also supplied by Reynolds Metals Co. on production order #E-44760. The extruded tube assembly was supplied by Precision Extrusions, Inc. The heliarc welded configuration consisted of a length of drawn tube, as described above and a flat piece of aluminum.

FIGURE 3.2.1.1. Sample Coupon

The chemical analysis of the material used in Tests 1 and 2, as reported by Allis-Chalmers Research Labs and ALCOA were as follows:

TABLE 3.2.1.
CHEMICAL ANALYSIS OF SAMPLE MATERIAL
USED IN TESTS 1 & 2

-----	REPORTED BY ALLIS-CHALMERS RESEARCH LABS.	REPORTED BY ALCOA RESEARCH LABS.
Ni	1.0	1.13
Fe	.20	.39
Si	.18	.12
Cu	.20	.13
Pb	.00	--
Ag	.00	--
Sn	.00	--
Zn	.00	--
Mg	.02	--
Ti	.02	--
Mn	.00	--
B	.00	--
Cd	.00	--
Co	.00	--
Al	Balance	Balance

Chemical analysis of sample materials used in Test 3 were as follows:

TABLE 3.2.2.

CHEMICAL ANALYSIS OF SAMPLE MATERIAL USED IN TEST 3*

AS REPORTED BY REYNOLDS METALS CO.		AS REPORTED BY PRECISION EXTRUSIONS, INC.
Ni	.96	.98
Fe	.59	.51
Si	.10	.07
Zn	.02	.05
Mn	.01	.05
B	.001	--
Cd	.003	--
Co	.004	--
Li	.002	--
Mg	.01	.05
Cu	.01	Trace
Cr	.01	.05
Ti	.01	.05
Pb	--	.05
Sn	--	.05
Al	Balance	Balance

* NOTE: No chemical analyses of sample materials used in this test were made at Allis-Chalmers. Also, no chemical analyses were furnished for the tubes and welded configuration.

Mechanical properties of material tested in Tests 1 and 2, as reported by Allis-Chalmers Research Labs, were as follows:

Tensile Strength	17,550 psi
Yield Strength (0.2% offset)	8,500 psi
% Elongation	29.3
R.H.	57.5
% Reduction of Area	61.0

Mechanical properties of the sheet sample used in Test 3 as reported by Reynolds Metals Company were as follows:

Tensile Strength	25,000 psi
Yield Strength	21,400 psi
% Elongation in 2"	9.5%

No mechanical properties were available for the other samples used in Test 3.

The samples used in Tests 1 and 2 were cut parallel to the rolling direction of the sheet. The sample size was 2" x 1/2" x 1/8" and they were machined to the dimensions previously shown in Figure 3.2.1.1. The sample surface area exposed to the corrosive environment was 12.9 cm². This figure disregards the sample edges because the position of the coupons in the holder is such that the edges do not contact the corrosive liquid to any extent and consequently the corrosion on the edges is negligible.

The sizes and shapes of the samples used in Test 3 were as shown in Figure 3.2.1.2. The sample surface area computations were made according to the dimensions shown in the sketches in Figure 3.2.1.2. and were as follows:

Area of coupon	18.1 cm ²
Area of tubes 1 and 2	31.9 cm ²
Area of extruded tube assembly	84.2 cm ²
Area of welded configuration	32.3 cm ²

All test samples were degreased in acetone and weighed before commencing the tests.

PLATE - BEFORE MACHINING

PLATE AFTER MACHINING

TUBES #1 & #2

EXTRUDED TUBE ASSEMBLY

FIGURE 3.2.1.2. Corrosion Sample Dimensions - Test 3

3.2.2. Test Description

The operating conditions during all three tests are presented in the following table:

TABLE 3.2.3.
OPERATING CONDITIONS DURING STATIC TESTS 1, 2 and 3

	TEST 1	TEST 2	TEST 3
Temperature (°F)	500	500	500
Pressure (psia)	681	681	681
pH	approx. 7	4.9-6.1	approx. 7
Conductivity (micromhos)	----	.4-5.0	----
ppm of Suspended Solids- (as Al ₂ O ₃ .H ₂ O)	----	1.0-12.8	----
Total Exposure Time (days)	47.5	36.9	21.7

During Test 1 the autoclave water was not analyzed and replaced, except when necessary because of leakages. During Test 2 the water was analyzed for pH, conductivity and concentration of suspended solids at the end of each inspection period whenever the water had not leaked out of the autoclave completely. The autoclave was drained thoroughly, rinsed with demineralized water and refilled at the beginning of each test period. During Test 3 the water was not analyzed but the autoclave was drained, rinsed and refilled with fresh demineralized water every time prior to sample replacement.

During Test 1 many operational difficulties were experienced due to miscellaneous assorted failures of the test equipment. Minor repairs had to be made on the autoclave and extra controls had to be installed. All of these shutdowns resulted in considerable extra handling of the samples and delays of the test.

During Test 2 again operating difficulties due to faulty gasketing and controls were experienced. The autoclave water had leaked out completely several times during the test, thus introducing factors of uncertainty as to the exposure time attained and corrosion effects in the steam and water phases.

During Test 3 the autoclave performed very satisfactorily and the test conditions were met continuously.

Test 1 was operated for a total of 47.5 days. The samples were inspected and weighed six times as follows: after 13.4, 22.2, 29.2, 35.2, 43.0 and 47.5 days of exposure.

Test 2 was operated for 36.9 days with sample inspections after 7.8, 11.6, 13.9, 22.8, 30.9 and 36.9 days of exposure.

Test 3 operated for 21.7 days with sample inspections after 7.9, 13.8 and 21.7 days of exposure.

3.2.3. Test Results

The results of Tests 1, 2 and 3 appear in Tables 3.2.4., 3.2.5. and 3.2.6. and in Figures 3.2.3.1., 3.2.3.2. and 3.2.3.3. The corrosion attack was evaluated as described in Section 3.1.

TABLE 3.2.4.

CORROSION TEST RESULTS IN mg/cm² FOR SAMPLES FROM TEST 1

EXPOSURE TIME (DAYS)	SAMPLE NUMBERS			
	1001	1002	1003	Average
13.4	1.98	2.55	1.49	2.01
22.2	2.34	2.61	1.89	2.28
29.2	2.59	2.84	2.09	2.51
35.2	2.73	2.97	2.26	2.65
43.0	2.87	3.07	2.44	2.79
47.5	2.83	3.05	2.35	2.74

TABLE 3.2.5.

CORROSION TEST RESULTS IN mg/cm² FOR SAMPLES FROM TEST 2

EXPOSURE TIME (DAYS)	SAMPLE NUMBERS			
	1101	1102	1103	AVERAGE
7.8	1.88	1.81	1.96	1.88
11.6	2.18	2.12	2.25	2.18
13.9	2.28	2.21	2.36	2.28
22.8	2.59	2.41	2.56	2.52
30.9	2.62	2.46	2.67	2.58
36.9	2.69	2.50	2.76	2.65

TABLE 3.2.6.

CORROSION TEST RESULTS IN mg/cm² FOR SAMPLES FROM TEST 3

EXPOSURE TIME (DAYS)	SAMPLE IDENTIFICATION						
	PLATE (BEFORE MACHINING)	PLATE (AFTER MACHINING)	TUBE 1	TUBE 2	EXTRUDED TUBE ASSEMBLY	WELDED CON- FIGURATION	AVERAGE
7.0	1.24	----	1.54	1.52	1.59	----	1.47
13.8	1.59	----	1.90	1.91	2.01	----	1.85
21.2	----	2.11	2.21	2.23	2.33	----	2.22
7.8	----	----	----	----	----	1.44	----

FIGURE 3.2.3.1., Static Corrosion Test

FIGURE 3.2.3.2. Static Corrosion Test

FIGURE 3.2.3.3. Static Corrosion Test

Results from all these tests show a divergence of the individual sample data after a short initial period. However, the curves eventually approach the same slope. The divergence phenomena is a characteristic in all aluminum corrosion tests. The corrosion rates during Test 1 as indicated by the slopes in the mg/cm² versus days plot in Figure 3.2.3.1. over the test period of from 29.2 to 43.0 days of exposure was as follows:

SAMPLE	1001	1.07 mils per year
	1002	.88 mils per year
	1003	1.34 mils per year
	Average	1.08 mils per year

The corrosion rates obtained in Test 2 during the last test period of 6 days (36.9-30.9=6) were as follows:

SAMPLE	1101	.62 mils per year
	1102	.35 mils per year
	1103	.80 mils per year
	Average	.59 mils per year

The initial corrosion rates indicated for Test 2 are somewhat higher than the ones indicated for Test 1. However, during the latter portion of these tests the rates approach the same value. These differences in the initial corrosion rates may be due to the uncertainties introduced by the frequent breakdowns and leakages during both tests. The corrosion curves for Test 3 are in good agreement with the previous results. The slopes of the curves after the initial period approach those obtained in the previous tests. The corrosion rates during the final test period of Test 3 are as follows:

Plate (after machining)	- 3.5 mils per year
Tube 1	- 2.1 mils per year
Tube 2	- 2.1 mils per year
Extruded Tube Assembly	- 2.2 mils per year

One point only on the graph was obtained for the welded configuration. It also is located in the same vicinity as the curves of the other shapes.

See Figure 3.2.3.4. for average comparison curves of all three tests. Curves appear to have similar slopes after the initial corrosion periods. These differences in initial rates may be due 1), as mentioned before, to the leakages and consequently uncertainties as to the time period involved at the beginning of Tests 1 and 2; and 2) the refreshment rates of the water in the autoclave. The water was drained after each inspection period during both Tests 2 and 3 but was not drained during Test 1. Consequently an inhibiting action caused

FIGURE 3.2.3.4. Comparison Graph - Average Corrosion Rates

by an increase in the concentration of the aluminum corrosion products in the water may have taken place.

It can be generally stated that the appearances of the samples exposed in both Test 1 and 2 were identical for the duration of the tests. The sample surfaces at the first inspection period were covered with a uniform gray oxide film which showed longitudinal streaks of lighter and darker gray. These marks were deduced to be previous cold working or rolling marks. As time progressed, the color of the films on the sample surfaces darkened but kept the same general distribution. It was noted after the test that the samples were covered with little black dots, which might be indications of segregation of the material or distribution of the nickel.

During Test 3 the sample surfaces had appearances as described here.: During the first and second inspection periods it was noted that the surfaces of the sheet sample were streaked longitudinally. To determine the extent or cause of these marks, 2/3 of one face of the sample was machined down slightly to show a clean surface. The end portion of the machined surface was polished on emery paper to remove machining marks. This is illustrated in Figure 3.2.1.2. Then the sample was reinserted in the autoclave for an additional 7.8 days of exposure. After removal it was noted that the streaks were again apparent on the machined surface, although, they were not as well defined as before. It was concluded that the streaks may have been caused by cold working. The results shown in Figure 3.2.3.3. indicate an increase in the corrosion of this sample after machining. This increase may be due to the more rapid attack of the new uncorroded surface exposed. See Figures 3.2.3.5. and 3.2.3.6. for photographs of both sides of this sample.

The heliarc welded configuration was exposed in the autoclave only during the last test period. At the end of the test the spots that were welded appeared very dark while the rest of the surfaces were gray. See Figure 3.2.3.7.

The tubular samples appeared rather dark gray in color with little black dots covering the surfaces. Some white oxide spots were also apparent. See Figure 3.2.3.8. for illustration of the tubular samples after test.

FIGURE 3.2.3.5. Plate After 21.7 Days of Exposure (NP 031-15)

FIGURE 3.2.3.6. Plate After 21.7 Days of Exposure – Machined and Polished Face (NP 031-16)

FIGURE 3.2.3.7. Welded Configuration After 7.85 Days of Exposure (NP 031-20)

The extruded tube assembly appeared noticeably lighter in color than the tubular samples; a very light gray color was noted on the flat portion of the sample. The sample surface was also covered with little black dots, somewhat smaller than those noted on the tubes. It is possible that these dots indicate distribution of the Ni.

The extruded tube assembly after corrosion is shown in Figures 3.2.3.9. and 3.2.3.10.

Following is a comparison between corrosion rates obtained in Tests 1 and 2 under identical operating conditions and during identical exposure periods (0-36.9 days). This comparison includes the higher initial corrosion rates.

<u>TEST #</u>	<u>SAMPLE #</u>	<u>CORROSION RATE (Mils/year)</u>
1	1001	3.96
	1002	4.29
	1003	3.30
	Average	3.85
2	1101	3.86
	1102	3.59
	1103	3.96
	Average	3.80

As the above results indicate, the corrosion rates obtained during these two tests are in good agreement, despite the operational difficulties encountered during both tests and despite the differences in the initial corrosion rates.

The corrosion rates obtained in Test 3 agree very well with the results obtained in the other two tests. The corrosion rates obtained for the plate material, drawn tube and extruded tube assembly, supplied by the different manufacturers are almost identical, which indicates that the different fabrication processes do not have much effect on the corrosion rates of the finished materials. It also suggests that the factors attributable to differences in fabrication facilities and procedures of the different manufacturers are almost nil. It indicates, too, that the shape of the test samples in static tests does not have any noticeable bearing on the corrosion rates.

FIGURE 3.2.3.8. Tubes #1 and #2 After 21.7 Days of Exposure (NP 031-17)

FIGURE 3.2.3.9. Extruded Tube Assembly After 21.7 Days of Exposure (NP 031-18)

FIGURE 3.2.3.10. Flat Portion of Extruded Tube From Above Assembly (NP 031-19)

3.2.4. Conclusions

The corrosion data on the 8001 aluminum, obtained during the three tests described, indicate a long-term corrosion rate for this alloy at Pathfinder conditions of from 0.3 to 2.2 mils per year. It was found that manufacturing and fabrication procedures do not influence the static corrosion rates to any extent. It was also determined that sample shape under static conditions does not have any noticeable bearing on the corrosion behavior of this alloy.

