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Argonne National Laboratory

SUMMARY OF CORROSION INVESTIGATIONS OF HIGH-TEMPERATURE ALUMINUM ALLOYS

October 1957 to December 1959

by

Norbert R. Grant

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SUMMARY OF CORROSION INVESTIGATIONS OF
HIGH-TEMPERATURE ALUMINUM ALLOYS

October 1957 to December 1959

by

Norbert R. Grant

Reactor Engineering Division

September 1961

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SUMMARY OF CORROSION INVESTIGATIONS ON
HIGH-TEMPERATURE ALUMINUM ALLOYS -
OCTOBER, 1957 TO DECEMBER, 1959

by

Norbert R. Grant

I. INTRODUCTION

The development of an aluminum alloy that did not undergo catastrophic disintegration up to 360°C by Draley and Ruther⁽¹⁾ gave great promise of finding a low-cost cladding material of low neutron cross section. A wealth of early testing indicated that a few aluminum alloys could be used in reactors, but these tests were of short duration. Also, the corrosion rates measured, although not catastrophic, were too high to allow the use of the material for long-term fuel elements without further investigation.⁽²⁾ These facts pointed out the need for, first, long-term dynamic tests in high-purity water, and, second, similar tests with inhibitors to reduce the corrosion to the lowest possible level. Draley and Ruther⁽³⁾ have shown that an extremely good inhibitor is phosphoric acid. Thus, a series of long-term dynamic loop tests were run, both with high-purity water and phosphoric acid. The main alloy tested was aluminum X-8001, although a few other alloys were also tried.*

In conjunction with the dynamic tests, a surface boiling and several static autoclave experiments were made with the X-8001 alloy. To complete the program, two types of X-8001 clad fuel plates were tested in the ANL loop at MTR.

II. SUMMARY

Long-term dynamic tests have provided additional information on the corrosion rate of aluminum X-8001. In five tests, this rate varied from near zero to 15 mdd (mg/dm²/day). The most important factors affecting corrosion were water velocity, pH (including a water additive), temperature, and surface-area-to-water volume ratio. The effect of several of these was known previously, but some had not been thoroughly investigated. In general, for this series of tests, there was a benefit by

*See Appendix for alloy compositions. The designation of the 1% nickel alloy was changed by the Aluminum Corporation of America from M-388 [as used in a previous report⁽²⁾] to X-8001. The latter will be used throughout this report.

decreasing the pH from 7 to 5. This benefit was magnified greatly if phosphoric acid was used to decrease the pH. However, when the pH was extended to 4.5 with phosphoric acid, the corrosion, although extremely low, was no longer a uniform type of attack. The effect of increasing temperature was to increase the corrosion rate, as had been noted previously.

The effect of the ratio of corroding aluminum surface area to volume of circulating water was directly measured for the first time. The test at 260°C indicated that for the dynamic section of the loop the metal loss decreases as this ratio increases. This helps to explain the reason for higher corrosion results in tests such as the in-reactor test loop in MTR, where this ratio is quite low.

Other variables which have a lesser or negligible effect were also investigated. Surface boiling caused a higher corrosion, although the question of how much this is due to increased surface temperature is not known. Tests of in-reactor fuel plates also gave similar results, but also have the same question. Coupling effects are negligible unless the water quality becomes very poor.

III. LONG-TERM DYNAMIC TESTS

A series of five tests were run, each for a period of seven months. The main purpose of these runs was to determine if any unusual effects would occur due to the additional five months in test. In addition, it was hoped that a comparison could be made with the two-month tests run earlier. The alloy tested in all of the runs was aluminum X-8001.

Three dynamic loops were available for these tests, all having similar characteristics, as shown in Figure 1.

Fig. 1. General Flow Diagram for ANL Dynamic Corrosion Loops

Loops 1 and 3 are small loops equipped with Westinghouse Model 30-A canned rotor pumps and have a total circulating volume of 21.6 and 26.8 liters, respectively. Loop 2 is powered with a Model 100-A canned rotor pump which circulates a volume of 42 liters. Approximately 1% of the total flow passes through an ion exchange bed during normal operation with high-purity water. When a special pH is to be maintained, the flow through a bed will vary, depending on the water quality. The fresh water added for makeup during a test is negligible compared with the volume of a loop. Whenever a loop is shut down to remove samples, all of the water is removed and discarded. After the samples have been replaced in a loop, it is evacuated, then filled with freshly deionized, degassed, and deoxidized water.

The test conditions are listed in Table I. Water conductivity and pH were measured at room temperature. Control of pH was accomplished by varying the flow through an ion exchange column. In the cases in which no phosphoric acid was present, only a cation resin bed was used to lower the pH. In the case in which phosphoric acid was present, a mixed-bed resin containing H^+ -regenerated cation resin and $H_2PO_4^-$ -regenerated anion resin was used. In each of the tests the corrosion product, hydrogen, was allowed to remain in the loop, and, thus, the concentration gradually increased during each cycle. Table I indicates the range of maximum concentrations that the hydrogen reached in each cycle throughout the test. Since the largest area of new aluminum surface was available during the first cycle of each test, the highest hydrogen concentration also occurred in that cycle. The column entitled "Surface Area to Volume" indicates the total exposed aluminum area per unit volume of circulating water (including bypass system). Since the cross section of the holder and the flow of loop water determine the velocity of the water past the samples, each loop has its own sample holders. Loops 1 and 3 have holders to give nominal velocities of 5.5 and 2.1 meters/sec and Loop 2 to give 6.7 meters/sec. The semistatic section (called 0 meters/sec) is a large piece of pipe through which a low, continuous flow of primary water is maintained.

Table I

LOOP CONDITIONS FOR LONG-TERM TESTS

Test No.	Loop and Run No.	Temperature (°C)	pH Range	Resistivity Range (megohm-cm)	H ₃ PO ₄ Added	Range of Maximum H ₂ Concentration Reached per Cycle (cc/liter)	Surface Area to Volume, (cm ² /liter)	Range of Flow, (liter/min)	Velocities Tested (m/sec)
A	1-5	260	5.0-6.8	0.11-0.82	No	560-190	58.0	136-140	5.5, 2.1
B	3-6	260	7.0-7.2	1.61-2.87	No	920-265	51.0	106-121	5.5, 2.1
C	1-6	315	5.5-6.2	0.35-0.80	No	1000-290	58.0	117-136	5.5, 2.1
D	3-7	315	5.2-5.7	0.23-0.62	Yes	160-30	54.5	117-125	5.5, 2.1, 0
E	2-2	315	4.2-5.8 (avg. 4.8)	0.14-0.51	Yes	125-52	57.0	272-300	6.7, 0

Sample holders were fully loaded at the start of each test. During the seven-month run, each loop was shut down once a month for removal of exposed coupons and addition of new ones (Test E schedule varied from this procedure and will be discussed later.) The samples that were loaded into the loop at the start of the test will hereafter be referred to as original samples, and those added during the test in place of some removed for analysis will hereafter be referred to as replacement samples. In order to determine metal loss of the exposed coupons, either the boric acid or iodine-methanol method was used. New samples added to the holder had been cleaned in either caustic solution with acid rinse, or in a hot acid pickling bath.*

A. Test A (260°C, pH 5.0 to 6.8)

As was explained previously, control of pH was maintained by circulating the bypass water through a cation resin only. Thus, as aluminum ions enter the water, they are exchanged for hydrogen ions; with the excess of H^+ , the water is acidic. As the amount of corrosion decreases, it becomes more and more difficult to maintain a low pH and the value approaches that for neutrality. Although little difficulty was encountered in the previously reported two-month test at these conditions, the lowest pH value reached during the last two periods of this seven-month test was 6.0.

The appearance of the samples as removed from the loop after six months may be seen in Figure 2. Only the two sets of samples having 185 days are original samples; the rest are replacements.

Fig. 2. X-8001 Samples from Test A, pH 5-6, 260°C

*See Appendix for description of the cleaning procedures and methods of determining metal loss.

Although previously during a two-month test the oxide at these conditions was adherent, here there was a loose light grey film throughout the entire test. After oxide removal, the metal surface was not pitted, but instead had many tiny little bumps. These bumps almost covered the 123-day samples at both velocities used, but concentrations were slightly less on previous and later samples. The bumps appeared to have some type of protection, while the area around them corroded at a more rapid rate. The results of the test are indicated in Figure 3. As had been experienced in earlier tests, the corrosion rates and metal losses of the replacement samples were higher than for the original samples.

Fig. 3. Corrosion of Aluminum X-8001 Alloy in 260°C, pH 5 to 6 Water

B. Test B (260°C, pH 7)

For a number of reasons, the sample size was cut in half for this and all subsequent runs: (1) the iodine-methanol method of analysis had been accepted as being useful, and this limited the weight of each sample; (2) by doubling the number of samples loaded into the loop, it would be possible to remove four samples at each shutdown for each velocity, thereby increasing confidence in the data; and (3) more samples would be available from the limited quantity of material of the new alloys being produced. Since the surface area in the loop would not be altered, it was felt that the corrosion of the samples should not be affected.

