

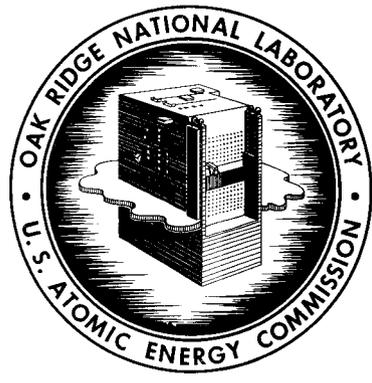
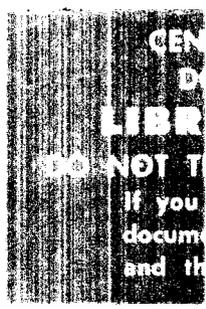


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ORNL-3056
UC-80 - Reactor Technology

EFFECT OF HEAT FLUX ON THE CORROSION OF ALUMINUM BY WATER. PART II. INFLUENCE OF WATER TEMPERATURE, VELOCITY, AND pH ON CORROSION-PRODUCT FORMATION

J. C. Griess
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Printed in USA. Price **\$1.00**. Available from the

Office of Technical Services
Department of Commerce
Washington 25, D. C.

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REACTOR CHEMISTRY DIVISION

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DATE ISSUED

FEB 10 1961

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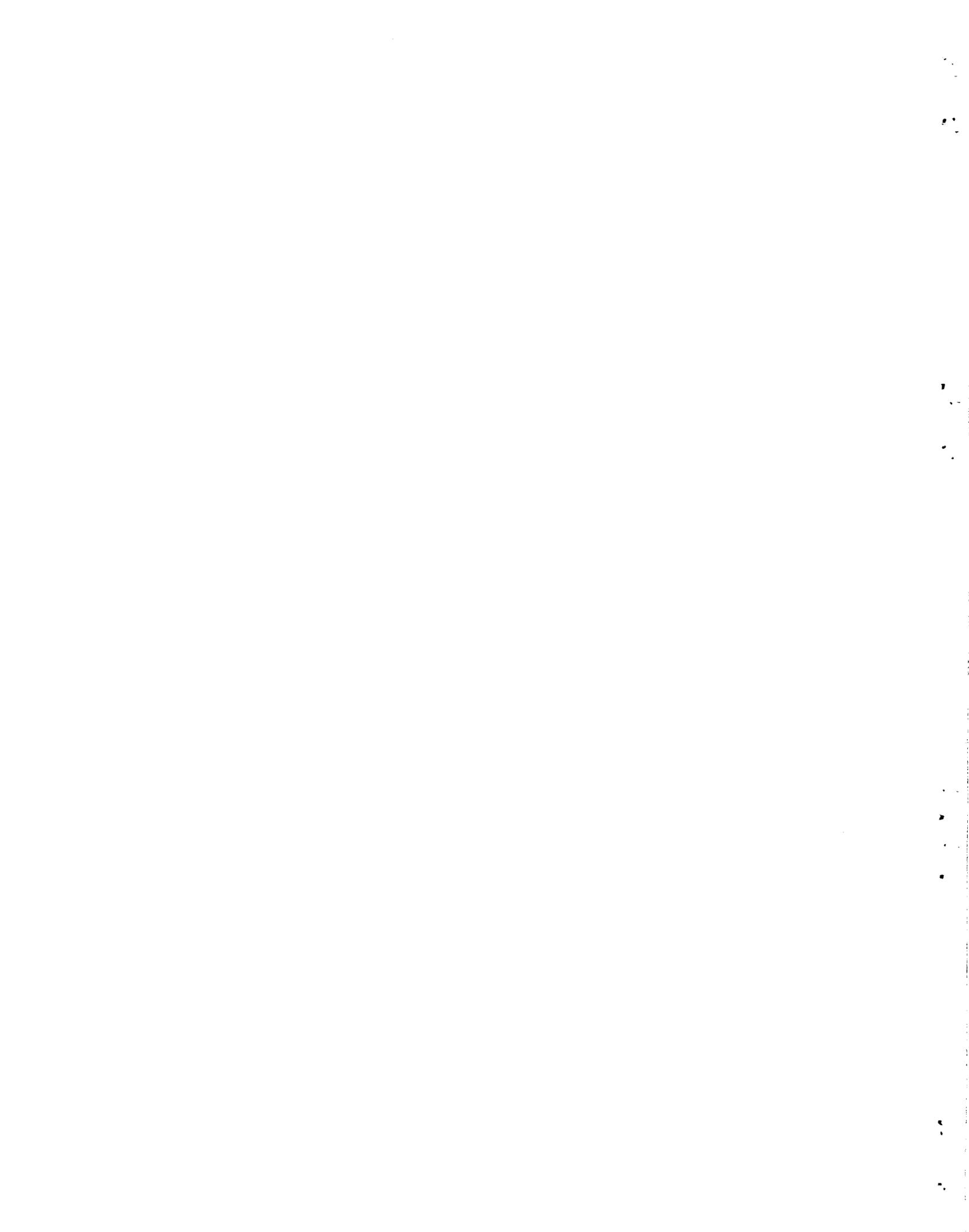