3.3. Tests on 8001 Al + 2.5% Magnesium Alloy

Two static corrosion tests were made on this alloy in order to determine its corrosion characteristics in still 500°F water. The purpose of the first test was a quick determination of the corrosion resistance while the second test was made in order to reproduce and confirm results obtained in the first test.

3.3.1. Test Material Description

The sample material was supplied by the Reynolds Metals Co. with the following identification numbers: 5078-1B and 5078-1C. The sample sheet was produced from a laboratory ingot of approximately 2" x 4" x 5" size. The ingots were scalped approximately 3/16" per face, reheated and hot rolled to .160" thickness. It was subsequently cold rolled without any intermediate thermal treatment to 0.100" and given a final anneal.

The chemical analysis of the sample material as reported by the Reynolds Metals Co. and the Allis-Chalmers Research Labs follows:

TABLE 3.3.1.
CHEMICAL ANALYSIS OF SAMPLE MATERIAL

	REPORTED BY ALLIS- CHALMERS RESEARCH LAB.	REPORTED BY REYNOLDS METALS CO.
Si	.10	.06
Fe	.4-.5	.57
Cu	.03-.05	.02
Mg	2.-3.	2.39
Ni	.7-.9	1.10
Mn	.00	----
Cr	.00	----
Pb	.00	----
Ag	.00	----
Sn	.00	----
Zn	.00	----
Ti	.00	----
B	----	.001
Co	----	.001
Cd	----	.003
Li	----	.008
Al	Balance	Balance

The mechanical properties, as determined by Allis-Chalmers and Reynolds Metals, were as follows:

TABLE 3.3.2.
MECHANICAL PROPERTIES OF SAMPLE MATERIAL

	REPORTED BY ALLIS- CHALMERS RESEARCH LABS.	REPORTED BY REY- NOLDS METALS CO.
Tensile Strength (psi)	29,900	31,600
Yield Strength (0.2%0.S.) (psi)	-----	13,900
% Elongation in 2 inches	27	22
Rockwell 15-T Hardness	61	62

The corrosion specimens were of 1-7/8" x 1/2" x 3/32" size. The surface area of the samples, disregarding the edges, was 12.1 cm².

The coupons were degreased and etched in 2% HNO₃ before being placed in the autoclave.

3.3.2. Test Description

The tests were performed at the operating conditions indicated in the following table:

TABLE 3.3.3.
OPERATING CONDITIONS DURING STATIC TESTS 1 AND 2

	TEST 1	TEST 2
Temperature (°F)	500	500
Pressure (psia)	681	681
pH	6.8-7	approx. 7
Total Exposure Time (Days)	14.0	14.7

Water analysis was made after the first test only and was as follows:

TABLE 3.3.4.
WATER CONDITIONS AT END OF TEST 1

CONCENTRATION (ppm)	
Al	0.06
Fe	1.20
Mg	0.25
Ca	Trace
Ni	Not Detected

During the first test the water in the autoclave was not changed. During the second test the autoclave was drained and refilled with fresh demineralized water at beginning of each test period.

During the first test the samples were examined 3 times ... after 4.7, 10.8 and 14.0 days of exposure, but weight change measurements were made only at end of test. During the second test the samples were examined and weighed 4 times ... after 3.0, 7.0, 11.0 and 14.7 days of exposure.

3.3.3. Test Results

The corrosion rates were calculated according to the "Autoclave Sample Corrosion Rate Calculation Procedure" outlined in Section 3.1. The corrosion test results at the end of the 14 day exposure for samples from the first test were as follows:

TABLE 3.3.5.

CORROSION TEST RESULTS IN mg/cm² FOR SAMPLES FROM TEST 1

<u>SAMPLE NUMBER</u>	<u>CORROSION (mg/cm²)</u>
AA	76.8
AB	76.0
AC	101.6
Average	84.8

The average overall corrosion rate was approximately 606 mdd or 321 mils per year.

The results of the second test were as follows:

TABLE 3.3.6.

CORROSION TEST RESULTS IN mg/cm² FOR SAMPLES FROM TEST 2

<u>EXPOSURE TIME (DAYS)</u>	<u>SAMPLE NUMBERS</u>			
	<u>1051</u>	<u>1052</u>	<u>1053</u>	<u>AVERAGE</u>
3.0	6.8	6.1	6.2	6.4
7.0	23.5	20.1	18.8	20.8
11.0	46.9	40.3	37.0	41.4
14.7	63.9	55.0	49.5	56.1

See Figure 3.3.3.1. for a plot of the results from Test 2. The slopes of the mg/cm² versus days curves indicate corrosion rates of 85 to 116 mdd or 45-61 mils per year for the individual samples over the last test period. The average overall corrosion rate is 38 mdd or 202 mils per year.

It can be generally stated the the appearances of the samples from both tests were very similar. After 3.0-4.7 days of exposure, samples were covered with a heavy charcoal gray oxide coating. After 10.8 - 11.0 days of exposure, presence of intergranular corrosion and small cracks were evident. At the end of the tests the samples were in a very poor condition, showing considerable corrosion and cracking. Boehmite had started to crack and flake off the sample surfaces. One sample was cross-sectioned and polished to give a better indication of the thickness of the corrosion product film and depth of penetration of the corrosive attack.

The corrosion product film was distributed rather evenly along the sample surfaces and showed approximately 30% loss of the original aluminum. Photographs of the samples were taken. See Figures 3.3.3.2., 3.3.3.3., 3.3.3.4., 3.3.3.5., and 3.3.3.6. for illustration of the individual corroded samples after 14.7 days of exposure, the 3 samples after 3 days of exposure, and a cross-section photograph of a sample after 14.7 days of exposure.

3.3.4. Conclusions

Evaluation of the results yields an approximate static corrosion rate of 321 to 202 mils per year over the 14 to 14.7 day period for samples of the 8001 Al + 2.5% Mg Alloy. These high corrosion rates and the presence of excessive amounts of corrosion products with large cracks definitely indicate that the 8001 Al + 2.5% Mg alloy cannot be considered as fuel element cladding material under Pathfinder conditions.

3.4. Tests On X2219 Alloy Clad With M 400

A total of 3 corrosion tests were performed on this alloy. The initial test was made in order to establish the corrosion behavior of the material. The second test was a confirmation test. The third test was made mainly

FIGURE 3.3.3.1. Static Corrosion Test

FIGURE 3.3.3.2. Sample 1051 After 14.7 Days of Exposure

FIGURE 3.3.3.3. Sample 1052 After 14.7 Days of Exposure

FIGURE 3.3.3.4. Sample 1053 After 14.7 Days of Exposure

FIGURE 3.3.3.5. Samples After Three Days of Exposure

FIGURE 3.3.3.6. Cross Section of Sample After 14.7 Days of Exposure (NP 004-2)

in order to observe copper diffusion phenomena; however, good corrosion test data was also obtained.

3.4.1. Test Material Description

The sample material used in these tests was supplied by ALCOA as Alclad M-400 (X2219) under code number S-173183. The material was fabricated in ALCOA'S Research Laboratory using standard practices. Then the material was solution heat treated and aged according to their standard practices for X2219 alloy. The material was supplied in the T6 temper. The samples were cut from a sheet bearing A-C code number 26-A.

The chemical composition of the X2219 material was as per specifications, according to ALCOA. The composition of the cladding was as follows:

Fe	.99%
Ni	.98%

Mechanical properties of the material were not investigated.

The samples used in Test 3 were heated at 932°F for 100 hours in a muffle furnace. Then these samples were machined to varying thicknesses of the M-400 Cladding. Sample #13 was all or nearly all X2219. The other samples had progressively increasing thicknesses of the M-400 cladding, sample #1 having the thickest cladding. The samples were then cut to 1" x .5" x .125" size. The sample specimens for Tests 1 and 2 were machined to 2" x .5" x .125" size as shown in Figure 3.2.1.1.

All samples were degreased in acetone before commencing the tests.

3.4.2. Test Description

Operating conditions during the tests were as follows:

TABLE 3.4.1.
OPERATING CONDITIONS DURING STATIC TESTS 1, 2 and 3

	TEST 1	TEST 2	TEST 3
Temperature (°F)	500	500	500
Pressure (psia)	681	681	681
pH	approx.7	5.75-6.05	5.35-6.4
Total Exposure Time (days)	18.4	28.3	33.6
ppm of Suspended Solids (as Al ₂ O ₃ H ₂ O)	----	2.5-4.0	1.0-13.5
Conductivity (Micromhos)	----	.4->5.0	.4->5.0

During Test 1 the water in the autoclave was not analyzed and was drained and replaced only during the second inspection period. During Tests 2 and 3 the autoclave water was analyzed for pH, conductivity and the amount of suspended solids at the end of each test period.

During Test 1 the samples were inspected after 3.8, 7.6, 13.4, and 18.4 days of exposure. During Test 2 the samples were inspected after 6.8, 13.6, 20.5 and 28.3 days. During Test 3 the samples were inspected after 8.1, 17.9, 25.7 and 33.6 days of exposure.

3.4.3. Test Results

Results yielded by Test 1 are as shown in the following table and Figure 3.4.3.1.

FIGURE 3.4.3.1. Static Corrosion Test

TABLE 3.4.2.
CORROSION TEST RESULTS IN mg/cm² FOR SAMPLES FROM TEST 1

EXPOSURE TIME (DAYS)	SAMPLE NUMBERS			AVERAGE
	1060	1061	1062	
3.8	.30	.29	.40	.33
7.6	.60	.57	.81	.66
13.4	.97	.93	1.14	1.01
18.4	1.19	1.11	1.33	1.21

The corrosion rates in the final test period, as indicated by the slopes of the curves in Figure 3.4.3.1., were as follows:

Sample #1060	2.27 mils per year
1061	1.94 mils per year
1062	2.00 mils per year
Average	2.07 mils per year

The test results obtained from Test 2 are shown in Table 3.4.3. and Figure 3.4.3.2.

TABLE 3.4.3.
CORROSION TEST RESULTS IN mg/cm² FOR SAMPLES FROM TEST 2

EXPOSURE TIME (DAYS)	SAMPLE NUMBERS			AVERAGE
	1063	1064	1065	
6.8	1.67	1.71	1.74	1.71
13.6	2.21	2.25	2.27	2.24
20.5	2.51	2.51	2.60	2.54
28.3	2.71	2.70	2.81	2.74

The corrosion rates in the final test period of 7.8 days, as indicated by the slopes of the curves in Figure 3.4.3.2., were as follows:

Sample #1063	1.39 mils per year
1064	1.29 mils per year
1065	1.42 mils per year
Average	1.37 mils per year

FIGURE 3.4.3.2. Static Corrosion Test

The initial corrosion rates indicated by this test are higher than the ones indicated by Test 1 during the same time period of exposure. However, during the last test period the corrosion rates were slightly smaller for Test 2 than for Test 1. These differences may be due 1) to the fact that the autoclave water was drained during each inspection period in this test but was not drained consistently during Test 1. The resulting higher refreshment rate may account for a higher corrosion rate during the initial period of Test 2. 2) Test 1 at final shut-down may not have attained a steady-state corrosion condition.

The corrosion test results obtained from Test 3 are shown in Table 3.4.4. and Figure 3.4.3.3.

TABLE 3.4.4.
CORROSION TEST RESULTS IN mg/cm² FOR SAMPLES FROM TEST 3

EXPOSURE TIME (DAYS)	SAMPLE NUMBERS						AVERAGE
	1	3	5	6	8	13	
8.1	1.90	1.83	1.78	1.81	1.67	1.62	1.77
17.9	2.38	2.28	2.17	2.25	2.07	1.99	2.18
25.7	2.64	2.54	2.41	2.48	2.29	2.21	2.43
33.6	2.77	2.64	2.53	2.65	2.39	2.35	2.56

The corrosion rates during the last test period (25.7-33.6 days of exposure) for samples from Test 3 were as follows:

Sample #1	.85	mils per year
#3	.71	mils per year
#5	.85	mils per year
#6	1.12	mils per year
#8	.68	mils per year
#13	.95	mils per year
Average	.85	mils per year

Corrosion rates of the individual samples are approximately the same, the samples with most cladding having a slightly higher initial rate than the samples with least cladding. See Figure 3.4.3.3. The spread of curves for the individual test specimens from one test

FIGURE 3.4.3.3. Static Corrosion Test

batch has been found to be a characteristic in aluminum corrosion testing and consequently the spread indicated in Figure 3.4.3.3. may not have any special significance as far as corrosion behavior of the cladding and base material is concerned.

It is noted from Figure 3.4.3.3. that after the high initial corrosion period the curves appear almost parallel for all 6 sample coupons. This tends to indicate that the static corrosion rates for both the X2219 and the M-400 alloys are nearly the same, since sample #13 was nearly all X2219 alloy and the other samples had varying thicknesses of M-400 cladding.

The samples exposed in Tests 1 and 2 were observed to have a similar and very satisfactory appearance after the tests. The surfaces were covered with a uniform gray oxide coating. Previous cold work or rolling marks in the transverse direction to the length of the samples were more predominantly apparent on one face of the sample coupons than on the other. See Figures 3.4.3.4. and 3.4.3.5. for illustrations of this phenomenon.