The appearance of the samples as removed from the loop is shown in Figures 4 and 5. The original samples include the first three sets on the left of Figure 4, and the one set on the left of Figure 5. There was not

as much loose oxide as in Test A. The samples that were cleaned with boric acid often exhibited a very rough surface, including some of the bumps, as in the previous test. The bumps were most prominent on the 94-day samples, then appeared in decreasing quantities, and were completely absent on the 180-day and 212-day samples.

Days in Test:

153

153

153

29

59

92

123

55 m/sec

21 m/sec

Fig. 4. X-8001 Samples from Test B, pH 7, 260°C

Days in Test:

212

32

59

88

118

151

182

5.5 m/sec HOLDER

21 m/sec HOLDER

Fig. 5. Final Withdrawal of X-8001 Exposed in 260°C Water at pH 7

Figure 6 shows the final results of the test. This time the corrosion of original samples and that of the replacements was very similar. The actual metal loss was similar to that for the replacement samples of the previous run (Figure 3). For the first time the iodine-methanol method was used to determine metal loss. Half of the samples were analyzed with this method and the other half with the boric acid method. Although Figure 6 is a composite of all of the samples, the results of the two methods always checked within 10%, mostly within 5%.

Fig. 6. Corrosion of Aluminum X-8001 Alloy in 260°C Water at pH 7

C. Test C (315°C, pH 5 to 6)

This was an attempt to repeat Test A with the only change being an increase in temperature. The smaller samples were used, but the surface area was still the same as Test A. It was a little easier to maintain the lower pH than in the 260°C test, since an increased amount of corrosion caused more exchange of ions in the bypass system. There was practically no oxide on the low-velocity samples after the first month (Figure 7). After this time the oxide became more adherent, but on most samples there were areas that still had practically no oxide (Figures 8 and 9). The cleaned metal surface of the high-velocity samples began to show pitting after three months. With further testing, the pits acquired a groove-like appearance, accompanied by a very nonuniform type of corrosion. The lower velocity samples also began to show a similar appearance after six months.

Fig 7 X-8001 Samples from Test C, pH 5-6, 315°C, 30 Days

Fig 8 X-8001 Samples from Test C, pH 5-6, 315°C, 119 Days

Fig. 9. X-8001 Samples from Test C, pH 5-6, 315°C, Final

The final results are shown in Figure 10. This time the metal losses of the replacements were somewhat lower than for the original samples, but the corrosion rates were higher. It is interesting to note that, although the original samples corrode along a very smooth decreasing curve, the replacement samples follow a more linear rate.

Fig. 10. Corrosion of Aluminum Alloy X-8001 at 315°C, pH 5 to 6

D. Test D (315°C, pH 5.5 with H₃PO₄ Added)

This was the first long-term dynamic test with phosphoric acid to decrease the pH. The control of the pH was very good and seldom varied more than one or two tenths of a unit from the average value of 5.5. The oxide on the high-velocity samples started with a brown color which changed during the last two months of exposure to a reddish brown. The low-velocity samples had the same color initially, but this turned to a typical grey oxide (as seen in high-purity water at a much lower temperature) after three months. The semistatic samples were the typical grey color throughout the test.

Figure 11 shows the samples as removed at the end of the test. Only those tested for 211 days are original samples. The six-month and seven-month high-velocity samples showed small holes through the oxide that apparently were pits in the metal. The maximum depth of the pits was approximately 0.025 mm. Although no photographs were made of the pits on these samples, they were taken for Test E (pH 4.5).

Fig. 11. Dynamic Corrosion of Aluminum
X-8001 Alloy in 315°C Water at
pH 5.5 (H_3PO_4 Added)

Since a different type of oxide was formed in phosphoric acid, the boric acid method for analysis was ineffective for its removal. Thus, all samples for this and most subsequent tests were analyzed by the iodine-methanol method. The results of the test are shown on Figure 12. The metal loss and corrosion rates were significantly less than for Test C. Even the results for the replacement samples appeared to indicate equal or lower corrosion rates than the original samples, with the exception of the scatter of results for the 2.1-meter/sec samples. Except for the pitting, the results were very encouraging.

Fig. 12. Corrosion of Aluminum Alloy X-8001 at 315°C, pH 5.5 (H_3PO_4 Regenerated Resin)

E. Test E (315°C, pH 4.5 with H_3PO_4 Added)

There were several variations in this run from the previous tests: (1) the cycles were not uniform - samples were removed at the end of 2, 4, 7, 10, and 24 weeks; (2) several alloys were tested including X-8001, X-2219, and Alcoa alloys 192263, 192264, and 192265; and (3) the test was run in Loop No. 2, which has a sample holder that permits a velocity of 6.7 meter/sec instead of the 5.5 meter/sec tested previously.

The X-8001 alloy samples had a grey oxide throughout most of the test (Figure 13). All except 169-day samples are replacement samples. Pitting through the oxide was noticeable after four weeks and continued until the end of the test, at which time one of the high-velocity samples had an appearance as shown in Figure 14. A cross section through one of the largest pits is shown in Figure 15. The depth of the pit is approximately 0.09 mm. The etched surface indicates no attack at grain boundaries. The X-2219 alloy samples had a reddish-grey oxide on the high-velocity samples, and a typical grey on the semistatic ones.

Fig. 13. Dynamic Corrosion Test on Aluminum Alloys
315°C, pH 4.5 (Phosphoric Acid)

Fig 14 Sample of X-8001
Alloy, Test E,
6 7 m/sec, 169 days

The small white spots in Figure 13 for this alloy are not pits through the oxide, but are small flecks of a light grey oxide. For the other three alloys tested, the low nickel content alloy (No. 192263) had similar characteristics to the X-8001, including pitting. The other two alloys had mostly a typical grey oxide and showed no evidence of pitting through the oxide. One of the unfortunate aspects of using the iodine-methanol method for determining metal loss is that the metal surface cannot be inspected, as it can when using the boric acid method.

The results of the test are shown in Figures 16, 17, and 18. It may be noted that for X-8001 the corrosion of the original samples is drastically reduced from that in Tests C and D, whereas the rate for the high-velocity replacement samples is almost the same as Test C. The corrosion rates for X-2219 is almost the same as for X-8001. The results of the other three alloys are so scattered that it is almost impossible to determine a corrosion rate. A very important effect is that the increase in alloying has caused a marked decrease in the corrosion of the replacement samples.

F Effect of Loop 1 Tests on Pumps and Heaters

It had been believed that oxide dissolved by the water may tend to deposit on hot surfaces. In an attempt to verify this, the loop heaters were removed after Test C. Their appearance is shown in Figure 19. The scale was adherent until it had dried thoroughly, but then it fell off. A closer look at the scale (Figure 20) indicated a white spinel-type crystal over a dark grey flake oxide. The material was slightly magnetic, indicating the presence of some magnetite in the scale.

The pump was also removed from the loop, and similar deposits were located in the intake pipe of the pump (Figure 21) and on the pump impeller (Figure 22). The oxide on the outer portion of the impeller exhibited almost none of the spinel crystals and was highly magnetic, whereas that toward the center of the impeller had similar properties as that on the heaters (Figure 23). No heated surfaces were involved in regard to these areas of deposition.

As Polished

100X

Etchant - 10% Na OH

250X

Fig. 15. Cross-section of Pit Formed in Sample of X-8001 After Dynamic Corrosion Test for 169 Days at pH 4.5 Phosphoric Acid at 315°C, 6.7 m/sec

FIG 18
CORROSION OF SPECIAL ALUMINUM ALLOYS IN 315°C WATER AT pH 4.5
(H₃PO₄ ADDED)

Fig 19. Line Heaters as Removed from Loop No. 1

Fig. 20. Close View of Oxide Deposit on Heaters of Loop No. 1

Fig. 21. Close View of Pump Intake Pipe, Loop No. 1

Fig. 22. Loop No. 1 Pump Impeller -
21,000 hours of Operation

Fig. 23. Close View of Pump Impeller, Loop No. 1

Though no examination of the inside of the tubes in the regenerative heat exchanger or cooler was made, no tendency of these $\frac{1}{4}$ -in. tubes to plug was noticed. Examination of the top of the ion exchange resin at a later date indicated a small quantity of oxide had been filtered out at that point.

G. Summary of Long-term Testing

Although the results of the early tests were never repeated, some useful information was gained in these long-term tests. First, there is apparently no need to worry about the alloy suddenly entering a period of catastrophic attack, at least not for a minimum of seven months. The first two tests at 260°C indicated an improvement in corrosion resistance due to the presence of excess hydrogen ions in the water. The improvement might have even been greater if this excess could have been maintained throughout the entire test. Without phosphate ions in the water, the corrosion at 260°C leaves a fairly uniform metal surface, but at 315°C a definite roughening of the surface exists after seven months. The use of phosphoric acid at a pH of 5.5 decreases the corrosion rate by a factor of two and the metal loss (after seven months) by a factor of four (Table II). A slight pitting problem began toward the end of the test, and was even more serious at pH 4.5. It is unfortunate that although the low-pH test had a very desirable corrosion rate, the metal attack is no longer uniform. There has been no noticeable attack on the stainless steel components of the loops due to the use of phosphoric acid.

Table II

SUMMARY OF LONG-TERM DYNAMIC CORROSION TESTS ON X-8001 ALLOY

Test No	Temp, °C	pH	Corrosion Rate, mdd, at			Weight Loss at 215 Days, mg/cm ² , at		
			5 5 m/sec	2 1 m/sec	Static	5 5 m/sec	2 1 m/sec	Static
I	260	7	12 0	3 6	-	38 0	18 8	-
II	260	5 to 6	8 0	4 7	-	26 2	18 8	-
III	315	5 to 6	15 4	10 6	-	62 0	40 0	-
IV	315	5 5 (H ₃ PO ₄)	8 0	3 6	1 3	17 4	10 5	3 8
V	315	4 5 (H ₃ PO ₄)	1 5 [†]	-	0 7	5 4* [†]	-	2 4*

*169 days

[†]6 7 m/sec

IV. OTHER DYNAMIC TESTS

During the time the long-term tests were being run, four tests of shorter duration were made to investigate different alloys and to determine the effect of exposed surface area on corrosion. The test conditions are listed in Table III. Methods of maintaining pH, hydrogen volume, flow, and coupon removal and analysis were similar to those described in the previous section.

Table III
LOOP CONDITIONS FOR OTHER DYNAMIC TESTS

Test No	Loop and Run No	Temperature (°C)	pH Range	Resistivity Range (megohm-cm)	Additive	Range of Maximum H ₂ Concentration Reached per Cycle (cc/liter)	Surface Area to Volume (cm ² /liter)	Range of Flow (liter/min)	Velocities Tested (m/sec)
F	2-1	288	8.9-9.3	0.21-0.24	NH ₄ OH	210 to 136	41.5	228-318	5.5, 0
G	3-8	315	4.9-6.0	0.35-0.65	H ₃ PO ₄	1150 to 480	72.0	113-121	5.5, 2.1
H	1-8	315	6.6-6.9	1.98-2.80	None	900 to 320	75.8	102-121	5.5, 0
I	1-7	260	6.3-7.0	1.27-3.50	None	190 to 20	Varied	110-117	6.7, 0

A. Test F (288°C, pH 9 with NH₄OH Added)

This test was started as a part of a cooperative testing plan by ANL and three other laboratories interested in aluminum corrosion. This test and one in another laboratory were the only ones completed; however, the results from the latter were inconclusive because of pump trouble. It would have been preferable to run the test at 260°C in order to have a comparison with data presented previously in this report. However, the assignment for this laboratory was 288°C, pH 9, and if the overall plan had been followed, the results would have had more meaning.

The Aluminum Company of America Research Laboratory furnished two lots each of X-2219 and X-8001 alloys so that a comparison could be made for two separate melts of material in the same test. The loop was shut down for coupon removal after 7, 35, 63, and 84 days. As a result of this staggering of time, the replacement samples had exposures of 21, 49, and 77 days.

The appearance of the original dynamic samples was poor. Leading edges of the X-8001 were eroded, and there were some areas on the samples where there was relatively little oxide. On these areas, the metal surface was very rough, possibly due to erosion. Dynamic replacement samples had essentially the same appearance. The X-2219 coupons had very little oxide and were extremely pitted. The replacement samples were even worse in appearance. The X-8001 semistatic samples exhibited some pitting on edges, and the X-2219 samples were pitted on all surfaces (see Figure 24). The results with the X-8001 original samples indicated a corrosion rate not much higher than that at 260°C, pH 7, whereas the corrosion rate of the replacement sample was much closer to that of the original samples in Test A (see Figure 25).

Fig. 24. Aluminum Alloy Samples from Test F, pH 9, 288°C, Semistatic Section.

Fig. 25. Corrosion of Aluminum X-8001 Alloy in 288°C Water at pH 9

The results with X-2219 were very difficult to determine. The boric acid method would not remove the oxide, and a precipitate was formed when the iodine-methanol method was used. After some experimentation, it was found that the precipitate was soluble in ammonium hydroxide. Because of this extra difficulty, the confidence in the results is not as great as for those with X-8001 alloy. However, the rates did turn out to be low for the original X-2219 samples, and somewhat higher for the dynamic replacement samples (see Figure 26): The difference in corrosion between the two melts of the same alloy turned out to be negligible for both alloys.

B. Test G (315°C, pH 5.5 with H₃PO₄ Added)

It has always been desirable to have an alloy that has a better high-temperature strength than X-8001. This was one of the reasons for the interest in X-2219. It was known that aluminum alloys made by powder metallurgy procedures were stronger at elevated temperatures than the wrought material. There was some development done by Argonne and ALCOA on making an alloy with the same composition as X-8001 from powder material. In 1957, some of this material was purchased from ALCOA under the designation of M-457.

FIG. 26
CORROSION OF ALUMINUM X2219 ALLOY IN 288°C WATER AT pH 9

Since the results of Test D were so successful for the X-8001 alloy, it was decided to test the M-457 at the same conditions, that is, at 315°C in pH 5.5 water using phosphoric acid. Another alloy tested was 198X, a 1% nickel-0.1% titanium alloy of aluminum developed by the Metallurgy Division of Argonne. Coupons of X-8001 were added to give a comparison with Test D.

Unfortunately, the M-457 alloy did not work too well. After one month, six of the samples at all three velocities had blistered and/or split open (see Figures 27 and 28). Although the blistered samples were removed after each shutdown, this type of reaction continued throughout the remaining three months of the test. There was a sufficient number of apparently unaffected samples of M-457 to allow corrosion measurements to be made, but the results of the measurements indicated that most of these samples had suffered some type of accelerated attack.

In the meantime, some very good results were achieved with the X-8001 and 198X alloys being tested (see Figure 29). The corrosion of the X-8001 was even less than for Test D, and that for the 198X was practically negligible.

Fig. 27. Dynamic Corrosion Test of M-457 Aluminum 315°C 30 Days
pH 5.5 (Phosphoric Acid) (Loop No. 3, Run No. 8)

41A

41C

41L

42A

43A

Fig. 28 Some Selected Samples of 457 Alloy Tested at 315°C, pH 5.5 (H_3PO_4) for 30 Days

FIG. 29
CORROSION OF ALUMINUM ALLOYS IN 315°C WATER AT pH 5.5
(H_3PO_4 ADDED)

One very simple explanation for the improvement in the X-8001 corrosion rates is probably due to the fact that the high corrosion of the M-457 provided the equivalent of a large surface-area-to-volume ratio, thereby effectively inhibiting the corrosion of the X-8001 alloy and possibly the 198X alloy. (For a discussion on the surface-area-to-volume effect on corrosion, see Test I).

Although the results with M-457 were discouraging, it is believed that the fault lay, not in the alloy, but in the preparation. If the compacting of the powder during rolling was not sufficient to remove the void volume, pressurized water could enter these voids during a test and the corrosion product hydrogen or the aluminum oxide formed could cause swelling of the sample, and eventually cracking. During the operation of the test for the M-457 alloy, 55% of the 5.5-m/sec samples, 70% of the 2.1-m/sec samples, and 85% of the semistatic samples failed (original samples only). On a time basis for all velocities, 8% failed in the first month, 23% in the second, 30% in the third, and 7% in the last, for a total of 68%.

C. Test H (315°C, pH 7)

Samples of six aluminum alloys were given to Argonne by the Martin Company to be tested in a dynamic loop. The alloys were made from pure aluminum, and each contained 1% titanium plus various amounts of nickel from 0.5 to 5.0% (see Table IV). The samples, along with X-8001 aluminum, were tested in high-purity water at 315°C at velocities of 5.5 and approximately zero meters per second. The samples received from Martin Company were already machined to the dimensions required for the dynamic sample holder. Since only six samples were supplied for each alloy except ST-2, plans were made to remove one sample of each alloy at each velocity for three cycles. Duplicate samples of X-8001 and ST-2 were removed for four cycles.

Table IV

ALLOY COMPOSITIONS FOR TEST H

Alloy	Added Elements, wt-% (Balance Al)						No. of Samples Tested
	Ni	Ti	Si	Fe	Nb	Cu	
X-8001	1.0	-	0.16	0.5	-	0.17	30
ST-2	2.0	1.0	-	-	-	-	42
FL-17	0.5	1.0	0.3	-	0.5	-	6
BM-5	5.0	1.0	-	-	-	-	6
BM-6	4.0	1.0	-	-	-	-	6
BM-7	3.0	1.0	-	-	-	-	6
BM-8	4.0	1.0	0.2	-	-	-	6

All samples 50% cold worked.

Results of the test are shown on Table V. Almost all of the special samples lost less metal than the X-8001, but the rates varied. Representative rate curves are shown in Figure 30.

Almost every ST-2 sample had strings of tiny blisters, which is usually an indication of inclusions rolled into the material. Two of the replacement samples were corroded so severely (see Figure 31) that measurements of metal loss could not be made. One-half of the total number of FL-17 samples blistered, one severely. Two BM-5 and one BM-8 samples blistered slightly. All of the samples tested had a non-adherent oxide after the first month.

The only alloy that appears to be any better than X-8001 was the BM-5. However, it is questionable whether it would be worth adding 4% nickel to X-8001 to receive the slight increase in corrosion resistance.