The samples exposed in Test 3 were also observed to have a very satisfactory appearance which was characterized by a smooth gray oxide coating. The following is a comparison of results from the three tests described. These three tests were operated under similar conditions and the comparison is made over identical exposure periods. (13.4-18.4 days):

FIGURE 3.4.3.4. Sample Coupon After 18.44 Days of Exposure (NP 025-26)

FIGURE 3.4.3.5. Reverse Side of Above Sample Coupon – After 18.44 Days of Exposure (NP 025-25)

TABLE 3.4.5.
CORROSION RATE COMPARISONS FOR ALL 3 TESTS ON
X2219 CLAD WITH M-400 ALLOY

TEST NUMBER	SAMPLE NUMBER	CORROSION RATE (MILS/YEAR)
1	1060	2.69
	1061	2.27
	1062	2.80
	Average	2.59
2	1063	2.27
	1064	1.94
	1065	2.00
	Average	2.07
3	1	2.22
	3	2.22
	6	2.22
	5	1.70
	8	1.70
	13	1.48
	Average	1.92

Figure 3.4.3.6. is a composite graph of the average corrosion results obtained during these three tests. Table 3.4.5., as well as Figure 3.4.3.6. indicate similar long-term corrosion rates for all tests. However, some variations are noted during the initial corrosion periods, as mentioned before.

3.4.4. Conclusions

The results of these 3 tests indicate that the X2219 alloy clad with M-400 aluminum is comparable in its static corrosion resistance to the 8001 aluminum alloy. However, it has been found by other investigators that the X2219 has poor performance under high flow velocity conditions and in inhibited systems. Therefore the X2219 alloy was not deemed advisable for use as the Pathfinder reactor core material.

COMPARISON GRAPH FOR STATIC TESTS
ON X2219 ALLOY CLAD WITH M400

FIGURE 3.4.3.6. Comparison Graph

3.5. Summary of Static Test Results

The static tests of the three different aluminum alloys described in preceding sections 3.2., 3.3. and 3.4. represent all of the static corrosion testing work done at Greendale Laboratories on aluminum alloys. These tests indicated that the 8001 and X2219 clad with M-400 aluminum alloys were better, from the corrosion standpoint, than the 8001 + 2.5% Mg alloy. Generally, it can be stated that the static corrosion curves of the 8001 and X2219 clad with M-400 alloys have a similar shape - all display a high initial corrosion rate which lasts up to about 10 days of exposure. This rate is then followed by a lower long-term or steady-state corrosion rate.

It was noted that the corrosion curves of the individual samples tested simultaneously in each test diverged somewhat during the initial corrosion period. However, eventually the slopes became parallel as the exposure time increased. This divergence or spread of the corrosion curves has been found to be a characteristic in aluminum corrosion testing. The spread was considerably less than observed in tests made under dynamic conditions.

A composite graph of the average corrosion rates for each test made on 8001 and X2219 clad with M-400 alloys is shown in Figure 3.5.1. The results indicate similar corrosion rates for both alloys, the X2219 clad with M-400 having a slightly higher corrosion rate during the latter portion of the tests. Variations are noted during initial corrosion periods of the tests, but as exposure time increased, the corrosion rates or slopes of the curves tended to approach the same values. This is particularly apparent in the X2219 clad with M-400 tests.

The effects of refreshment on the corrosion rates are also apparent from Figure 3.5.1.; the tests during which the autoclave water was not drained and refilled exhibiting lower initial corrosion rates. The refreshment consisted of draining, rinsing and refilling of the autoclave with fresh demineralized water during each shut-down period. In the non-refreshed tests the dissolved and suspended corrosion products were not removed and consequently may have had a slight inhibiting action. The refreshment effects are very well

FIGURE 3.5.1. Comparison Graph

shown in the X2219 clad with M-400 alloy tests. In the 8001 alloy tests this effect is not very definite, probably because of the difficulties experienced with the autoclave operation, as described before.

It can be generally stated that the static corrosion rates obtained at Greendale agree very well with results from tests performed under similar test conditions at various other civilian and government laboratories.

4. DYNAMIC CORROSION TESTS MADE AT GREENDALE LABORATORIES

4.1. General

Corrosion testing information discussed in this section deals with 8001 aluminum alloy exposed to dynamic test conditions approaching those expected in Pathfinder. Three test loops of identical design and size were used for these tests. The loops were put into operation as follows: Loop 1 was started in June, 1958, Loop 2 in September, 1958 and Loop 3 in December, 1958.

The test program was devised in such a manner as to: 1) determine corrosion characteristics of the alloy in high purity water at high temperatures and high flow rates; 2) determine reproducibility of the corrosion data obtained during initial tests, as well as the relationships between data obtained from tests in the three different loops; 3) investigate various methods of corrosion rate reduction, such as increasing the aluminum-surface-area-to-water-volume-ratio, static prefilming of specimens at various temperatures, pH variations, inhibitor additions, etc.; 4) investigate the effects of specimen shape on their corrosion behavior; 5) investigate other aluminum alloys that might show more promise for this application.

In accordance with this plan, five tests on plain aluminum samples were made in the three loops. During each test, eight corrosion specimens were tested.

Loop 1 failed during the second test and, as a result, a reproducibility test in this loop was not made. The loop was out of operation for a considerable length of time due to miscellaneous failures. Before interruption of the aluminum corrosion testing program, the loop was modified for testing of round shaped specimens.

After establishing the corrosion rate of the 8001 aluminum and ascertaining the reproducibility of the data, the testing program was directed toward reduction of the corrosion rates to a lower and more acceptable value for the Pathfinder fuel core design. Loop 2 was used to test effects of an increased aluminum-surface-area-to-water-volume-ratio, while Loop 3 was used to test statically prefilmed samples.

The following sections 4.2., 4.3. and 4.4. present detailed descriptions, and discussions of results from each of the dynamic tests.

Corrosion test results were evaluated by weight change measurements and specimen appearance changes. The sample coupons were usually weighed without cleaning or descaling. Uniform corrosion rates were assumed in the corrosion rate calculations. Pitting, intergranular (none observed) and localized attack were not considered.

At the end of the tests, corrosion film was stripped off the samples in a saturated boric acid solution as follows: the samples were soaked in saturated boric acid solution for at least one minute. Then, a.c. current of 0.02 amperes per square centimeter of sample surface was passed through the sample for a period of one to two minutes. Temperature during stripping was maintained between 68 and 86 F. After stripping, samples were brushed with a stiff bristle brush, rinsed in demineralized water, dried, and weighed.

During the initial weight gain period, corrosion was calculated according to the procedure outlined in section 3.1. After the initial period, when weight was lost, the calculations were made in a straightforward manner. Long-term corrosion rates, referred to in the following text, were calculated over a specific test time - usually over the last test period. The long-term rates are significant from a reactor design standpoint, since these rates represent steady-state conditions.

It was realized that the weighing method of evaluation is inaccurate because some of the corrosion film is lost due to high flow conditions in the loops. Therefore, an eddy current device was constructed for non-destructive measurement of corrosion. Difficulties were encountered, however, in stabilizing the gauge. As a result, the data obtained by means of this device was scattered to such an extent that it was useless. Numerous attempts were made to rectify this problem, but they were unsuccessful. It was concluded from the work of other investigators that in spite of inherent inaccuracies of the weighing method of evaluation, the curve of weight loss per area versus exposure time is reasonably representative of the corrosion rate.

The stripped sample weights obtained at the end of each test indicate the amount of metal actually lost or corroded over the entire test. The corrosion curves when transposed parallel to the correction points (obtained by stripping and indicated on the graphs) would approximate the actual corrosion rate. However - only the overall corrosion rate, over the entire test exposure, would be changed. The long-term rate, which is figured after steady-state conditions are obtained, would not be changed.

4.2. Plain Aluminum Tests

The purposes of these tests were:

- 1) To investigate corrosion behavior of 8001 aluminum alloy in high purity water at high temperatures and high flow velocities.
- 2) To establish reproducibility of corrosion test results in each test loop.
- 3) To compare and correlate corrosion data obtained at Greendale with results from other laboratories.

A total of five tests were performed in three identical dynamic corrosion test loops operating continuously between inspection periods.

The average operating conditions during the tests were as follows: 500°F, 1200 psi, pH 5.8 - 7.0 and flow rates ranging from 24 to 31 fps. The corrodent or corrosive medium was distilled and demineralized water. The total exposure times for samples exposed in the five tests ranged from 70 to 95 days. The loops were shut down for sample inspections at approximately 10 to 20 day intervals after initial corrosion periods had been attained.

4.2.1. Test Material Description

The sample material tested was 8001 aluminum alloy from the same lot as that tested in Static Tests 1 and 2. See section 3.2.1. of this report for further description of the material.

The sample coupons used in tests numbered 1 in all three loops were annealed at 650 F. Coupons used in Tests 2 in Loops 2 and 3 were heat treated in a muffle furnace at 500 F for 73 hours. The samples were then slowly cooled (4 hours) to room temperature.

The chemical analysis of the material is shown in Table 3.2.1.

The mechanical properties, sample size and preparation were the same as in Static Tests 1 and 2 of this alloy.

All samples were marked with identifying numbers, degreased in acetone, desiccated, and weighed before insertion in the corrosion loops.

4.2.2. Test Equipment Description

Corrosion studies were conducted in three dynamic corrosion

test loops which were made to the same specifications. Figure 4.2.2.1. is a flow diagram of the corrosion test loops. There are essentially two streams of flow. The main stream includes the pump and the sample holder, while the purification stream includes two heat exchangers, a sintered metal filter, a conductivity cell and an ion exchanger. A mixed bed resin is used in the ion exchanger. The feed and make-up water is distilled and passed through a demineralizer and a deoxygenating resin before entering the loop. The entire loop is made of 304 stainless steel.

Water volume in the main section of loop is 2.3 liters, the volume in the purification section is 11.3 liters. The aluminum-surface-area-to-water-volume-ratio is $45.5 \text{ cm}^2/\text{liter}$, considering the total system volume.

For the sake of clarity and illustration, three photographs of the loops are presented. Figure 4.2.2.2. shows a general view of the three test loops. Figure 4.2.2.3. is a close-up of the circulating pump, the heat exchangers and the ion exchanger. Figure 4.2.2.4. is a close-up of the test section which contains the sample holder.

The sample holder assembly and contents include a set of sample coupons, sapphire holding rods and stainless steel end pins as shown in Figure 4.2.2.5. The photograph shows nine samples as originally used in Loop 1. However, sample holders were modified since then to permit higher flow rates. All holders contained eight sample coupons during the tests described.

4.2.3. Test Description

All five of these tests were made under the average operating conditions shown in Table 4.2.3.1.

FIGURE 4.2.2.1. Dynamic Corrosion Loop Flow Diagram

FIGURE 4.2.2.2. General View of Corrosion Test Loops (A-C 196423)

FIGURE 4.2.2.3. Corrosion Loop Showing Circulating Pump, Heat Exchangers and Ion Exchanger (A-C 196424)

FIGURE 4.2.2.4. Test Section of the Corrosion Test Loop (A-C 196425)

FIGURE 4.2.2.5. Sample Holder Assembly (A-C 199718)

TABLE 4.2.3.1.

AVERAGE OPERATING CONDITIONSPLAIN 8001 ALUMINUM TESTS

TEST NUMBER	1	1	1	2	2
LOOP NUMBER	1	2	3	2	3
TEMPERATURE (°F)	500	500	500	500	500
PRESSURE (psi)	1200	1200	1200	1200	1200
pH	6.2-6.9	6.3-6.7	6.6-7.1	5.8	5.9-6.4
FLOW RATE (fps)	23.6	28.1	30.8	28	27
CONDUCTIVITY (micromhos)	.45-.92	.2-.8	.3-.67	.4-.6	.4-.6
A/V (cm ² /liter)	45.5	45.5	45.5	45.5	45.5
TOTAL EXPOSURE TIME (days)	73.9	95.0	80.8	69.7	73.1

The following five subsections describe details of the loop operation:

4.2.3.1. Operating Conditions In Loop 1 During Test 1

This was the first dynamic test performed at our laboratory. Unfortunately, the loop was shut down and started up frequently because of adjustments and repairs required.

Samples were inspected after 33.8, 47.5 and 73.9 days of exposure. Water purity during the test, expressed as conductivity in micromhos versus exposure time in days, is plotted in Figure 4.2.3.1.

4.2.3.2. Operating Conditions In Loop 2 During Test 1

Loop 2 was operated for 104 hours at the expected test conditions prior to sample insertion. During this break-in period, the instrument control and equipment were tested for dependability. Proper adjustments were made in order to avoid the unfortunate shutdowns, which occurred when operating Loop 1.

The samples were inspected four times during this test. The inspections were made after 53.9, 77.9, 88.8 and 95.0 days of exposure.

The water purity, indicated by a continuous reading conductivity recorder, is plotted versus exposure time in Figure 4.2.3.2.

FIGURE 4.2.3.1. Loop 1, Test 1 . . . Water Conditions

FIGURE 4.2.3.2: Loop 2, Test 1 . . . Water Conditions

FIGURE 4.2.3.3. Loop 3, Test 1 . . . Water Conditions

After 53.9 days of exposure, it was noted that samples were held rather loosely in the holder. It was assumed that the coupons had changed dimensions due to corrosion, which resulted in a loose fit. In order to eliminate possible sample vibration, thin strips of aluminum foil were inserted between sample holder and sapphire holding rods. At the next inspection shutdown, it was observed that the foil had disintegrated completely and some aluminum oxide was apparent on the sample surfaces, as well as on the sample holder and sapphire rods. This oxide was light gray, flaky and non-adherent. The foil was not replaced during the next period.

4.2.3.3. Operating Conditions in Loop 3 During Test 1

Some difficulties were experienced when starting the loop; but after rectifying the troubles, the loop was operating properly.