Table V
RESULTS OF CORROSION TEST H
Original Samples

Alloy	Average Weight Loss, mg/cm ²								Weight Loss Rate, mdd		
	Velocity, m/sec: 5.5				0				5.5	0	
	Time, days:	31	60	88	118	31	60	88	118		
X-8001		19.2	31.6	38.8	43.6	3.3	4.3	5.6	7.1	21.2	3.8
ST-2		14.9	23.6	28.9	35.6	3.0	4.4	5.8	7.5	20.0	4.6
FL-17		-	26.4	-*	38.0	-	2.3	5.5	9.2	20.0	12.3
BM-5		-	21.5	25.4	29.3	-	3.9	5.4	7.6	12.7	6.3
BM-6		-	19.6	30.4	33.9	-	3.9	5.1	7.8	24.9	7.2
BM-7		-	22.3	27.2	37.6	-	3.9	5.3	7.2	26.4	7.2
BM-8		-	21.8	30.0	38.2	-	3.9	6.3	10.1	28.3	11.2

Replacement Samples

Alloy	Average Weight Loss, mg/cm ²						Weight Loss Rate, mdd	
	Velocity, m/sec: 5.5			0			5.5	0
	Time, days:	30	58	87	30	58	87	
X-8001		16.1	26.9	31.1	4.7	7.0	9.0	23.2
ST-2		10.2*	20.9	27.2	5.2	7.5*	7.6	28.0

*One sample in set severely blistered or corroded. No measurement of metal loss made on that sample.

FIG. 30
DYNAMIC CORROSION TEST ON MARTIN ALUMINUM ALLOYS 315°C, HIGH PURITY WATER

58 Days, Semistatic

30 Days, 5.5 m/sec

Fig. 31. Dynamic Corrosion Test at 315°C in High Purity Water
Martin ST-2 Aluminum Alloy

The blistering of some of the samples was probably due to poor rolling techniques, or allowing contamination of the metal prior to rolling. The two ST-2 samples that failed may have come from a section of the ingot that was low in alloying elements. Although nothing is known about the mechanical properties of these alloys, none of them appears to be sufficiently superior to X-8001 aluminum to warrant further investigation.

D. Test I (260°C, pH 7)

In an effort to determine more exactly what effect the surface area had on the previous tests at 260°C, a special test was made with this being the only variable. Buildup of hydrogen was limited to 200 cc/liter by venting during the tests when large sample surface areas were exposed.

A series of runs was made by placing a various number of samples in the loop, starting with only two samples (1.6 cm²/liter) in the dynamic holder, and ending with full dynamic and semistatic holders (101 cm²/liter). Each test was for 170 ± 2 hr and was started with fresh water. The results may be seen on Figure 32. The samples in the semistatic section obviously are not affected by the change in surface area, but those in the dynamic section are quite sensitive to the amount of corroding aluminum surface, especially at the lowest values of cm²/liter. Incidentally, this is the range in which the MTR tests (W6, W7, W9,⁽²⁾ W10, and W11) were run.

There was a marked difference in the appearance of the samples from one end of the surface area range to the other. At the conclusion of the first run, the two samples tested were covered by a light blue powder over a light grey flaking scale. Those samples that were

tested with a very high surface area present had an adherent medium to dark grey scale. In all previous tests at 260°C, the loose powder has been an indication of high corrosion, whereas the adherent scale was usually an indication of lower corrosion.

Fig. 32. Effect of Surface Area to Volume Ratio On The Corrosion of Aluminum Alloy X-8001 - One Week at 260°C in Distilled Water

V. EFFECT OF SURFACE BOILING ON CORROSION

In addition to obtaining information in dynamic test loops and static autoclaves, it was considered important to determine the corrosion of X-8001 alloy as a result of boiling on the surface of the metal. A test facility and the first test made were described in a previous report.⁽²⁾ Briefly, the pressure vessel was designed to operate at 20.4 atm and hold up to twenty-five samples. These samples consisted of 1500-watt bayonet-type, stainless steel heaters clad with the X-8001 alloy. Power to the heaters was controlled so that they could be operated at full, one-half, or one-quarter power levels, equivalent to heat throughputs of 6.7, 3.3, and 1.7 watts/cm². A small flow of water was passed through an ion-exchange resin bed by natural circulation to maintain the water quality desired.

A. Test at 215°C with H₃PO₄ Added to a pH of 3.5

The total time of the test was 304 days. Samples were withdrawn at regular intervals at each power level. Typical appearances of the sam-

ples are shown in Figure 33. A light area at top indicates the end of the hot portion of the heater, which suffered negligible corrosion. The actual color of the oxide was light green for the samples exposed for a short time, gradually getting darker to a dark green for these 10-month samples.

The cladding was carefully removed from each heater, the heater and clad were weighed, and the aluminum was dissolved by the iodine-methanol method. The oxide was weighed and actual metal loss determined. Because of problems of handling, the results from some samples were lost. The metal losses of the remainder of the samples were so slight that scatter is extreme (see Table VI and Figure 34).

◊ Fig. 33. Boiling Corrosion Test on X8001 Aluminum at 215°C 304 Days

Table VI

RESULTS OF BOILING CORROSION TEST IN H_3PO_4

Sample No.	Power (watts/cm ²)	Exposure Time, (days)	Weight Loss (mg/cm ²)
11	0 ↓	61	0.40
12		119	0.32
13		182	0.48
14		304	0.61
21	1.7 ↓	61	0.68
24		304	0.37
31	3.3 ↓	61	0.58
32		119	0.67
34		243	0.82
35		304	0.43
41	6.7 ↓	61	0.69
42		119	0.53
43		182	1.20
45		304	0.86

FIG. 34
RESULTS OF BOILING CORROSION TEST ON ALUMINUM X8001 AT 215°C, pH 3.5
(H_3PO_4 ADDED)

B. Effect on Stainless Steel Coupons

Since little was known about the effect of this solution of pH 3.5 on stainless steel, coupons of this material were placed in baskets suspended from the top flange of the vessel. Although the baskets were always below the water level, steam bubbles from the heaters were constantly passing

through and around the stainless steel specimens. Materials tested were Types 304, 347, and 405 stainless steels. Various mechanical and physical changes of the basic metal were made, and the actual test was conducted on the following:

1. Stock Type 304 stainless steel - rolled sheet;
2. Sensitized Type 304 stainless steel - heated to 680°C, held for one hour, furnace cooled; oxide layer machined off;
3. Bent Type 304 stainless steel - bend radius = 4 times thickness;
4. Bent Type 347 stainless steel - bend radius = 4 times thickness;
5. Type 304 stainless steel welded to Type 405 stainless steel with Type 308 stainless steel weld rod;
6. Type 405 stainless steel welded to Type 405 stainless steel with Type 308 stainless steel weld rod;
7. Type 304 stainless steel bolted to X-8001 aluminum with stainless steel bolt - one sample stainless steel and aluminum of same length, one sample with short piece of aluminum.

All of the samples (except coupled specimens) were removed and weighed during shutdowns. Since the oxide layer was rather thin, it was neglected, and the weight loss used as actual metal loss. The first four types had only small weight losses and thus small corrosion rates (see Figure 35). The Type 405 stainless steel, however, lost approximately ten times as much weight (see Figure 36).

FIG. 35
CORROSION OF TYPES 304 AND 347 STAINLESS STEEL AT 215°C, pH 3.5
(H_3PO_4 ADDED)

FIG. 36
CORROSION OF WELDED TYPES 304 AND 405 STAINLESS STEEL AT 215°C, pH 3.5
(H_3PO_4 ADDED)

The appearances of the samples varied for each type. Overall pictures are represented in Figures 37 and 38 for one- and ten-month exposures.

1. The stock Type 304 stainless steel obtained a dark green coating during the first month; this became slightly darker during the test. At the end of eight months, a slight microscopic pitting was noted.

2. The sensitized Type 304 stainless steel developed a thin multi-colored tarnish during the first month. This changed to a green color during the sixth month. Large microscopic pits appeared at the end of eight months, and cracks were evident at ten months. Figure 39 indicates two of the worst areas as magnified 100X.

3. The bent Type 304 stainless steel sample had the same oxide as sample type 1 above. No cracks were visible at 100X magnification around the stressed area. Microscopic pitting on the whole sample was similar to sample type 1.

4. The results of the bent Type 347 stainless steel sample was the same as 3 above.

Fig. 37. Static Corrosion Test on Stainless Steel at 215°C, 30 Days
Dilute Phosphoric Acid, pH 3.5

304 SS (Stock)

304 SS (Sensitized)

304 SS Welded to 405 SS
with 308 SS Rod 405 SS Welded to 405 SS
with 308 SS Rod 304 SS Coupled to
X-8001 Aluminum

Fig. 38. Static Corrosion Test on Stainless Steel at 215°C, 304 Days
Dilute Phosphoric Acid, pH 3.5

Before Corrosion Test

After Corrosion Test

After Corrosion Test

Fig. 39

Micrographs of Typical Areas of Sensitized Type 304 Stainless Steel Corrosion Tested for 304 Days at 216°C in pH 3.5 Phosphoric Acid (100X)

5. The sample of Type 304 stainless steel welded to Type 405 stainless steel had a similar oxide on the Type 304 stainless steel side as described previously; the Type 405 stainless steel side had a black coating throughout the test. Microscopic pitting became noticeable on the Type 304 stainless steel and weld area after eight months. Type 405 stainless steel was extremely corroded on sharp edges by the end of the test.

6. The sample of Type 405 stainless steel welded to Type 405 stainless steel exhibited the same corrosion indicated for Type 405 stainless steel in sample type 5.

7. The coupled samples of Type 304 stainless steel and X-8001 aluminum exhibited the same corrosion indicated previously for the sample type 1 (Type 304 stainless steel) and the zero power heaters (X-8001). No unusual attack was visible at contact areas between the materials.

C. Summary

The advantages for X-8001 aluminum in this medium are obvious when the results of this test are compared with that in high-purity water. Since no rate could be determined for this test, it was not possible to get definite reduction in corrosion rate. However, as compared to a 3.4-mdd rate for 6.7 watts/cm² in high-purity water, a reduction factor of 10 is apparently possible. Danger exists in use of a stainless steel system with the X-8001: the 400 series stainless steel is very poor, and care would have to be exercised in use of Type 304 stainless steel to make certain no sensitized areas exist. Type 347 stainless steel appears to be satisfactory; however, there were only two samples of this type, and the test is too preliminary to make a final evaluation.

VI. STATIC TESTS

A. Corrosion in Boric Acid and Polyborate Solutions

Interest was expressed in the use of sodium octaborate ($\text{Na}_2\text{B}_8\text{O}_{13} \cdot 4\text{H}_2\text{O}$) and boric acid as soluble poisons, both for emergency shutdown of a reactor and for control during operation. When this experiment was begun, the primary interest was its application to the ALPR (Argonne Low Power Reactor), and thus all of the tests were made at 215°C with X-8001 aluminum.

Two concentrations of the borates and control samples in high-purity water were used. The following concentrations were recommended by the ALPR physicists(4):

0.69 g boron/liter = 3.3 g octaborate/liter = 3.96 g boric acid/liter

0.41 g boron/liter = 1.9 g octaborate/liter = 2.28 g boric acid/liter.

The test was started with four samples in each solution. One of these original samples was withdrawn each month and replaced with a new sample, and the assembly placed into a fresh solution. Average pH and resistivity values during the experiment are shown in Table VII.

Table VII

WATER CONDITIONS FOR STATIC CORROSION TESTS
IN BORIC ACID AND POLYBORATE SOLUTIONS

Solution	Initial pH	Average Final pH	Initial Resistivity (ohm-cm)	Average Final Resistivity (ohm-cm)
High-purity water	7.0	7.2	3,200,000	190,000
1.9 g octaborate/liter	8.6	8.6	2,000	2,650
3.3 g octaborate/liter	8.6	8.6	1,200	1,700
High-purity water	7.0	6.6	6,000,000	50,000
2.28 g boric acid/liter	5.7	6.3	440,000	31,000
3.96 g boric acid/liter	5.5	6.0	330,000	38,000

After testing, the last original sample and the replacement samples tested in the 2.28 g boric acid/liter solution showed localized pitting near contact points with the stainless steel holder. Samples treated in the stronger boric acid solution showed no pitting. The octaborate samples for both concentrations had coatings that varied from a loose black powder to an adherent black tarnish (see Figure 40). Only the original samples showed pitting, but in this case it was on all surfaces. All of the samples treated in high-purity water had a good adherent grey scale, which is typical of this alloy at this temperature.

Fig. 40. Autoclave Testing of X-8001 Aluminum in Degassed Sodium Octaborate Solutions for 120 Days at 215°C

The samples autoclaved in the boric acid solution were treated by the boric acid stripping technique to determine weight loss. Because of the nature of the oxide upon the samples autoclaved in the octaborate solution, this method was not successful, and determinations were made by dissolving the aluminum in an iodine-methanol solution. The metal loss rates are shown in Figures 41 and 42. (Note: "Metal loss" scale increases by factor of 10 from Figures 41 to 42.) There is a definite increase in corrosion rate with the increased concentration of octaborate, due to an increase in pH and possibly the formation of a nonprotective oxide. The reason for the large increase of corrosion for the replacement samples over the original samples is not known, although this same effect has been seen during some dynamic tests on this alloy. The decrease in rate by the stronger boric acid solution is probably due to the decrease in pH. There is quite a bit of scatter for the replacement samples in boric acid solutions also, but they do not appear to cause a higher corrosion rate than the original samples.

FIG. 41
STATIC CORROSION TEST OF X8001 ALUMINUM IN BORIC ACID SOLUTION AT 215°C

FIG. 42
STATIC CORROSION TEST OF X8001 ALUMINUM IN SODIUM OCTABORATE AT 215°C

These results indicate that the use of sodium octaborate should be avoided in systems that contain alloy X-8001, and probably other aluminum alloys. Although no attempt was made to measure breakdown of the octaborate molecule at this temperature, this is indicated by the rise in resistivity of the solutions and the black appearance of the corroded specimens. The use of boric acid with X-8001 at 215°C appears quite satisfactory.

B. Corrosion in Dilute H₃PO₄ Solutions

In order to evaluate roughly the effect of phosphoric acid addition to water on X-8001 aluminum, a series of tests were conducted at 230, 260, 315, and 360°C and with solutions of pH 3.5, 4.5, and 7.0 (high-purity water). Two samples were tested at each condition. In order to keep the pH of the solution from going too far astray, the solutions were renewed at the end of 1, 3, 9, 28, 42, and 56 days. Even with this precaution, the pH values rose noticeably (see Table VIII). Weight gain measurements were made on the samples at some of these solution changes, and plots of these changes form smooth curves at the lower three temperatures (see Figure 43). At 360°C there appears to be a breakaway for the samples in the two phosphoric acid solutions. This is probably due to the fact that blistering developed on the samples and caused loss of the protective coating (see Figure 44).

Table VIII

RESULTS OF STATIC CORROSION TEST IN DILUTE H₃PO₄

Test Temperature, °C	pH		Weight Loss, mg/cm ²		Weight Loss Rate, mdd
	Initial	Final (Range)	28 days	71 days	
230	7.0	6.2-8.7	1.47	2.62	2.7
	4.5	5.1-6.1	1.49	1.56	0.2
	3.5	4.9-5.7	0.40	0.48	0.2
260	7.0	6.5-7.1	2.10	3.35	2.9
	4.5	5.8-6.4	2.35	3.54	2.7
	3.5	5.1-6.9	0.84	1.08	0.5
315	7.0	6.3-7.1	3.31	6.22	6.7
	4.5	6.1-7.1	2.78	4.85	4.7
	3.5	5.7-6.4	2.28	2.87	1.4
360	7.0	6.0-7.2	5.59	9.35	8.7
	4.5	5.9-7.0	4.03	9.66	12.7
	3.5	5.4-6.8	3.18	15.12	27.6

FIG. 43
CORROSION OF X8001 ALUMINUM IN DILUTE PHOSPHORIC ACID

One sample operating at each condition was removed at the end of 28 days, the rest were continued to a total of 71 days. Weight losses were determined by the iodine-methanol method and rate measurements made over the two points (see Table VIII).

No reliable conclusion is possible from the test because of the continuously changing phosphoric acid concentration and the small number of samples. Addition of the acid at 360°C appeared to have done more harm than good, whereas at the other temperatures the addition of phosphoric acid indicated a definite improvement in corrosion over high-purity water.

Fig. 44. Static Corrosion of X-8001 Alloy in Neutral Water and Dilute Phosphoric Acid for 71 Days

C. Corrosion of Bolted Couples in High-purity Water

Several tests were made to determine the coupling corrosion of X-8001 aluminum-Type 304 stainless steel. Coupons fastened with Type 304 stainless steel bolts and nuts were used in the first test with uncoupled coupons of each material included in each autoclave as controls. Test conditions were at 260, 315, and 360°C, in degassed and air-saturated, high-purity water. Samples were inspected monthly for 219 days.

Corrosion of the individual coupons and couples did not vary from tests previously made. Some fracturing of the scale on the aluminum occurred (see Figure 45), and later in the test some blistering was noted on the coupons at 360°C. However, no unusual attack was noticeable on the aluminum around the nut or next to the stainless steel.

Fig. 45. Autoclave Testing of X-8001 Aluminum-304 Stainless Steel Bolted Couples and Individual Samples After 60 Days

D. Corrosion of Riveted Couples

1. Corrosion in High-purity Water

A riveted couple has been used in the EBWR dummy elements (see Section VII). The couples are made of the same materials as used in the above test, but are fastened with a stainless steel rivet. A test was made at 288°C in degassed and air-saturated water for 257 days, and samples were inspected monthly. A new variable tested here was the effect of having different sizes of samples coupled together, that is, a short piece of stainless steel with a long piece of aluminum, and the reverse. Figure 46 shows these samples after 257 days of exposure. No unusual corrosion was noted except for the sample with long stainless steel and short aluminum in air-saturated water. Here, severe attack took place on the aluminum around the rivet and at the edges. Several notches were actually eaten into the aluminum for a depth of approximately one to two millimeters. Of all the possible combinations tested, galvanic attack was noticeable only in this one case, i.e., small aluminum area exposed and low-resistivity water.