The loop was shut down four times during the test. Sample coupons were inspected after 31.5, 54.6, 67.6 and 80.8 days of exposure. Water purity in the loop, as indicated by a continuous reading conductivity recorder, is plotted in Figure 4.2.3.3.

4.2.3.4. Operating Conditions In Loop 2 During Test 2

The loop performed very satisfactorily during this test. Loop was shut down for sample inspection after 8.2, 17.9, 33.0, 44.8, 57.7 and 69.7 days of operation. Water purity is plotted versus exposure time in Figure 4.2.3.4.

After 44.8 days of operation during this test, the loop filter was removed and deposits found on the sintered metal filter element were collected. The material was filtered, dried and analyzed. Major constituents identified were Al, Ni and Fe. No attempt was made to interpret influence of elements on corrosion of aluminum. See Table 4.2.3.4.1. for a description, spectrographic and X-ray diffraction analyses of the material. This deposit had formed during both Test 1 and 2 over a total of 139.8 days of operation. Both tests were run under similar conditions.

4.2.3.5. Operating Conditions In Loop 3 During Test 2

The loop performed very satisfactorily during this test. Loop was shut down for sample inspection after 10.8, 26.3, 36.3, 47.2, 60.2 and 73.1 days of sample exposure. The water purity versus exposure time is plotted in Figure 4.2.3.5.

After 47.2 days of operation during this test, the deposits accumulated on the loop filter element were collected and analyzed. The material had formed during both Test 1 and

FIGURE 4.2.3.4. Loop 2, Test 2 . . . Water Conditions

TABLE 4.2.3.4.1.

LOOP FILTER CRUD ANALYSES AND DESCRIPTION

ANALYSES AND DESCRIPTION		LOOP #2	LOOP #3
Spectrographic Analyses:	Cu	.1	.2-.3
	Sn	Approx. .05	Approx. .05
	Pb	Approx. .05	Approx. .05
	Zn	Less than .05	Less than .05
	Fe	.6-.8	10.0-20.0
	Al	10.0-20.0	10.0-20.0
	Ni	3.0-5.0	6.0-8.0
	Mn	.00	.1-.2
	Si	Approx. .2	Approx. .3
	Cr	Approx. .2	1.0-2.0
	Mo	Approx. .3	Approx. .6
	Ca	Approx. .1	Approx. .1
	Mg	Approx. .1	Approx. .2
	P	Less than .2	Less than .2
	B	.2-.3	.2-.3
	Ti	Approx. .02	.10-.15
X-ray Diffraction Analyses:		Bohmite, α -Al ₂ O ₃ ·H ₂ O	Bohmite, α -Al ₂ O ₃ ·H ₂ O
	Bayerite, β -Al ₂ O ₃ ·H ₂ O	Magnetite, Fe ₃ O ₄	
	Aluminum, Al	Aluminum, Al	
Color	Brown	Grayish Brown	
Magnetism	Slightly	Slightly	
Hardness	Medium Soft	Medium Soft

FIGURE 4.2.3.5. Loop 3, Test 2 . . . Water Conditions

Test 2 over a total operating time of 127.7 days. Both tests were run at similar conditions and with similar materials. The deposit appeared about same as that collected from Loop 2 filter. Analysis indicated significant amounts of aluminum, nickel, chromium and iron. See Table 4.2.3.4.1. for results. It was deduced that the iron might have come from the wear on the pump. This assumption was substantiated after the test, when the pump was disassembled and examined. Considerable wear was observed on the pump impeller and rotor shaft.

4.2.4. Test Results

The corrosion test results obtained for individual samples during the five tests are tabulated in Tables 4.2.4.1., 4.2.4.2., 4.2.4.3., 4.2.4.4. and 4.2.4.5. The average corrosion rates from the first tests in each loop are plotted in Figure 4.2.4.1. Figure 4.2.4.2. is a plot of the average corrosion rates obtained during the second tests in Loops 2 and 3. Severity of the corrosion attack was determined by methods outlined in Section 4.1. of this report.

During the progress of the tests, some samples were brushed with a stiff bristle type brush to remove loose, non-adherent oxide particles from the sample surfaces. These particles eventually would have been lost in sample handling. It was found that brushing of the samples slightly increased the values of the weight losses. This produced a small vertical displacement of the corrosion curve, but did not change the slope of the curve.

Continuous conductivity indications during loop operation were obtained by means of a continuous recorder. Figures 4.2.3.1., 4.2.3.2., 4.2.3.3., 4.2.3.4., and 4.2.3.5. depict water conditions, expressed as conductivity in micromhos versus exposure time in days. It is observed in Figures 4.2.3.2. and 4.2.3.3. that after initial start-up of the new loops, about 10 days of operation were necessary to achieve stable water conditions. After this period, a similar trend in water conditions is observed in all tests; the start-up of each test period being characterized by a high conductivity which rapidly decreased and stabilized to a value below 0.5 micromhos in less than a day.

Turbidity measurements were made of the suspended material in the loop water produced during the test. Identity of material causing the turbidity was not established, but the crud analysis shown in Table 4.2.3.4.1. presents a possible composition of the suspended material. See also sections 4.2.3.4. and 4.2.3.5. for further description of the material. The influence of the elements found in the analyses on the corrosion of aluminum was not investigated.

TABLE 4.2.4.1.

CORROSION IN MG/CM² OF LOOP #1 - TEST #1 SAMPLE COUPONS

EXPOSURE TIME (DAYS)	SAMPLE NUMBER								AVERAGE
	1042	1043	1044	1045	1047	1048	1049	1050	
33.75	17.79	15.71	16.42	14.06	8.77	8.81	7.15	7.13	11.95
47.52	25.00	22.67	23.10	21.03	17.15	17.31	14.23	13.63	19.26
73.89	36.46	33.87	33.32	32.15	27.71	27.81	26.12	25.18	30.33
After Stripping	-----	49.4	-----	-----	-----	-----	-----	39.3	44.3

TABLE 4.2.4.2.

CORROSION IN MG/CM² OF LOOP #2 - TEST #1 SAMPLE COUPONS

EXPOSURE TIME (DAYS)	SAMPLE NUMBER								AVERAGE
	1007	1009	1010	1011	1012	1013	1014	1015	
53.92	16.93	11.82	10.89	10.90	11.19	11.98	14.45	13.97	12.77
77.91	25.91	19.47	19.19	18.90	18.96	20.33	24.79	24.55	21.50
88.79	33.30	27.35	26.50	26.10	26.50	27.35	29.90	30.40	28.45
95.00	34.60	29.70	29.15	28.90	29.00	30.10	33.30	33.40	31.20
After Stripping	49.1	43.6	41.7	-----	42.1	43.3	-----	46.3	44.4

TABLE 4.2.4.3.

CORROSION IN MG/CM² OF LOOP #3 - TEST #1 SAMPLE COUPONS

EXPOSURE TIME (DAYS)	SAMPLE NUMBER								AVERAGE
	1016	1017	1018	1019	1020	1021	1022	1023	
31.48	4.47	4.10	4.49	4.78	6.19	4.82	5.36	7.19	5.17
54.63	17.52	13.60	13.98	14.88	14.81	12.52	13.48	14.33	14.40
67.57	22.35	17.75	17.52	19.34	18.41	15.93	17.68	19.31	18.53
80.79	30.55	24.20	24.40	26.30	23.70	21.50	24.00	25.40	25.05
After Stripping	-----	37.7	37.8	39.7	38.1	35.5	37.3	38.5	37.7

TABLE 4.2.4.4.

CORROSION IN MG/CM² OF LOOP #2 - TEST #2 SAMPLE COUPONS

EXPOSURE TIME (DAYS)	SAMPLE NUMBER								AVERAGE
	1078	1079	1080	1081	1082	1083	1084	1085	
8.20	1.44	1.61	1.77	1.80	1.82	1.88	1.81	1.79	1.74
17.90	1.90	2.20	2.26	2.19	2.38	2.12	2.26	2.36	2.21
32.95	0.15	1.35	2.21	2.52	2.42	2.51	1.77	1.05	1.75
44.82	3.28	1.45	0.83	1.30	1.21	1.22	0.11	2.67	1.51
57.70	8.57	6.37	4.12	4.17	3.86	3.37	5.01	7.69	5.40
69.73	12.82	10.42	7.98	8.08	7.54	7.11	8.97	11.78	9.34
After Stripping	25.1	22.8	20.5	----	20.3	20.4	22.5	24.9	22.4

TABLE 4.2.4.5.

CORROSION IN MG/CM² OF LOOP #3 - TEST #2 SAMPLE COUPONS

EXPOSURE TIME (DAYS)	SAMPLE NUMBER								AVERAGE
	1086	1087	1088	1089	1090	1091	1092	1093	
10.76	1.95	2.28	1.98	2.03	2.12	2.16	1.83	0.79	1.89
26.25	1.31	1.81	1.39	1.62	1.65	1.75	1.34	0.22	1.39
36.30	9.66	5.08	5.08	5.90	2.18	2.50	3.68	4.23	4.79
47.20	11.04	6.51	6.62	7.58	4.41	4.21	5.49	6.64	6.56
60.16	15.91	11.73	10.77	11.49	8.48	8.11	10.58	12.25	11.17
73.11	19.47	14.46	13.83	14.52	11.12	10.82	14.20	15.49	14.23
After Stripping	35.6	-----	30.5	31.4	29.1	28.0	30.9	31.6	31.0

Turbidity indications expressed as ppm of $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, obtained during Test 2 in Loop 2, are shown in Table 4.2.4.6.

TABLE 4.2.4.6.

TURBIDITY DURING TEST 2 IN LOOP 2

EXPOSURE TIME (DAYS)	TURBIDITY - ppm of SUSPENDED SOLIDS AS $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$
17.90	2.50
32.95	10.12
44.82	13.60
57.70	6.00
69.73	1.50

Figure 4.2.4.3. is a plot of the concentration of suspended solids in Loop 2, Test 2 as a function of time. Corrosion results in mg/cm^2 are also plotted against time on the same graph. This graph illustrates an interesting phenomenon. It is noted that as corrosion rate decreases slightly, concentration of suspended solids increases sharply - up to 45 days. At this time, the aluminum corrosion rate increases while turbidity decreases. The turbidity as well as the sample weight change measurements were made at the end of each test period before draining of loops and subsequent sample removal. It is unfortunate that the loops had to be drained during each inspection shutdown period, because the suspended solids were lost. Draining and subsequent filling of the loops with demineralized water also added to the refreshment rates. Despite this drainage, the graph shows a relationship between the corrosion attack and suspended solids concentration as could be expected, if the system had not been drained.

This seems to suggest that a change in the nature or composition of the corrosion film might have occurred which could have contributed to the rapid formation of a suspension up until 45 days of exposure. After this time, another change in the nature of the film may have occurred with a resulting smaller dissolution rate. Further investigation along these lines would be very interesting and desirable. The five corrosion tests indicated similar corrosion behavior after initial periods of up to 45 days of exposure. During the initial period, weight is gained. The film is apparently built up faster than it is removed by the high flow rates. After the initial period, between 25 and

45 days, a sharp increase in corrosion rates is observed - the film being removed more rapidly by the high flow conditions. The curves in the mg/cm² versus days plots have essentially the same slopes or corrosion rates after the initial period. The initial period is of little importance in determining long-term corrosion characteristics; consequently, no attempts were made to observe the break-off points during tests numbered 1.

The average corrosion curves shown in Figures 4.2.4.1. and 4.2.4.2. for all five tests after the initial period have slopes as follows:

Loop 1, Test 1	23 mils per year
Loop 2, Test 1	24 mils per year
Loop 3, Test 1	22 mils per year
Loop 2, Test 2	17 mils per year
Loop 3, Test 2	15 mils per year

It can be noted that tests numbered 1 are related and tests numbered 2 are related. There also is a relation apparent between Tests 1 and 2 in the same loops.

The differences of 2 mils per year between the results obtained during Tests 1 and 2 in Loops 2 and 3 may be attributable to the individual loop characteristics as well as the slight differences in flow velocities.

It was expected that Tests 1 would produce lower corrosion attack on the sample specimens than Tests 2, because of the corrosion attack on the new loops themselves and the consequent increase in the dissolved and suspended solids in the loop water. However, it was found that this supposition was reversed, which leads to the conclusion that corrosion of the loops themselves and the corrosion products from the stainless steel corrosion may have contributed to the accelerated attack on the aluminum. The frequency of start-ups and shutdowns during Tests 1 may also have contributed to the higher initial corrosion rates during the first series of tests in all loops.

It can be generally stated that the appearance of all of the sample coupons in all of the tests was about the same after certain specific periods of exposure to the corrosive conditions.

After about the first ten days of exposure, the sample surfaces were characterized by a black adherent oxide coating with some small bluish-gray colored pock marks. As time progressed, these pock marks increased in size and number and larger areas of bluish-gray colored uneven surfaces became apparent. Further observation of these films, after about 30 - 40 days of exposure, indicated that there were probably three corrosion film layers. A black film next to the metal surface, a decidedly gray layer on

FIGURE 4.2.4.1. Dynamic Corrosion Tests 1

FIGURE 4.2.4.2. Dynamic Corrosion Tests 2

TURBIDITY IN ppm OF SUSPENDED SOLIDS AS $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$
AND
AVERAGE CORROSION IN mg/cm^2
VERSUS
EXPOSURE TIME IN DAYS
LOOP 2 TEST 2

FIGURE 4.2.4.3. Turbidity and Corrosion Test

the black film, (noted particularly around the exposed bare metal areas), and a light blue film on the outside of the samples. The blue and gray scales seemed less adherent than the black film. Close to the end of the test, at between 40 - 60 days of exposure, a point was reached where only two films were again apparent - a bluish-gray film and a light non-adherent bluish film. The samples by this time had pitted quite severely.

The leading and trailing edges of all samples showed some erosion effects. The leading edges of the leading samples in all holders exhibited the most severe erosion and also were the first on which erosion was noted. Figure 4.2.4.4. illustrates the corrosion of Loop 3, Test 1 samples. The top curve represents the leading sample. Because of the weighing method of evaluation, no differentiation is possible between the corrosion and erosion effects. However, it was definitely apparent that the accelerated upward trend of the curve representing the leading sample was due to erosion.

Progress of the corrosion attack can be followed by examining the series of photographs presented in Figures 4.2.4.5. to 4.2.4.22. Flow direction in all photographs is from left to right and top to bottom.

Figure 4.2.4.5. shows Loop 2, Test 2 samples after 17.9 days of exposure, while Figures 4.2.4.6. and 4.2.4.7. show close-ups of the leading and trailing coupons respectively. The samples at this stage are covered with a black coating which in places is changing to a bluish-gray color. This is particularly apparent on the leading sample. Some bluish pock marks are apparent on all sample surfaces. A slight erosion effect can be noted on the leading edges.

Figure 4.2.4.8. shows the same samples after 33.0 days of exposure. Figure 4.2.4.9. is a close-up of the leading sample, while Figure 4.2.4.10. is a close-up of the sample positioned in the middle in Figure 4.2.4.8. The sample surfaces bear a similarity to their earlier appearances, but they are becoming increasingly covered by a bluish-gray film. At this stage of corrosion, three differently colored films are noted; the black film previously observed is being covered by the bluish-gray film. A decidedly gray colored oxide is noted around the pock and scratch marks. The erosion effects have become more obvious.

Figure 4.2.4.11. illustrates Loop 3, Test 2 samples after 36.3 days of exposure at about the same stage in the corrosion process as the above Loop 2 samples. Figures 4.2.4.12. and 4.2.4.13. are enlargements of the leading sample and the sample positioned in the middle row at right in Figure 4.2.4.11. The sample surfaces exhibited similarly colored films, although the oxide pattern and color distribution was somewhat different.

FIGURE 4.2.4.4. Corrosion Test

FIGURE 4.2.4.5. Loop 2, Test 2 . . . Samples After 17.9 Days of Exposure (NP 033-24)

FIGURE 4.2.4.6. Loop 2, Test 2 . . . Closeup of Leading Sample After 17.9 Days of Exposure (NP 033-26)

FIGURE 4.2.4.7. Loop 2, Test 2 . . . Closeup of Trailing Sample After 17.9 Days of Exposure (NP 033-28)

FIGURE 4.2.4.8. Loop 2, Test 2 . . . Samples After 33.0 Days of Exposure (NP 042-9)

FIGURE 4.2.4.9. Loop 2, Test 2 . . . Closeup of Leading Sample After 33.0 Days of Exposure (NP 042-14)

FIGURE 4.2.4.10. Loop 2, Test 2 . . . Closeup of Middle Sample After 33.0 Days of Exposure (NP 042-12)

FIGURE 4.2.4.11. Loop 3, Test 2 . . . Samples After 36.3 Days of Exposure (NP 042-7)

FIGURE 4.2.4.12. Loop 3, Test 2 . . . Closeup of Leading Sample After 36.3 Days of Exposure (NP 042-17)

FIGURE 4.2.4.13. Loop 3, Test 2 . . . Closeup of Sample Positioned at Right-Center in Above Group (NP 042-15)

Figure 4.2.4.14. shows Loop 2, Test 2 samples at the end of the test after 69.7 days of exposure. The samples were covered with a bluish-gray adherent film and a light non-adherent bluish oxide. Figures 4.2.4.15. and 4.2.4.16. show enlargements of the leading sample and the sample positioned in the middle in Figure 4.2.4.14. The surfaces are rather uneven and show a "fish-scale" effect possibly caused by sample vibration or flow characteristics.

Figure 4.2.4.17. shows Loop 3, Test 2 samples at the end of the test after 73.1 days of exposure. Figures 4.2.4.18. and 4.2.4.19. are close-ups of the leading sample and the sample positioned in the middle row at right in Figure 4.2.4.17. The samples have the same coloring as those shown in Figure 4.2.4.14., but the "fish-scale" or flow effect is somewhat different. These are the same samples as shown in Figures 4.2.4.11., 4.2.4.12., and 4.2.4.13.

Figure 4.2.4.20. illustrates Loop 2, Test 1 samples after 77.9 days of exposure. Figures 4.2.4.21. and 4.2.4.22. are enlargements of the samples positioned in the top row, middle and the bottom row at left. These samples show very definite pitting and erosion patterns.

The following five subsections describe some of the peculiarities of each test which may have some bearing on the results obtained.

4.2.4.1. Loop 1, Test 1

As described in section 4.2.3.1. of this report, Loop 1 was started up and shut down frequently during Test 1 because of miscellaneous repairs and adjustments required. This irregular sequence of operation or cycling, particularly during the beginning of the test, may account for high initial corrosion rates exhibited by samples from this test. Some spalling and consequent increase in corrosion may have occurred, thus increasing initial as well as overall corrosion rates.

4.2.4.2. Loop 2, Test 1

As described in section 4.2.3.2., a thin aluminum foil was inserted between the sapphire holding rods and sample holder in order to avoid sample vibration. It is possible that introduction of the foil deterred corrosion rate of the coupons slightly by creating a higher concentration or saturation of aluminum in vicinity of test specimens. This may account for the dip apparent in the point in Figure 4.2.4.1., for Loop 2, Test 1 at 77.9 days of exposure. If sample vibration was resulting in higher apparent corrosion rates, then the foil might possibly have kept the samples firmly in the holder, resulting in a

FIGURE 4.2.4.14. Loop 2, Test 2 . . . Samples After 69.7 Days of Exposure (NP 050-12)

FIGURE 4.2.4.15. Loop 2, Test 2 . . . Closeup of Leading Sample After 69.7 Days of Exposure (NP 050-8)

FIGURE 4.2.4.16. Loop 2, Test 2 . . . Closeup of Sample Positioned in the Middle in Above Group (NP 050-10)

FIGURE 4.2.4.17. Loop 3, Test 2 . . . Samples After 73.1 Days of Exposure (NP 050-1)

FIGURE 4.2.4.18. Loop 3, Test 2 . . . Closeup of Leading Sample After 73.1 Days of Exposure (NP 050-5)

FIGURE 4.2.4.19. Loop 3, Test 2 . . . Closeup of Sample Positioned at Right-Center in Above Group (NP 050-6)

FIGURE 4.2.4.20. Loop 2, Test 1 . . . Samples After 77.9 Days of Exposure (NP 025-43)

FIGURE 4.2.4.21. Loop 2, Test 1 . . . Closeup of Sample Positioned at Top-Center in Above Group (NP 025-9)

FIGURE 4.2.4.22. Loop 2, Test 1 . . . Closeup of Sample Positioned at Bottom-Left in Above Group (NP 025-10)

decreased corrosion rate. The foil was not replaced during the next test period, and it is observed that the next inspection results yielded an increase in weight loss. Further investigation in order to establish vibration effects of the samples while loop was operating was not made.

4.2.4.3. Loop 3, Test 1

Corrosion test results for the individual samples from this loop are plotted in Figure 4.2.4.4. The top curve showing largest weight loss represents the leading sample. This higher loss on the leading sample was observed also in the other tests and is due to greater erosion effects on the leading edge of the sample.

The curves are representative of the general trend in aluminum corrosion test results, showing a divergence of individual sample data after a period of time.

4.2.4.4., 4.2.4.5. Loop 2 and Loop 3, Tests 2

There were no significant departures from the proper operation and no detectable deviations in results were noted during these tests.

4.2.5. Conclusions

Purposes of tests described in section 4.2. of this report, as outlined in the introduction, were:

- 1) To establish the corrosion characteristics of 8001 aluminum in high purity water at high temperatures and high flow rates,
- 2) To ascertain reproducibility of results, and
- 3) To compare and correlate corrosion data obtained at Greendale with results from other laboratories.

From experience gained during these tests it appears that, under conditions of high temperature and high flow rates, the corrosion film builds up to a certain thickness, after which it is rather rapidly and unevenly removed from the sample surfaces by the high flow velocities.

Average corrosion rates, after initial corrosion period of up to 45 days of exposure, vary between 15 and 24 mils per year. The differences, as explained in section 4.2.4. are due to:

- 1) Variations in the initial corrosion rates due to conditioning of the loops, and

2) Individual loop characteristics.

Other investigators have also found that results from different corrosion loops usually show some variations that can be attributed to the above reasons.

It is rather difficult to compare the results obtained at Greendale with work performed at other laboratories because of variations in experimental equipment and variations in test conditions, particularly flow rates. The evaluation methods employed, the treatment of samples, as well as the methods of data collection, all present limiting features to date comparisons. However, the corrosion test results obtained at Greendale are in good agreement with results reported from recent investigations by other civilian and government laboratories.

Tests conducted by Oak Ridge National Labs and by Du Pont indicate that 8001 aluminum, exposed to similar dynamic high purity water conditions, will corrode 25 - 40 mils per year.

At Hanford, dynamic tests were performed to determine aluminum corrosion with heat transfer through the aluminum. These results predict corrosion rates for Pathfinder fuel cladding of approximately 50 mils per year.

The corrosion rates of 8001 aluminum exposed to the water conditions to be maintained in Pathfinder are too high for an economical design and operation of the reactor. Methods to reduce the high corrosion rates have been investigated by Greendale Labs as well as at other laboratories. The following sections 4.3. and 4.4. of this report deal with two of the methods investigated at Greendale Labs.

4.3. Increased A/V Tests

A relationship has been found to exist between corrosion rates of the aluminum sample coupons being tested and the quantity or concentration of aluminum corrosion products circulating in corrosion testing loops. This relationship is frequently expressed as the aluminum-surface-area—to-water-volume-ratio, usually referred to as A/V.

The area-to-volume-ratio phenomenon has been found useful as a method of corrosion rate reduction for aluminum exposed in high purity water at high temperatures and high velocity flows. Purpose of the tests made at Greendale was to evaluate this method in hopes of reducing the high corrosion rates obtained in the plain aluminum tests described in section 4.2. A total of three tests were performed in Loop 2. The tests were numbered 3, 4 and 5. First test was conducted with the excess aluminum area located in a by-pass stream and without the purification system. Second test was made with the excess area located in the main piping, up-

stream from test specimens, and the purification stream operating. Last test was identical to the second test and was made in order to ascertain reproducibility of the low corrosion rates obtained in the previous test.

The tests were conducted under the operating conditions of 500°F, 1200 psi, pH 5.5 - 7.0, flow rates 26 - 28 fps and total exposure times of 57 - 126 days. The A/V in the first test was 2620 cm²/liter and during the last two tests 1346 cm²/liter.

4.3.1. Test Material Description

The sample material tested was 8001 aluminum alloy from the same lot as that used in the Plain Aluminum Tests and in Static Tests 1 and 2.

The sample coupons for all three tests were cut from a sheet parallel to its rolling direction. The coupons were then machined into test specimens of 2" x .5" x .125" size according to Figure 3.2.1.1.

The specimens used in both Test 3 and Test 4 were heat treated in a muffle furnace for 288 hours at 500°F. The specimens used in Test 5 were heat treated at 650°F for 545 hours. All specimens were gradually cooled to room temperature in about four hours.

The chemical analysis of the material is tabulated in Table 3.2.1. Mechanical properties of the material are described in section 3.2.1. of this report.

All samples were marked with identifying numbers, washed in acetone, desiccated and weighed prior to insertion in the sample holder.

4.3.2. Test Equipment Description

All three tests described in section 4.3. were made in Loop 2. In order to achieve a higher than normal aluminum-surface-area-to water-volume-ratio (A/V) in the system, an excess aluminum area was placed in the loop. During Test 3, the purification stream was not operating and the excess aluminum area was placed, for conveniences sake, in the by-pass stream. During Tests 4 and 5, the excess area was located in the main piping, upstream from the test specimens, and the purification stream was operating.

The following subsections describe the loop modifications for the three excess A/V tests.

4.3.2.1. Loop 2, Test 3

The loop piping and components were re-arranged prior to

beginning of this test in order to arrive at an A/V ratio of 2620 cm². In order to follow the modifications, refer to Figure 4.2.2.1. which shows the normal flow diagram in the loop.

The mixed bed ion exchange resin was removed from the ion exchange vessel and a rack made of 8001 aluminum sheets, held together by stainless steel rods, was inserted into the vessel. See Figure 4.3.2.1. for sketches of the rack. The cooling water to loop heat exchangers was shut off and the loop filter and conductivity cell were taken out of the system in order to avoid damage to and failure of these components and their seals. Essentially, then, the system consisted of the main stream, as during previous tests, and a by-pass stream containing the excess aluminum section. Flow rate in the by-pass piping was small, and it joined the main piping on the downstream side of test specimens. The system was thoroughly insulated and was operated at 500°F and 1200 psi.

Total surface area of the eight aluminum test samples was 103 cm². Surface area of the rack was 5850 cm². Total aluminum surface area in the system was 5953 cm². Water volume in the main-stream piping and components was 2.27 liters, and volume in the by-pass stream piping and components was 11.33 liters. Total system volume was 13.60 liters. The area-to-volume ratio was 2620 cm²/liter considering main-stream volume only. The area-to-volume ratio was 484 cm²/liter considering total system volume. The area-to-volume ratio used in previous tests was 45.5 cm²/liter considering main-stream volume only and 7.6 cm²/liter considering total system volume.