2. Corrosion in Phosphoric Acid Solutions

At approximately the same time, another coupling test was started with similarly fastened short pieces of the same materials. The conditions for this test were room temperature, pH 3.5 phosphoric acid solution, and 288°C, pH 3.5 and 4.5 phosphoric acid solutions. Samples were inspected monthly during the 212-day test. The sample tested at room temperature indicated little corrosion except for some small white spots of oxide on the aluminum adjacent to the stainless steel coupon. The sample exposed to 288°C water at pH 4.5 exhibited pitting over the entire aluminum surface, as experienced previously in a dynamic test (Section III-E). No unusual pitting occurred around the rivet (see Figure 47). The sample at pH 3.5 was just the opposite in its behavior in that no pitting occurred on the coupon in general, while a large quantity did occur around the rivet (see Figure 48). This apparently was due to galvanic attack.

E. Corrosion of ALPR Fuel Plate Coupons

During fabrication of the ALPR fuel plates, a coupon was cut from the end of each plate for corrosion testing.⁽⁵⁾ These coupons contained no fuel but consisted of three layers of the X-8001 aluminum alloy clad material bonded during the manufacturing process. A total of 798 coupons was obtained.

Fig. 46. Autoclave Test of X-8001 Aluminum-304 Stainless Steel Couple in 288°C Water 258 Days (A 4647)

Fig. 47. X-8001 Aluminum and 304 Stainless Steel Riveted Couple
212 Days at 288°C in H_3PO_4 at pH 4.5

14X

Fig. 48. X-8001 Aluminum and 304 Stainless Steel Riveted Couple
212 Days at 288°C in H_3PO_4 at pH 3.5

14X

Before the corrosion test was started, the coupons were cleaned in acetone and every twentieth one was weighed to provide a basis for metal-loss information. The corrosion test was carried out at 288°C in a large autoclave with distilled, deionized water. (Although the reactor operates at a bulk water temperature of 215°C, the corrosion test was made at 288°C to accelerate the corrosion of the coupons.) The manner in which coupons were added and removed from the test is indicated in Table IX.

Table IX
CORROSION TESTING OF ALPR COUPONS

Period, Days	Total Days	Coupons Removed	Coupons Blistered (of those removed)	% Blistered	Total Coupons in Test	Comments
0	0	0	0	0		Start with 466 coupons
7.0	7.0	0	0	0	466	
7.0	14.0	110	0	0	466	Add 136 coupons
14.2	28.2	21	0	0	492	
14.0	42.2	25	1	4	471	
14.5	56.7	25	1	4	446	
14.0	70.7	22	0	0	421	
15.3	86.0	22	2	9	399	
15.2	101.2	75	14	19	377	Add 196 coupons
13.1	114.3	25	0	0	498	
13.0	127.3	25	4	16	473	
14.0	141.3	25	6	24	448	
14.0	155.3	423	82	19	423	
		798	110	14		

Small blisters began forming near the edges of a few of the samples almost at once. The percentage that blistered increased for awhile, and then apparently leveled off near the end of the test. It is believed that the blistering was caused by an incomplete bond between layers of metal near the edge

of the fuel plate when it is manufactured or by a high silicon content at the edge causing poor corrosion resistance. Since this material was removed from the plate before it was placed in an assembly, these results are not necessarily an indication that the plates in the reactor were blistered. At the end of the 169 days, the remaining weighed coupons were separated from the unweighed ones. The remaining weighed coupons were continued in test at 288°C in a small autoclave, with some removed periodically for examination.

After 291 days of testing had been completed, thirty-nine weighed coupons were stripped of oxide by the boric acid technique and determinations of metal loss were made. The resultant curve, which appears to have a parabolic form, is illustrated in Figure 49. The indicated tangent to the curve has a corrosion rate of 1.9 mdd, which is slightly lower than that experienced previously for X-8001 aluminum under similar conditions. Approximately 35% of all the weighed coupons were blistered; of those subjected to test for less than 169 days, 16% were blistered, and of those for more than 169 days, 47% were blistered.

FIG. 49
CORROSION OF ALPR FUEL PLATE COUPONS AT 288°C

The surface-area-to-water volume ratio during the first 169 days ranged from 33 to 26 cm²/liter, and for the remainder of the test from 1460 down to 254 cm²/liter, because of the use of a much smaller autoclave.

The results of the test indicate that the lot of X-8001 aluminum used for the fuel plate cladding had good corrosion resistance. Although the bond near the outer edge of the coupons was not too good, this is not necessarily an indication that the fuel plates were not bonded at the edges, or that they were blistered.

VII. IN-REACTOR TESTS

A. EBWR Dummy Fuel Elements

Dummy elements were used to fill the outer row of the EBWR core during the first two years of operation.⁽⁶⁾ These dummies consisted of X-8001 aluminum formed into a square tube, with top and bottom adapter fittings made of Type 304 stainless steel. The fittings were fastened to the aluminum with stainless steel rivets. Design was such that the water inside the tube was almost stagnant. There was a maximum of thirty-four of these dummy elements in the core. This was equivalent to approximately 38 cm²/liter of core water. Reactor bulk water temperature was 252°C.

Two of these dummies were removed after approximately six months of operation. Examination in a cave indicated a loose red-brown oxide on the outside of the tube, and a typical adherent light grey oxide on the inside. Spectrographic analysis of the oxides showed three times the nickel content on the inside as compared to the outside, and three times as much iron on the outside.

Samples cut from the tube were descaled by the boric acid method. Interpolation of micrometer measurements indicated a scale thickness of 0.025 mm. The metal surface exhibited no unusual corrosion. Pitting was slight, the largest pit being approximately 0.3 mm in diameter and 0.01 mm deep.

Examination of the area around the rivets showed a serious galvanic attack on the aluminum (see Figures 50 and 51)

One year later (approximately six months of EBWR power operation), two more dummy elements were removed and examined. There was more loose oxide than previously observed on the outside surfaces, and the scale on the inside surfaces was a darker grey. Microscopic examination of three specimens indicated that approximately 0.076 mm had corroded from each side of the aluminum. The largest pit found was approximately 0.5 mm in diameter and 0.05 mm deep. No other significant changes were noted from the first set examined.⁽⁷⁾

B. Coupons Tested in CP-5 with H₃PO₄

In order to study the in-reactor corrosion of three aluminum alloys in phosphoric acid, a test was conducted in a vertical irradiation facility in CP-5. The alloys tested were X-8001, M-400, and X-2219. The solution used had an initial pH of 3.0 and the average temperature of the tests was 260°C.

FRONT - 4X

FRONT - 2X

BACK - 2X

Fig. 50. EBWR Dummy Assembly from
Core Position D13

BACK - 4X

BACK - 2X

FRONT - 2X

Fig. 51. EBWR Dummy Assembly from
Core Position K2.

A special holder was designed that would hold nine samples and could be easily disassembled by remote operation. Three samples of each alloy were placed into a holder and loaded into an autoclave (see Figure 52).

Fig. 52. Sample Holder for Aluminum Corrosion Test in CP-5

The autoclaves were filled with the pH 3.0 phosphoric acid solution and sealed shortly before being loaded into the reactor. Maximum thermal neutron flux in the reactor was 2×10^{13} nvt at 2-Mw operation. Upon completion of the test, the autoclave was opened in a cave. The samples were removed and their weight losses were determined by the iodine-methanol method (see Table X).

Table X

RESULTS OF CP-5 IN-PILE TEST OF ALUMINUM ALLOYS

Run No.	Avg Temp (°C)	Total Thermal Neutron Exposure (nvt)	Days at Temp	Alloy	Metal Loss (mg/cm ²)
26	246	3.88×10^{19}	22	X-8001	1.51, 1.75
27	260	7.45×10^{19}	43	X-8001	- -
				M-400	1.37, 1.25, 1.58
				X-2219	1.38, 1.95, 0.81
30	274	12.6×10^{19}	73	X-8001	3.16, 3.09, 3.48
				M-400	5.32, 4.76
				X-2219	5.62, 5.52

Two major problems were encountered during the procedure. During Run No. 26 a small leak developed and about half of the liquid was lost. Thus, during this run only the X-8001 samples were completely covered with solution for the entire in-reactor time (see Figure 53A). During dissolution of some of the samples in the alcohol solution, an organic precipitate formed on the oxide. Since the weight of the oxide must be known accurately for weight-loss determination, the results for these samples had to be discarded. The X-2219 samples from Run No. 30 were pitted (see Figure 53B). Similar appearances have been noted for this alloy at 260°C in high-purity water. The pH of the remaining solution was approximately 6.3 for each test.

A rough estimate of corrosion rates indicates 2.8 mdd for the X-8001, 11.8 mdd for the M-400, and 13.1 mdd for the X-2219. The rate for X-8001 compares roughly with that in the out-of-reactor test (Section VI-B). As in the earlier test, the results were very inconclusive because the small number of samples and the variation of pH (phosphoric acid content) with time. There is no indication that the corrosion of in-reactor samples was any worse than that of out-of-reactor samples in similar phosphoric acid solutions.

C. MTR-W-10 Test on a BORAX-IV-type Fuel Plate

Two types of small fuel plates were manufactured and tested in the ANL-2 loop in the MTR to determine their in-reactor corrosion characteristics. The first of these was a BORAX-IV-type plate. The complete results and description of the test loop have been described previously.⁽⁸⁾ A schematic drawing of the test loop is shown in Figure 54.

Four fuel elements were manufactured by the ANL Metallurgy Division for this test. BORAX-IV-sized, X-8001 aluminum tube plate extrusions were cut down to four rows of tubes. The plates were sealed at one end and loaded with thorium-uranium pellets (93.4 wt-% ThO_2 and 6.54 wt-% U_3O_8 , 93% enriched). (These were excess from the reactor loading.) The pellets were bonded to the tubes with lead, an aluminum plug placed in the top, and the top end of the tubes were sealed. The finished plates were 40.6 cm long and 5.17 cm high (see Figure 55). These miniature plates were manufactured essentially in the same manner as those manufactured for BORAX-IV.

Two plates were selected for this test - one each for the in-reactor and the out-of-reactor sections of the loop. Careful physical measurements of the plates were made. They were cleaned with acetone and loaded into cartridges designed for this test (see Figure 56).

Calculations were made to determine the temperature and pressure at which local boiling could be achieved on a portion of the plate. Based on the results, the loop operating conditions were set at 40.7 atm and 241°C (bulk water temperature). The plates were put into the loop and remained there for seven MTR cycles (see Table XI). (Each cycle is of three weeks duration which includes one to five days for refueling.)

A. Run No. 26

X-8001 ↑

X-2219 ↑

M-400 ↑

B. Run No. 30

Fig. 53. In-pile Corrosion of Aluminum Alloys

Fig. 54. Schematic Drawing of ANL-2 Loop in MTR

Fig. 55. BORAX-IV Prototype Fuel Plate
(Dimensions in cm)

Fig. 56. Holding Cartridge with W-10 Fuel Plate (Dimensions in cm).

Table XI

OPERATING CONDITIONS FOR MTR-W-10

Total Exposure	122 days, 2365 Mwd
Temperature	90.6% between 238°C to 243°C during irradiation
Flow	227 liters/min, equivalent to 3.4 to 4.0 meters/sec at sample
Surface-area-to-volume Ratio	6.4 cm ² aluminum/liter circulating water
Water Resistivity	1.4 to 3.5 megohms
Water pH	5.9 to 7.6 (average 6.5)

After the irradiation period, the plate was pulled out of the flux zone for three cycles to cool. It was then removed from the loop and shipped to Argonne, Illinois, for examination.

Both the in- and out-of-reactor plates were removed from their cartridges and examined. Physical measurements were made in the as-removed condition, and again after the oxide was removed by the boric acid technique. The stripping of the in-reactor plate was accomplished quite successfully by remote control in a cave. After obtaining all possible data on the whole plates, they were opened by removing the clad for examination of the thoria-urania pellets.

The appearance of the in-reactor plate in its three stages is shown in Figure 57. The red color of the oxide indicated that boiling occurred from the start of the fuel for a distance of about 5 in. on the plate. Chemical analysis of the fuel confirmed this observation. The out-of-reactor plate in the as-removed condition is shown in Figure 58.

The metal losses for the plates were 15.9 mg/cm² for the in-reactor and 8.57 mg/cm² for the out-of-reactor. Extrapolated over 74 days above 218°C, this gives rates of 21.5 mdd for the in-reactor tests, and 11.6 mdd for the out-of-reactor test. The metal loss of the in-reactor plate given above is an average value for the entire sample. The oxide thickness varied from 0.13 mm at the boiling section to 0.045 mm. Chemical analysis of the fuel indicated a burnup of 1.03 to 0.1% (average 0.41% of total metal atoms) and a heat flux of 157 to 15.6 watts/cm² (average 61.7 watts/cm²) along the length of the in-reactor plate. The appearance of the thoria-urania pellets indicated some cracking but was uniform for both plates.

After removal of the oxide, the aluminum surface had a rough appearance where boiling took place. Temperature drop through the scale caused the temperature inside the tube to exceed the melting point of lead in this area.

Fig. 57. BORAX-IV Prototype Fuel Plate Before And After Irradiation

Fig. 58. BORAX-IV Prototype Fuel Plate Tested in Out-of-Reactor Section

This allowed the tubes to collapse slightly in some unsupported places, such as at the crack between two fuel pellets. Although this is not considered serious, it could be detected by microscopic examination. The plate was pitted slightly between the boiling and the nonboiling areas. The nonboiling section and the out-of-reactor plate had a relatively smooth surface comparable to that observed in loop tests under similar conditions.

The corrosion of the in-reactor plate was not significantly different from that of coupons tested in the same loop.⁽²⁾ The coupons had a rate of 31.7 mdd after 95 days at 243°C to 249°C at 4.9-meter/sec flow. The water quality and surface-area-to-water volume ratio were approximately the same for both tests.

D. MTR-W-11 Test on an ALPR-type Fuel Plate

The second of the MTR loop tests of this series was made on a miniature ALPR fuel plate. A complete description of the test has been published.⁽⁹⁾ Six plates were manufactured by the ANL Metallurgy Division, using the picture frame type of construction and following the same procedure used for the ALPR core.⁽⁵⁾ The core was an alloy of 80.5% 1100 aluminum, 17.5% uranium (93% enriched), and 2% nickel. The clad was X-8001 aluminum. The dimensions of each plate are shown in Figure 59. In order to achieve a satisfactory bond between the core and clad, a very thin coating of elemental silicon was used as a bonding agent. The bond integrity was checked by annealing at 550°C for one hour and examination by means of ultrasonic transmission.

Calculations had indicated that to achieve local boiling over a section of the plate and operate at a bulk water temperature of 215°C, a pressure of 25.8 atm would be required to allow for a margin of safety against burn-out. It was further approximated that operation for 13 cycles would allow a maximum burnup of 2% of the total core atoms. Two of the six plates were chosen for this test, cleaned with acetone, and loaded into the same cartridges used in the W-10 test. This had to be done by remote operation for the in-reactor cartridge. Both cartridges were shipped to Idaho and tested in the ANL-2 loop in the MTR for 11 reactor cycles (see Table XII).

During the eleventh cycle, a water sample was removed from the loop to measure pH and resistivity (both continuous monitors had broken down a week before). The water sample emitted 1.0 r/hr of beta-gamma radiation. A close inspection of the loop water activity monitor indicated a gradual rise in activity, starting two to three days before this sample was taken. After a Cs¹³⁸ analysis verified a rupture of the plate, it was withdrawn from the flux zone in the loop and allowed to cool. At no time during or after this incident did the activity in the loop water become high enough to scram the reactor or in any way interfere with the operation of MTR.

There were several prior incidents which may have contributed to the rupture of the plate. Bypass flow of the loop water through a sulfite (for oxygen removal) and mixed ion exchange resin beds was switched to the spare set during the previous scheduled shutdown. After this change, it was found that the pH still could not be maintained at 7, but rose to a value of 9. The resistivity dropped to 50,000 ohm-cm. Then the pressure drop across the in-reactor tube rose from 0.54 to 1.1 atm in 6 hr. Since this had happened previously, it was not considered too important. The conditions returned nearly to normal before reactor startup two days later. It was five days after startup that the plate rupture was noticed.

Fig. 59. ALPR Type Fuel Plate (Dimensions in cm.)

Table XII

OPERATING CONDITIONS FOR MTR-W-11

Total Exposure	227 days, 6293 Mwd
Temperature	91.2% between 213°C-218°C during irradiation; 93.7% above 204°C during irradiation
Flow	227 liters/min, equivalent to 3.4 to 4.0 meters/sec at sample
Surface-area-to-volume Ratio	5.8 cm ² aluminum/liter circulating water
Water Resistivity	0.8 to 3.4 meg-ohm-cm
Water pH	6.7 to 7.6 (average 7.1)
Hydrogen Dissolved in Water	11 to 31 cc/liter (average 23 cc/liter)

After two weeks of cooling, the fuel plates were removed from the loop and shipped to Argonne, Illinois, for examination. The plates were removed from the cartridges, photographed, and physical measurements were taken (see Figures 60 and 61). A typical view of the high-flux portion of the plate is shown in Figure 62. The area containing the rupture was cut from the plate. The remainders of the in-reactor plate and the out-of-reactor plate were stripped of oxide using the boric acid method.

Two blisters, approximately 0.63 cm in diameter, were evident on one side of the plate. One had visibly broken open (Figure 63), and the other appeared to be closed. After mounting, photographic inspection showed that the latter had small holes through the metal (see Figures 64 and 65). Corrosion in the blisters had proceeded between the meat and the clad. At the area of highest heat flux, the plate was swollen slightly, and micrographic examination revealed gas pockets in the core but no corrosion (Figure 66). The swelling was probably caused by a combination of high fuel temperature (estimated at 540°C) and a U²³⁵ burnup of approximately 50% in this area. The burnup just out of the swollen zone was approximately 40%. Visual examination of the metal surface of the plate revealed a very rough surface over the area of local boiling and a relatively smooth surface on the rest of the plate (similar to the surface of the out-of-reactor plate). No other evidence of failure of the bond was noted.

Since the in-reactor plate was sectioned before a weight measurement (after stripping) could be taken, the corrosion was determined by the change in thickness measured at several locations. The in-reactor plate had an average metal loss of 0.16 mm and the out-of-reactor plate had a metal loss of 0.13 mm. This is roughly equal to a corrosion rate of 28.5 mmd for the in-reactor plate.