4.3.2.2. Loop 2, Test 4

The loop piping and component arrangement during this test was same as during the "Plain Aluminum Tests" described in section 4.2. of this report.

The excess area in the form of a bent 8001 aluminum tubing of 13.125" length, 0.420" O.D. and .340" I.D. was inserted in the "J" section or sample holder section of the main loop piping, upstream from test specimens. Figure 4.2.2.4. presents an illustration of the "J" section.

Surface area of the tubing was 202.5 cm²; total aluminum surface area was 305.5 cm². The area-to-volume-ratio was 134.6 cm²/liter considering main-stream volume only. This A/V ratio was similar to that expected in Pathfinder.

4.3.2.3. Loop 2, Test 5

The loop arrangement, as well as size and location of the excess area during this test were identical to previous test.

FIGURE 4.3.2.1. Aluminum Rack Used in Loop 2

4.3.3. Test Description

The three tests described in this section were performed under the average operating conditions shown in Table 4.3.3.1.

TABLE 4.3.3.1.

AVERAGE OPERATING CONDITIONS

INCREASED A/V TESTS

Test Number	3	4	5
Loop Number	2	2	2
Temperature (°F)	500	500	500
Pressure (psi)	1200	1200	1200
pH	5.9-6.3	5.6-6.3	5.3-6.6
Flow Rate (fps)	27.6	28	27.0
Conductivity (micromhos)	5.0	.3-.6	.4-.7
A/V * (cm ² /liter)	2620	134.6	134.6
TOTAL EXPOSURE TIME (days)	57.0	107.0	126.1

* NOTE: These values of A/V consider main-stream volume only.

4.3.3.1. Operating Conditions In Loop 2 During Test 3

The loop performed very satisfactorily during this test. Samples were examined after 8.0, 18.9, 28.9, 41.9 and 57.0 days of exposure. Water in the loop was drained during each test period. Loop was filled with fresh distilled and demineralized water at beginning of each test period. Since the loop filter and ion exchanger were not operating during this test, conductivity and suspended solids content in the water during the test were higher than in any other loop test.

4.3.3.2. Operating Conditions In Loop 2 During Test 4

The loop performed very satisfactorily during this test. The samples were inspected after 10.9, 22.8, 35.7, 47.0, 56.7, 66.1, 79.5, 93.0, and 107.0 days of exposure. Water conditions during this test, expressed as conductivity in micromhos versus days of exposure, are plotted in Figure 4.3.3.1.

4.3.3.3. Operating Conditions In Loop 2 During Test 5

The loop was operating properly during this test. Samples were inspected after 11.4, 47.1, 64.6, 78.6, 96.4, 103.0,

and 126.1 days of exposure. Water purity during the test is shown in Figure 4.3.3.2.

4.3.4. Test Results

Corrosion test results obtained for individual specimens from each of the three tests are tabulated in Tables 4.3.4.1., 4.3.4.2. and 4.3.4.3. The average corrosion rates from all three tests are plotted in Figure 4.3.4.1. The corrosion rates were calculated according to the procedure outlined in section 4.1. of this report.

Average long-term rates or slopes of the curves shown in Figure 4.3.4.1. during final test periods in each loop were as follows:

Loop 2, Test 3	22.9 mils per year
Loop 2, Test 4	7.2 mils per year
Loop 2, Test 5	6.1 mils per year

As seen from above results of the last two tests and Figure 4.3.4.1., the corrosion rate of aluminum can be decreased by increasing the concentration of dissolved and suspended aluminum corrosion products in the test solution. However, there is a certain unexplained criterion involved which has not been investigated at the present time. It has been found, at Greendale as well as by other investigators, that in the increased A/V tests, in order to arrive at reduced corrosion rates the purification stream must be operative. The excess area contributes to an increase in the concentration of solids content in the circulating water, but the purification stream reduces solids concentration. These two factors are opposing in nature and no sound theoretical explanation has been derived to account for the observed improvement in corrosion behavior of aluminum under these conditions.

It must be remembered that the low corrosion rates observed in Tests 4 and 5 were obtained in a pressurized hot water loop and may not be applicable under Pathfinder conditions because:

- 1) The A/V effect is essentially a concentration or saturation phenomenon. In a pressurized hot water loop, heat is transferred from the hot water to the corrosion test specimens; the bulk water, as well as the water adjacent to the corrosion film, is saturated with aluminum corrosion products and consequently less dissolution of corrosion film or metal takes place - with a resultant decrease in corrosion rates.

FIGURE 4.3.3.1. Loop 2, Test 4 . . . Water Conditions

FIGURE 4.3.3.2. Loop 2, Test 5 . . . Water Conditions

TABLE 4.3.4.1.

CORROSION IN mg/cm^2 OF LOOP 2, TEST 3, SAMPLE COUPONS

EXPOSURE TIME (DAYS)	SAMPLE NUMBER								AVERAGE
	1113	1114	1115	1116	1117	1118	1119	1120	
8.0	0.82	0.98	0.90	0.92	0.93	0.91	0.87	0.83	0.89
18.9	3.89	4.19	3.75	5.20	5.36	5.07	5.36	4.42	4.66
28.9	10.26	10.88	10.27	11.43	11.08	9.92	10.66	10.04	10.57
41.9	15.93	16.36	15.51	16.81	15.70	14.61	15.15	14.76	15.60
57.0	22.10	22.30	21.10	23.40	21.40	19.85	20.50	20.70	21.40
After Stripping	41.3	41.2	41.1	43.4	41.8	41.3	41.6	41.1	41.6

TABLE 4.3.4.2.

CORROSION IN mg/cm^2 OF LOOP 2, TEST 4, SAMPLE COUPONS

EXPOSURE TIME (DAYS)	SAMPLE NUMBER								AVERAGE
	1121	1122	1123	1124	1125	1126	1127	1128	
10.9	2.17	2.25	2.19	2.30	2.27	2.30	2.31	2.27	2.26
22.8	2.92	3.20	3.07	3.22	3.08	3.08	3.20	3.07	3.10
35.7	0.93	1.50	1.88	2.09	1.73	2.46	3.16	2.02	1.97
47.0	1.02	0.60	0.26	1.64	1.46	2.42	2.94	1.67	1.50
56.7	2.36	0.18	1.79	0.87	0.89	2.10	2.51	0.72	1.43
56.1	3.79	1.17	2.86	0.29	0.41	1.80	1.95	0.20	1.56
79.5	5.23	2.07	4.94	0.59	0.14	1.53	1.33	1.57	2.18
93.0	7.00	3.62	6.22	1.83	1.24	0.99	0.34	3.40	3.08
107.0	9.78	5.82	9.88	3.90	3.33	2.64	1.51	5.51	5.00
After Stripping	28.5	24.9	27.8	23.6	24.3	22.5	22.0	23.8	24.7

TABLE 4.3.4.3.

CORROSION IN mg/cm² OF LOOP 2, TEST 5, SAMPLE COUPONS

EXPOSURE TIME (DAYS)	SAMPLE NUMBER								AVERAGE
	1157	1158	1159	1160	1161	1162	1163	1164	
11.4	2.43	2.49	2.23	2.24	2.29	2.37	2.40	2.41	2.36
47.7	2.85	3.47	2.61	2.16	3.02	3.16	1.84	0.74	2.48
64.6	1.77	2.68	1.48	1.34	2.54	2.77	2.10	0.36	1.88
78.6	0.32	1.73	0.60	0.34	2.02	2.25	0.99	1.26	1.19
96.4	1.44	0.08	1.88	2.22	0.36	0.80	1.51	4.45	1.59
103.9	2.33	0.20	2.30	2.77	0.09	0.46	2.01	4.95	1.89
126.1	5.04	2.68	4.75	5.31	1.78	2.26	5.87	8.02	4.46

FIGURE 4.3.4.1. Dynamic Corrosion Tests

- 2) In a reactor, however, heat is transferred through metal cladding, corrosion film and water film adjacent to the corrosion film to the bulk water. Temperature of adjacent water film is higher than that of the bulk water, consequently the adjacent water film is saturated with aluminum corrosion products to a lesser degree than the bulk water. Since a layer of lower concentration water is next to the corrosion film and metal, more of these may tend to go into solution — resulting in an increased corrosion rate.

The following three subsections describe in detail results obtained and observations made during each of the tests.

4.3.4.1. Loop 2, Test 3

From Figure 4.3.4.1., it is obvious that the large excess area in Test 3 did not produce any beneficial effects on the test specimens. The slope of the average corrosion curve from this test closely approaches that obtained during initial plain aluminum tests described in section 4.2. The initial corrosion periods for samples from this test were also somewhat shortened, which resulted in high overall corrosion rates. Lack of improvement in corrosion behavior during this test may have been due to several different factors or a combination of these:

- 1) Lack of water purification during the test...
- 2) Location of the excess area in the by-pass stream too far removed from test specimens...
- 3) The particular loop component and system flow arrangement...
- 4) The flow rate through the by-pass stream was small and a sufficiently high concentration of Boehmite may not have accumulated in the vicinity of the test specimens...
- 5) The drainage of the loop water during each inspection shutdown, and consequent loss of the dissolved and suspended corrosion products...
- 6) Some of the aluminum corrosion products may have plated or settled out in the heat exchangers which were inaccessible for inspection.

The loop make-up water was distilled and demineralized. Conductivity and turbidity of water in the loop increased to

higher than normal values during each test period. This indicated that the excess aluminum area or the rack was corroding as desired. However, because of the reasons listed above, attempts to reduce the corrosion rate in this test were unsuccessful. This seemed to indicate that the corrosion rate cannot be reduced by placing an excess area in a by-pass stream. However, at about this time, it was learned from investigators at AECL, Chalk River, that their experiments with the A/V factor yielded good results when the excess aluminum area was placed upstream from the test specimens and when the purification stream was operating. They also had obtained similarly poor results in a system with no continuous water purification provisions and with the excess area located downstream from test specimens.

It was expected that the extra aluminum corrosion products introduced in the system might plate out on the stainless steel loop, but no plate-out was noted at end of test.

The weight of the aluminum rack had increased 9.45 gm during the test. This corresponded to a corrosion rate of 2.8 mdd or 1.5 mils per year. After the test, the rack was covered with an uneven gray oxide film.

Progress of corrosion during Test 3 can be described in the following general way:

After the first eight days of exposure, the samples were covered with a grayish-black oxide film. On top of this film was a bronze colored coating. After 19 days of exposure, the bronze colored coating had given way to a flaky reddish film. The grayish-black film was again observed underneath this coating. Some of the non-magnetic reddish coating was very tightly adherent. This reddish coating may have been iron oxide from the corrosion of the stainless steel loop, since no purification components were used in this test. After 29 days of exposure, the samples appeared about same as before. Surfaces were very smooth with some bare metal apparent under the red oxide.

After approximately 42 days, the samples were covered with a rough grayish-blue non-adherent oxide film. Some reddish oxide coating was also noted on the samples. The gray film showed slight but uniform pitting. Some erosion was apparent on leading edges of all samples.

At the end of the 57-day test, the sample surfaces had a reddish, porous, non-adherent covering. Gray oxide was noted under this layer.

No analyses were made of the variously colored films covering the samples, but it seems reasonably safe to assume that the reddish material observed resulted from corrosion of the stainless steel loop piping.

No attempts were made to determine effects of the elements from stainless steel loop corrosion on corrosion of the aluminum.

4.3.4.2. Loop 2, Test 4

Test 4 was devised in such a manner as to locate the excess aluminum area upstream from and close to the test specimens. The purification stream was also placed back in operation.

Results of Test 4 indicated a definite improvement in both the appearances and corrosion rates of the sample coupons.

The weight of the aluminum tubing used as the excess area increased 1.1593 gm, which corresponds to a corrosion rate of 2.84 mils per year. The corroded aluminum tubing is shown in Figure 4.3.4.2. and an enlargement of the tubing is shown in Figure 4.3.4.3. The tubing was covered with a dark grayish-blue adherent oxide and some light bluish non-adherent film. Corrosion progress in Test 4 can be followed by referring to the following description and Figures 4.3.4.4. to 4.3.4.15.

After about 11 days of exposure, all samples were covered with a black uniform oxide.

After about 23 days, the samples appeared to have four different colored films: the black film observed previously ... some bluish-gray colored pock marks ... an ash-gray film replacing the black film ... and a light brownish-gray, non-adherent film unevenly distributed as the top layer. Slight erosion was noted on all leading sample edges. See Figure 4.3.4.4. for a view of the samples. Figures 4.3.4.5. and 4.3.4.6. are enlargements of the leading and trailing samples.

After 36, 47 and 57 days of exposure, the samples appeared very similar; their surfaces were characterized by three differently colored films: black, blue and gray. Some bare metal was noted, particularly on the leading two samples. Figure 4.3.4.7. illustrates the samples after 36 days of exposure. Figures 4.3.4.8. and 4.3.4.9. are close-ups of the leading and trailing samples.