Fig. 60. Irradiated W-11 Plate as Removed from Reactor

Fig. 61. Out-of-Reactor Plate as Removed from Loop

Fig. 62.

Typical View of High-Flux Region (4X)

Fig. 63.

Opened Blister (4X)

Fig. 64. Polished Section Through Ruptured Blister (13X)

Fig. 65. Polished Section Through Unruptured Blister (13X)

9X

(25X)

Fig. 66. Polished Section of Swollen Area

Burnup analyses made on 0.32-cm punchings from the in-reactor plate indicated a range from 58% of total U^{235} core atoms (1.1 cm from high flux end) to 7.5% (30.8 cm from high flux end). The maximum heat flux developed by the plate was from 218 watts/cm² at the start of the test to 82.5 watts/cm² at the end of the test. The heat flux at the rupture was approximately 50.5 watts/cm² at the end of the test.

The corrosion of the in-reactor plate was somewhat higher than for the W-10 test. There are two factors that could contribute to this increase. The first is the operation of the plate at high pH level. By control testing of a similar plate at Argonne in one of the corrosion loops, it is estimated that operation at pH 9 for a similar length of time (as incurred by the W-11 plate) could cause additional corrosion of 0.025 to 0.050 mm.

The second factor concerns the metal temperature of the plate in the high-flux section. Estimates of the surface temperature, based on measurements of thermal conductivity of the scale from this plate, indicated attained temperatures up to 315°C. This temperature would exist locally for a short period of time, since the pressure exerted on the scale would soon force it from the plate. However, repeated formation and sloughing of scale in this manner would cause a much higher rate of corrosion. Another indication of the high temperature at the plate surface was determined by X-ray diffraction of the scale. The scale from the high-flux (boiling) region of the plate contained approximately 50% corundum, while that out of the boiling region contained very little. One other contributing factor was the very high corrosion in the failed section after the clad had been penetrated. The inside of the metal was probably attacked by superheated steam, to which X-8001 has very poor resistance. Figure 64 gives some evidence of this accelerated attack on the inside of the clad. The influence of this factor is not evident in the results of this test, since corrosion was not measured by weight loss.

Prior to initiating this test of a miniature ALPR fuel plate, it had been calculated that the heat flux would exceed that predicted for ALPR. Rather than try to reduce the heat flux of the W-11 plate to the ALPR level (average 68 watts/cm²),⁽¹⁰⁾ it was decided to see whether this much higher flux would be harmful. Although the results are obvious, it would be expected that the ALPR could operate far beyond the effective core life before any problems experienced in this test would be encountered.

Once again, the corrosion for both the W-10 and W-11 tests is higher than that for the loop tests at Argonne because of the low ratio of surface area to circulating water volume in the MTR loop.

One important result of the W-11 test was that, although the element operated for about two days after failure, the amounts of uranium and fission products in the loop were not sufficient to raise the loop activity above the alarm point, nor caused a permanent high level contamination of the loop.⁽¹¹⁾

VIII. DISCUSSION

The question of the conditions under which X-8001 aluminum can be used for cladding fuel plates in a boiling or pressurized water reactor still has not been completely answered. Some of the results discussed in this report have helped to reveal a few of the conditions. The use of phosphoric acid down to a pH of 5.5 yields a substantial advantage. This permits metal temperatures as high as 315°C if other factors, such as water velocity, clad thickness, and core life, do not interfere. If the pH is lowered to 4.5, non-uniform attack presents a problem, and if lowered to 3.5 galvanic attack may occur. In the latter case, use of stainless steel alloys subject to sensitization would be limited. Future investigation at a pH of 5.0 would be advantageous in order to determine the lowest pH value for good corrosion resistance without pitting.

In high-purity water the corrosion of X-8001 aluminum at 315°C appears to be excessive and therefore the alloy is suitable only for short-term use. Even then there will be a great deal of spalling of oxide. At 260°C there is some loss of oxide at the highest velocity tested; however, the corrosion at this lower temperature is not as severe. One of the problems with this material is the loss of corrosion product to the system, whether it settles in the primary vessel or is carried out to the purification system or other components. With an all aluminum-clad core and control rods, deposition of aluminum oxide would probably not be a problem. However, mixing an aluminum core with stainless steel or Zircaloy cladding will cause higher scale thicknesses on the latter two than would be expected. In addition, EBWR experience has indicated that control rod drives located in the bottom of the primary vessel will require continuous flushing to keep activity levels and problems with sticking to a minimum.⁽¹³⁾

APPENDIX

A. Alloy Compositions (from ALCOA Analyses)

Alloy	Composition, wt-%									
	Ni	Cu	Fe	Si	Mn	Zn	Zr	V	Cr	Ti
X-8001	0.98	0.17	0.49	0.17	-	0.04	-	-	-	-
X-2219	-	6.07	0.16	0.08	0.31	-	0.16	0.08	-	-
192263*	1.38	0.03	1.44	0.08	0.06	0.02	-	-	0.02	0.02
192264*	2.64	0.02	0.34	0.10	0.05	0.02	-	-	0.35	0.02
192265*	4.34	0.076	0.38	0.08	0.05	0.02	-	-	0.02	0.03
M-457*†	0.99	0.20	0.56	0.11	0.00	0.00	-	-	0.01	-
198X††	1.00	-	-	0.001	-	-	-	-	-	0.10
M-400	0.98	0.00	0.99	0.07	0.01	-	0.00	0.01	-	-

*One melt

†0.50% oxide

††Made at ANL from pure aluminum base metal; nominal composition

B. Initial Cleaning Operations1. Caustic Method

The caustic method consisted of immersing the sample into: (1) a 10 wt-% NaOH bath for one minute; (2) a 10 vol-% HNO₃ bath for 2 min; (3) a rinse with distilled, deionized water; and (4) a rinse with acetone or ethanol. All solutions were at room temperature. This method was almost always used for X-8001 alloy samples as it removes all types of grease, chips, and burrs remaining on the samples. The method was also satisfactory for M-400 aluminum alloy samples, but not for high copper alloys, such as X-2219. The latter were thoroughly cleaned with acetone only.

2. Acid Etch Method

In the acid etch method, the sample was dipped for 20 sec into a solution of 50 cc HNO₃ (stock 70% acid), and 5 cc HF (stock 48% acid) diluted to 1 liter. The solution was kept at a constant temperature of 95°C. The sample was then placed in a 70% HNO₃ solution at room temperature for 5 to 10 min, after which the sample was rinsed with distilled, deionized water, then acetone. This method was useful for all types of aluminum alloys and exhibited no effect on corrosion results. This method

was used for only two tests (Test E and Test F). Its use was discontinued because of the difficulties and hazards involved in working with a hot HF solution.

C. Metal-loss Determinations

1. Boric Acid Method

The boric acid method was explained fully in a previous report.⁽²⁾ Briefly, the method requires the sample to be immersed in a saturated boric acid solution. An alternating current of 0.02 amp/sq cm of sample surface is passed between the sample and a platinum electrode for 30 to 60 sec. The samples are brushed in water to free the remaining heavy oxide. To complete the oxide removal, the sample is placed in a chromic-phosphoric acid bath at 85°C to 95°C for one hour. During this time, a 200-ma direct current is passed between the sample and a platinum anode.

2. Iodine-Methanol Method

This is a slight variation of a method found in the literature.⁽¹²⁾ The solution consists of 10 gm iodine per 100 ml CP methyl alcohol. At least 20 ml of solution/gm of aluminum is required for complete dissolution. The iodine acts as the catalyst for the aluminum-alcohol reaction. Temperature control is very important, and the dissolution proceeds best at 50°C $\pm$ 5°C. A higher temperature causes too rapid an evolution of hydrogen, and lower temperature results in very slow dissolution. The end of the dissolution can be noted by stoppage of the hydrogen evolution.

Loop samples were 4.95 cm high by 2.42 cm wide by 0.32 cm thick, and weighed a little less than 10 gm. After the sample was removed from the loop, it was carefully sheared into three pieces. The shear was especially designed so that no metal was lost during the cutting. Loss of oxide was not important since only the weight of the remaining aluminum was needed. The three pieces were placed into a small glass extraction thimble (specially made with a long hook to suspend it from a flask cap). The thimble and sample were heated in oven (110°C), desiccated until cool, and weighed. The thimble was placed into a flask containing two liters of iodine-alcohol solution. The flask was one of several in a large constant-temperature water bath maintained at 50°C. Each flask was fitted with a condenser. Six to eight hours were required to complete the dissolution.

After the aluminum was completely reacted, the thimble and oxide were removed from the flask, thoroughly washed with methanol, dried in an oven, desiccated until cool, and weighed. The difference of the two weights was the amount of aluminum left after corrosion, and this needed only to be subtracted from the original weight to determine the metal loss.

Two loop tests were run with duplicate samples so that the two methods of weight-loss determination (boric acid versus iodine-methanol) could be compared. Results were very favorable, with the difference always less than 10% and usually less than 5%.

This method was not successful for the X-2219 alloy. The copper sometimes reacted with the solution to form a complex precipitate which remained with the oxide. The only solvent for the precipitate was dilute NH_4OH , but the method was very slow. This introduced another error in that the copper in the oxide was also dissolved. After inaccurate results were obtained from several samples, the X-2219 samples were again analyzed by the boric acid method.

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