After both 66 and 80 days of exposure, a change in the color of the films was noted. The top layer was light bluish-gray, the next was dark bluish-gray and the layer closest to the metal surface was black. Some slight vibration or fish-scale

FIGURE 4.3.4.2. Aluminum Tubing Used as the Excess Area in Loop 2, Test 4 (NP 064-8)

FIGURE 4.3.4.3. Closeup of Section of Aluminum Tubing Used as the Excess Area in Loop 2, Test 4

FIGURE 4.3.4.4. Loop 2, Test 4 . . . Samples After 22.8 Days of Exposure (NP 058-9)

FIGURE 4.3.4.5. Loop 2, Test 4 . . . Closeup of Leading Sample After 22.8 Days of Exposure (NP 058-10)

FIGURE 4.3.4.6. Loop 2, Test 4 . . . Closeup of Trailing Sample After 22.8 Days of Exposure (NP 058-12)

FIGURE 4.3.4.7. Loop 2, Test 4 . . . Samples After 35.7 Days of Exposure (NP 061-10)

FIGURE 4.3.4.8. Loop 2, Test 4 . . . Closeup of Leading Sample After 35.7 Days of Exposure (NP 061-13)

FIGURE 4.3.4.9. Loop 2, Test 4 . . . Closeup of Trailing Sample After 35.7 Days of Exposure (NP 061-11)

effects were also observed. Figure 4.3.4.10. shows the samples after 80 days of exposure. Figures 4.3.4.11. and 4.3.4.12. are enlargements of the leading sample and the sample positioned in the middle row at right.

After 93 days, the samples appeared about the same; but some pin-holes were observed on a few samples at the leading edges.

At the end of the test, after 107 days of exposure, the samples were covered with a grayish film. Some vibration or fish-scale effects were observed. Figure 4.3.4.13. shows the samples at this time. Figures 4.3.4.14. and 4.3.4.15. are close-ups of the leading sample and the sample positioned in the middle row at right.

4.3.4.3. Loop 2, Test 5

Test 5 was identical to Test 4 in every respect. The results of Test 5 very closely resembled the results of Test 4. The aluminum tubing, used as the excess area, had gained 1.3030 gm over the 126.1 days of exposure — corresponding to a corrosion rate of 2.71 mils per year. This figure does not consider any losses of aluminum or aluminum corrosion products from the tubing.

The appearance of the tubing was similar throughout the test to the appearance of tubing used in Test 4.

Corrosion films on the sample specimens were of a similar appearance to those observed in Test 4 except for the vibration or fish-scale effects which were not noted during Test 5.

4.3.5. Conclusions

The last two tests described in this section have yielded the lowest dynamic corrosion rates attained in the entire Allis-Chalmers aluminum corrosion testing program.

It has been successfully demonstrated that the long-term corrosion rate of 8001 aluminum can be reduced by use of the A/V phenomenon. However, as mentioned in the previous section, the A/V phenomenon is really an expression of the corrosion product concentration in the circulating water. The relationships that exist between these concentrations and the corrosion rates is exceedingly complex and not well understood by any of the aluminum investigators at the present time. Nevertheless, it has been proven that high A/V ratios result in very low corrosion rates.

It has been found by other investigators, as well as at Greendale, that not only a large excess aluminum area in the loop is necessary, but also the following two factors

FIGURE 4.3.4.10. Loop 2, Test 4 . . . Samples After 79.5 Days of Exposure (NP 063-13)

FIGURE 4.3.4.11. Loop 2, Test 4 . . . Closeup of Leading Sample After 79.5 Days of Exposure (NP 063-8)

FIGURE 4.3.4.12. Loop 2, Test 4 . . . Closeup of Sample Positioned at Right-Center in Above Group (NP 063-10)

FIGURE 4.3.4.13. Loop 2, Test 4 Samples After 107.0 Days of Exposure (NP 064-2)

FIGURE 4.3.4.14. Loop 2, Test 4 . . . Closeup of Leading Sample After 107.0 Days of Exposure (NP 064-5)

FIGURE 4.3.4.15. Loop 2, Test 4 . . . Closeup of Sample Positioned at Right-Center in Above Group (NP 064-7)

are just as important in order to successfully reduce the corrosion rates of the test specimens:

- 1) Proper location of the excess area upstream from the test specimens, and
- 2) Continuous purification of a portion or all of the loop water.

A firm conclusion cannot be drawn as to the applicability of this method of corrosion rate reduction to the Pathfinder core design because of:

- 1) Design considerations as to placement of the excess aluminum area in the close vicinity of the core.
- 2) Heat transfer considerations. Direction of heat transfer in a pressurized hot water loop is reverse of that in a reactor as explained in the Test Results section.
- 3) Increase in solids content in the reactor water.

It is definitely apparent that a closer examination of the concentration or dissolution phenomena and other variables, particularly heat transfer effects, is needed if the A/V ratio method of corrosion rate reduction is to be applied in Pathfinder.

4.4. Prefilmed Sample Tests

The purpose of these tests was to attempt to reduce the high dynamic corrosion rate of the 8001 aluminum alloy at high temperatures and high flow rates. It was hoped that the prefilm coating might prolong the initial corrosion period and also deter the attack on the aluminum metal. Two dynamic tests, numbered 3 and 4, were made in Loop 3. Specimens used in Test 3 were prefilmed in a static autoclave at 500°F, which was also the dynamic corrosion test temperature. Specimens used in Test 4 were prefilmed at 600°F, which was 100°F above the dynamic test temperature. Total sample exposure times during these two tests were 72.6 and 134.0 days.

4.4.1. Test Material Description

The sample material tested was 8001 aluminum alloy from the same lot as that tested in the INCREASED A/V TESTS, PLAIN ALUMINUM TESTS and STATIC TESTS 1 AND 2. See section 3.2.1. of this report for further description of the material.

The sample coupons used in Test 3 were heat treated at 500 F for 244 hours in a muffle furnace. They were then slowly cooled to room temperature. The coupons used in Test 4 were heat treated at 650 F for 44 hours and were then rapidly cooled to room temperature.

Chemical analyses of the material is shown in Table 3.2.1. The mechanical properties and sample size are described in section 3.2.1. of this report.

The samples were stamped with identifying numbers, washed in acetone, desiccated and weighed prior to prefilming in the autoclave.

4.4.2. Test Equipment Description

Test equipment consisted of the autoclave as described in section 3.1. of this report and dynamic corrosion test Loop 3. Loop component and piping arrangement was the same as described in section 4.2.2. of this report.

4.4.3. Sample Prefilming

The samples used in both of the tests described in this section were prefilmed in the static autoclave. The prefilming conditions were as shown in Table 4.4.3.1.

TABLE 4.4.3.1.

STATIC PREFILMING CONDITIONS

	Test 3	Test 4
TEMPERATURE (°F)	500	600
PRESSURE (psi)	681	1543
pH	5.7	5.6
CONDUCTIVITY (micromhos)	< 5.0	< 5.0
EXPOSURE TIME (days)	7.1	3.1

The prefilming was performed in fresh distilled and demineralized water. The pH and conductivity measurements of the water, shown in Table 4.4.3.1. were made at end of prefilming period.

The coupons were desiccated and weighed before installation in the dynamic loop sample holder.

4.4.4. Dynamic Test Description

The two tests described in this section were performed under the average operating conditions shown in Table 4.4.4.1.

TABLE 4.4.4.1.

AVERAGE OPERATING CONDITIONS

PREFILMED SAMPLE TESTS

TEST NUMBER	3	4
LOOP NUMBER	3	3
TEMPERATURE (°F)	500	500
PRESSURE (psi)	1200	1200
pH	6.0	5.9-7.0
FLOW RATE (fps)	27.7	26.8
CONDUCTIVITY (micromhos)	.4-.8	.3-.8
A/V (cm ² /liter)	45.5	45.5
EXPOSURE TIME (days)	72.6	134.0

The loop was drained and refilled with fresh distilled and demineralized water during each sample inspection period.

The following two subsections describe the operational sequel and peculiarities during each test, which may have some bearing on the corrosion test results obtained.

4.4.4.1. Operating Conditions In Loop 3 During Test 3

Numerous shutdowns of the loop occurred during this test due to control, filter, pump and plant power failures. The loop was shut down for sample inspection after 17.1, 27.0, 37.0, 50.1, 61.7, and 72.6 days of sample exposure. Water conditions, expressed as conductivity in micromhos versus exposure time in days, are depicted in Figure 4.4.4.1. After about 37 days of exposure, the loop water appeared very dark in color. Black, magnetic deposits were collected on the loop filter element. It was assumed that this material indicated an impending failure of the canned rotor pump due to wear. This assumption was later substantiated when the pump failed and was taken apart for inspection.

After 50.1 days of operation, the sintered metal filter in the purification stream failed. Soft black spots and holes had developed in the filtering medium, and the element had

FIGURE 4.4.4.1. Loop 3, Test 3 . . . Water Conditions

partially separated from the top end-cap. Filter element was replaced.

4.4.4.2. Operating Conditions In Loop 3 During Test 4

Miscellaneous assorted operating difficulties, including plant power, loop control and pump failures, occurred during this test. These breakdowns may have introduced some more errors in the exposure time and temperature computations.

The test specimens were inspected after 12.6, 22.1, 35.6, 49.1, 65.4, 77.8 and 134.0 days of exposure. Water conditions in the loop are plotted in Figure 4.4.4.2.

4.4.5. Test Results

Corrosion test results for individual coupons obtained during the two prefilmed sample tests are tabulated in Tables 4.4.5.1. and 4.4.5.2. The average corrosion rates from both tests are plotted in Figure 4.4.5.1. The corrosion attack was evaluated according to section 4.1.

Average long-term corrosion rates during final test periods in each loop were as follows:

Loop 3, Test 3	48.4 mils per year
Loop 3, Test 4	14.2 mils per year

No attempts were made to interpret effects of elements from the stainless steel loop corrosion on the corrosion rates obtained.

Generally, the corrosion attack on the prefilmed sample coupons can be described as follows:

Initial corrosion stage was somewhat prolonged; but after the break-off point, the long-term corrosion rates increased to the same and higher values than during tests made on untreated samples. It was observed that before the break-off point was reached, the prefilm coating was peeling or spalling off, thus losing its protective characteristics.

The following two subsections describe in detail the results during each of the two tests.

4.4.5.1. Loop 3, Test 3

From Table 4.4.5.1. and Figure 4.4.5.1., it is apparent that during the final test period, the long-term corrosion rate was two to three times higher than that obtained on samples of the same material without prefilming. However, of the tests conducted at Greendale Laboratories, in only one was

CONDUCTIVITY - micromhos

FIGURE 4.4.4.2. Loop 3, Test 4 . . . Water Conditions

TABLE 4.4.5.1.

CORROSION IN mg/cm² OF LOOP 3, TEST 3, SAMPLE COUPONS

EXPOSURE TIME (DAYS)	SAMPLE NUMBERS								AVERAGE
	1075	1076	1094	1095	1096	1097	1098	1099	
7.14	1.70	1.63	1.74	1.68	1.70	1.71	1.75	1.67	1.70
17.06	1.96	2.00	2.07	2.12	2.15	1.99	2.01	1.99	2.04
27.00	1.47	1.74	1.67	1.80	1.77	1.60	1.53	1.50	1.63
36.99	1.29	0.27	0.67	0.23	0.25	0.13	0.26	0.88	0.50
50.10	7.59	5.96	5.97	4.56	4.63	5.15	4.89	6.39	5.63
61.67	14.35	12.52	12.29	11.12	11.24	11.82	11.51	12.32	12.14
72.64	24.75	22.75	22.55	20.85	20.95	21.60	21.30	22.45	22.15
After Stripping	35.3	33.6	33.3	31.5	31.9	32.4	32.2	32.6	32.9

FIGURE 4.4.5.1. Dynamic Corrosion Tests

the initial corrosion period extended for a longer time than the initial period during this test.

These results tend to confirm reports from AECL, Chalk River in which it was deduced that in order to achieve lower corrosion rates, the samples must be prefilmed statically at a higher temperature than the dynamic test temperatures. To confirm this deduction, Test 4 was performed.

Corrosion progress during Test 3 can be described in terms of sample appearance changes as follows:

After prefilming, the samples were covered with a uniform light gray film. After a total exposure of 17 days, the film had darkened slightly. Small bluish-gray pock marks were apparent on all sample surfaces.

After 27 days, the bluish-gray pock marks had increased in size and a bluish oxide was apparent, particularly along scratch marks on sample surfaces and on the leading edges. Pits on the surfaces revealing bare metal were noted.

After 37 days, a decidedly gray film was apparent on all samples. Some bare metal, fairly evenly distributed in a pattern of shallow pits was also noticed. Considerable erosion was apparent on the leading sample.

After about 50 days of exposure, a fish-scale pattern was noted on all surfaces. The areas of bare metal were larger and the bluish-gray oxide was pitted. Erosion was noted on leading edges of all samples.

After about 62 days, a very definite fish-scale pattern, distributed in even dark and light blue patches was observed. The pits had disappeared, and some very small spots of bare metal were noted.

No further change in the sample appearance was noticed at the end of the 72.6 day test.

4.4.5.2. Loop 3, Test 4

Samples used in this test were prefilmed in a static autoclave at 600 F. Results of this test again indicated a lengthening of initial corrosion period, but the long-term corrosion rate was lower than obtained in Test 3.

The sample appearance changes during the test can be described in the following manner:

After prefilming, the samples were covered with a light gray oxide film. Slight rolling marks were apparent on all samples. After 12.7 days of exposure, samples appeared gray in color with some blue spots around the leading edges. Some bare metal was apparent. The prefilm coating had apparently started to peel or spall off.

After 22.1 days, the prefilm coating was peeling or spalling off in patches, leaving both bare metal and a slight bluish colored film in its place.

After 35.6 days, the samples appeared as illustrated in Figure 4.4.5.2. The darker patches were the prefilm coating, while the lighter ones were of a light bluish-gray color. Figures 4.4.5.3. and 4.4.5.4. are enlargements of the leading sample and the third sample from the trailing end.

After 49.1 days, the prefilm coating had almost completely disappeared. The samples were noted to have 3 differently colored films.

No change in sample appearance was noted after 65.4 days of exposure.

After 77.8 days, the samples were covered with a bluish oxide of a light and dark shade. Some slight pitting of the surfaces was noted.

At the end of the test, after 134.0 days of exposure, the samples were of a bluish-gray color. The surfaces had even and closely spaced distribution of pits. The oxide film at some of the pits was cracked.

4.4.6. Conclusions

Results obtained from the prefilmed sample tests indicate that prefilming in an autoclave and in the 500 - 600°F range has no advantage for long-term applications. Such prefilming produces lower corrosion rates during the initial period of the test. Eventually, however, the corrosion attack is accelerated and the long-term corrosion rates for treated specimens approach the same or higher values than for untreated specimens.

TABLE 4.4.5.2.

CORROSION IN mg/cm² OF LOOP 3, TEST 4, SAMPLE COUPONS

EXPOSURE TIME (DAYS)	SAMPLE NUMBERS								AVERAGE
	1139	1140	1141	1142	1143	1144	1145	1146	
3.12	2.24	2.23	2.23	2.18	2.23	2.20	2.25	2.16	2.22
12.65	2.07	2.60	2.53	2.48	2.52	2.48	2.37	1.86	2.36
22.14	0.48	2.12	2.25	1.97	1.93	2.15	1.49	0.01	1.55
35.61	1.50	1.25	1.66	1.28	0.86	1.47	0.45	3.05	1.56
49.05	5.98	2.24	1.02	0.88	2.63	1.18	3.06	11.28	3.53
65.44	12.05	7.99	6.91	5.46	7.54	6.16	8.52	18.92	9.19
77.82	18.05	12.88	11.51	9.34	12.28	10.83	12.88	24.80	14.07
133.96	36.65	27.75	24.60	21.60	26.20	23.95	28.10	44.00	29.10
After Stripping	52.9	44.7	42.7	39.2	44.2	41.9	45.6	61.2	46.5

FIGURE 4.4.5.2. Loop 3, Test 4 . . . Samples After 35.6 Days of Exposure (NP 063-1)

FIGURE 4.4.5.3. Loop 3, Test 4 . . . Closeup of Leading Sample After 35.6 Days of Exposure (NP 063-4)

FIGURE 4.4.5.4. Loop 3, Test 4 . . . Closeup of Sample Positioned at Right-Center in Above Group (NP 063-6)

It is possible that a different prefilming temperature or technique might yield more acceptable results. However, due to the high flow conditions and frequent cycling, the prefilm coating is expected to wear or spall off rather rapidly.

In view of the test results and present state of knowledge in general about this method of corrosion rate reduction, prefilming of Pathfinder fuel elements cannot be recommended. Time considerations limit further investigation of this method for Pathfinder.

4.5. Summary of Dynamic Test Results

The tests described in preceding sections 4.2., 4.3. and 4.4. represent all of the experimental work done at Greendale in the dynamic corrosion testing of 8001 aluminum alloy. Figure 4.5.1. is a composite graph of the ten dynamic tests made at Allis-Chalmers. The curves designated by solid lines, in Figure 4.5.1., represent the plain aluminum tests; the ones with dashed lines are the increased A/V tests; and the curves with a dash-dot-dash designation are the prefilmed sample tests.

From these curves, it can be observed that the average corrosion rates after the break-off points during the five plain aluminum tests vary between 15 and 24 mils per year. The sample coupons prefilmed at 500 F indicated an average dynamic corrosion rate of 48 mils per year during the final stages of the test. The samples prefilmed at 600 F yielded an average corrosion rate of 14 mils per year after the break-off point. The initial corrosion stage during these tests was somewhat prolonged. However, spalling or peeling off of the prefilm coating was noted after a period of time which indicated that the beneficial effects of prefilming were not of a lasting nature. The increased A/V test, in which the excess area was located in the by-pass stream with no continuous purification provisions, yielded a corrosion rate of approximately 23 mils per year. The increased A/V tests in which the excess areas were located directly upstream from the test specimens and the purification streams were operative, indicated corrosion rates of 6 to 7 mils per year during the final test periods. Visual inspection of the test specimens and the results indicated in Figure 4.5.1. reveal a definite improvement in corrosion rates as well as the appearances of the test specimens.

The dynamic corrosion tests yielded corrosion rates 6 to 160 times greater than the static tests. This was concluded to be due mainly to the high flow velocities of the corrosive medium past the test specimen surfaces.

FIGURE 4.5.1. Comparison Graph

The divergence phenomenon of the corrosion curves of individual samples tested simultaneously in each test, was considerably more pronounced during the dynamic tests, than during the static tests.

The dynamic corrosion rates obtained at Greendale relate well to results from other laboratories as shown in section 2.2.

Time limitations for application to the Pathfinder reactor did not permit further experimentation with this alloy under different test conditions, such as: pH variations, inhibitor additions, etc. The program of dynamic corrosion testing of the 8001 aluminum was carried out as initially conceived. Some delays during the tests were encountered due to failures in various loop components, particularly pump failures. The pace of the corrosion testing program was also governed by length of time required to arrive at a steady-state corrosion rate in each test. Consequently, not enough test data on the 8001 alloy corrosion at Pathfinder conditions could be obtained by the time the Pathfinder core design was finalized.

It is consensus of opinions of investigators in the aluminum corrosion testing field, that the present state of knowledge about the dynamic corrosion characteristics of this material is not advanced enough to warrant an infallible statement concerning its suitability as cladding material at Pathfinder conditions. To our knowledge, there are no reports available at this time that provide sufficient information from which to adequately evaluate the corrosion properties of aluminum for boiling water reactors at Pathfinder conditions.

Consequently, it is exceedingly difficult to provide reactor core engineers with information adequate for design of aluminum clad fuel elements to be used in high temperature boiling water reactors, such as Pathfinder.

Considerable research and development efforts have been expended at various laboratories, as well as at Greendale, in order to decrease the dynamic corrosion rates of this alloy. Further extensive investigations should be made in order to inhibit the corrosion of aluminum to where corrosion rates obtained in pressurized water loops are less than the acceptable reactor design limits. The reason for this is lack of reliable information concerning the effects of such aspects as heat transfer and the increase in cladding temperature over the bulk water temperature, which contribute considerable deleterious effects on the corrosion behavior of the aluminum.

5. Conclusions

The present state of knowledge about corrosion behavior of 8001 aluminum in boiling water reactors, prevents recommendation of this material in reactors with high heat flux and with water temperatures approaching 500 F. However, based on current knowledge of aluminum corrosion behavior in water, the 8001 alloy probably can be used as cladding at more moderate temperatures and pressures. The corrosion behavior of 8001 aluminum is influenced by a large number of very complex and inter-related variable factors many of which are not thoroughly understood at present. It would be exceedingly difficult at this time, because of lack of sufficient knowledge regarding the corrosion of this alloy under reactor conditions, to predict adequately corrosion behavior of this material in the Pathfinder reactor. An accurate evaluation of aluminum corrosion information is further complicated because much of the earlier data led to misleading or limited conclusions. Considerably more research and development will be required, especially at 500 F, in order to understand more thoroughly such variables as water composition, flow velocity, effects of heat transfer, etc., which greatly influence corrosion behavior of the 8001 alloy.

Temperature has a great deal to do with corrosion rate of aluminum in boiling water reactors, but it has been shown that temperature of the water is not necessarily the controlling factor. Consideration must be given to the actual metal temperature which may be 100-140 F greater than the reactor water in contact with it. This increase in temperature results in high corrosion rates that are not satisfactory for the application of aluminum to power reactors operating at Pathfinder conditions.

The effect of pH on inhibiting corrosion of aluminum in boiling water reactors is not thoroughly understood, although it has been demonstrated that a pH of 4.5 maintained with phosphoric acid produces a condition where low corrosion rates are experienced. Nevertheless, there are considerable operating problems involved in maintaining low pH in reactor water.

Further research and development is required before aluminum can be used as a fuel cladding material for power reactors operating above 600 psi. Considerably more information must be obtained before a realistic understanding of aluminum as fuel cladding material for boiling water reactors can be achieved. There are several problems which should receive further investigation in order to help enlarge the understanding of aluminum for these applications. Methods must

be investigated for inhibiting corrosion of aluminum in high temperature water; perhaps with the addition of phosphoric acid. Investigation of other adequate inhibitors should also be made. In the event that phosphoric acid is used to maintain low pH, some of the operating problems associated with increased activity and decomposition of water must be explored in order to satisfactorily use this method. Likewise, corrosion of other materials in the reactor subjected to low pH water must also be investigated.

The problems associated with aluminum corrosion resulting from high heat fluxes through the aluminum cladding of reactor fuel elements must be investigated more completely in order to obtain sufficient knowledge about the temperature drops through the corrosion product and deposition films on the fuel element surfaces.

Further investigation must be made into the strength of aluminum alloys operating at temperatures considerably higher than the water temperatures of their respective reactors. Problems related to fabrication must be explored in regard to corrosion resistance as well as the problems that might result in increased or varying velocities across the fuel elements themselves.

6.0 BIBLIOGRAPHY

1. R. L. Dillon and R. J. Lobsinger, Summary Report on Corrosion of Aluminum in High Temperature Water...
HW-59778
2. J. A. Ayres, Evaluation of Aluminum for use in Reactors Cooled by High Temperature Recirculating Water...HW-61757, Rev., Feb. 1960
3. C. R. Breden, Evaluation of Aluminum Alloys for Reactor Application...May, 1959
4. J. E. Draley, W. E. Ruther, Aqueous Corrosion of 2S Aluminum at Elevated Temperatures...ANL-5001, Feb. 1953
5. C. Groot, R. M. Peekema, The Corrosion of Aluminum and its Alloys...HW-36692, May, 1955
6. J. E. Draley, W. E. Ruther, Corrosion Resistant Aluminum above 200 C...ANL5430, July, 1955
7. R. L. Dillon, R. E. Wilson, V. H. Troutner, High Temperature Aqueous Corrosion of Commercial Aluminum Alloys...HW-37636, January, 1956
8. W. E. Ruther, Corrosion Experiments with 2S Aluminum at 200 C...ANL-5500, March, 1956
9. J. E. Draley, W. E. Ruther, Corrosion Resistance and Mechanical Properties of Aluminum Powder Products...ANL-5927, March, 1959
10. C. R. Breden, N. R. Grant, Summary of Corrosion Investigations on High Temperature Aluminum Alloys (Feb.1955-Oct.1957)...ANL-5546, February, 1960
11. C. Groot, R. E. Wilson, The Intergranular Corrosion of Aluminum in Superheated Steam...HW-51797, May, 1956
12. J. E. Draley, C. R. Breden, W. E. Ruther, N. R. Grant, High Temperature Aqueous Corrosion of Aluminum Alloys...April, 1958
13. R. L. Dillon, V. H. Troutner, Observations on the Mechanisms and Kinetics of Aqueous Aluminum Corrosion...HW-51849, September, 1957

14. V. H. Troutner, High Temperature Aqueous Corrosion Product Films on Aluminum...HW-53389, November, 1957
15. E. L. Martinec, Corrosion of an Aluminum Nickel Alloy in a Reactor Test Loop...ANL-5783, September, 1957
16. R. J. Lobsinger, R. L. Dillon; Corrosion of Aluminum in Deionized Water...HW-52008, Group Progress Report, April to September, 1957
17. I. Cohen, Corrosion of Experimental Aluminum Alloys in High Temperature Water...WAPD-PWR-PMM-1247, August, 1957
18. J. A. Ayres, R. L. Dillon, Corrosion of Aluminum in Dionized Water...HW-53963, December, 1957 - Progress Report September-December, 1957
19. G. J. Bieffer, P. G. Anderson, Corrosion Behavior of Aluminum-Nickel-Iron Alloys in High Temperature Water Under Dynamic Conditions...AECL-763, December, 1958
20. F. H. Krenz, Corrosion of Aluminum-Nickel Type Alloys in High Temperature Aqueous Service...CORROSION, Volume 13, No. 9, pages 575t-581t. AECL-492, September, 1957.
21. G. J. Bieffer, Effects of Alloying Additions and Temperature on the Corrosion of Aluminum-Nickel-Iron Alloys in High Temperature Water...AECL-691, July, 1958
22. R. L. Dillon, Dissolution of Aluminum Oxide as a Regulating Factor in Aqueous Aluminum Corrosion...HW-61089, Aug. 31, 1959
23. J. E. Draley, W. E. Ruther, Experiments in Corrosion Mechanism: Aluminum at High Temperatures...ANL-5658, Dec., 1956
24. Alan B. Riedinger, Corrosion Behavior of Aluminum Alloys in High Temperature Pressurized Water...KAPL Memo ABR-2, March 20, 1957

25. J. E. Draley, W. E. Ruther, Aqueous Corrosion of Aluminum, Part 2 - Methods of Protection Above 200 C ...CORROSION, Volume 12, No. 10, p. 480t, October, 1956
26. I. Cohen, Corrosion of Experimental Aluminum Alloys in High Temperature Water...Report No. 6, WAPD-PWR-PMM-582, October 4, 1956
27. J. A. Ayres, Corrosion of Aluminum in Deionized Water...HW-45623, Supplement to the Progress Report, July-October, 1956, Supplement 1
28. M. D. Ferrier, Minutes of a Conference on the Corrosion of Aluminum in Water at High Temperatures - Held at Chalk River, Ontario, December 18-19, 1956 ...CRMt-700, June, 1957
29. A. Russell, Technique of Aluminum Corrosion Measurement...HW-49631, March 4, 1957
30. R. L. Dillon, A Simple Graphical Method for Computing Corrosion Temperatures in Reactor... HW-55045, February, 1958