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ABSTRACT

The influence of water temperature, pH, and velocity on corrosion and on corrosion-product formation on the surface of aluminum alloys subjected to a very high heat flux was determined. At a heat flux of 1.5×10^6 Btu/hr·ft² and with cooling-water temperatures and velocities in the ranges of 131 to 223°F and 32 to 48 fps, respectively, a tightly adherent layer of corrosion products (α -Al₂O₃·H₂O) formed on the surface of the aluminum specimens at a linear rate during 10-day tests. The rate at which the corrosion product formed (and the rate of temperature increase in the aluminum) was markedly influenced by the pH of the coolant. With high-purity water as the coolant, oxide films as thick as 1.5 to 2.0 mils formed in 10 days. When the pH of the cooling water was adjusted to 5 with nitric acid, oxide films less than 0.5 mil formed under the same conditions. From measured oxide thicknesses and temperature drops across the corrosion-product films, a thermal conductivity of 1 Btu/hr·ft²·°F/ft was calculated for the aluminum oxide film. The rate of oxide formation was independent of the alloy and the velocity in the range investigated. The temperature of the cooling water was a significant factor; the lower the water temperature the slower the rate of film formation.

Because of the manner in which the specimens were fabricated, quantitative corrosion measurements were not possible. However, it was qualitatively established that corrosion was not severe, and except in one case evidence of localized attack was not found. It was concluded that under the conditions expected to exist during operation of the High-Flux Isotope Reactor, aluminum would be a suitable material for cladding fuel elements.

INTRODUCTION

A new reactor for production of transplutonium elements will be built at ORNL. The reactor is designated the High-Flux Isotope Reactor (HFIR). To achieve the high neutron flux necessary to produce significant quantities of the transplutonium elements, a compact, relatively small core

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with high power density will be used. The reactor core will be an integral unit composed of a flux trap surrounded by two concentric rings of involute fuel plates. Each plate has a thickness of 0.050 in., which includes the uranium-aluminum alloy fuel and 0.010 in. of an aluminum alloy cladding on each side. The plates are separated by a 0.050-in. channel through which water flows at a rate of about 40 fps. This high flow rate is necessary to remove the heat from the fuel plates, since heat fluxes as high as 1.5×10^6 Btu/hr·ft² will exist during reactor operation. Under normal conditions cooling water will enter the reactor at a temperature of 120°F and will rise 70°F in passing through the core. The design features of the reactor are described in previously issued reports.^{1,2}

Since data on the corrosion of aluminum under conditions of very high heat flux did not exist, it was necessary to initiate an experimental program to determine how severe corrosion would be and what effect corrosion would have on heat transfer. The first test in this series has been reported,³ and the results indicated that corrosion leads to the formation of an adherent layer of corrosion products with low thermal conductivity on the water-cooled surfaces. Thus in a reactor operating at a constant power level, the continuous corrosion of aluminum cladding would result in a continuous increase in the temperature of the fuel plates. Since aluminum has low mechanical strength, which decreases rapidly as temperature increases, and since it has been reported that the corrosion rate of aluminum is approximately governed by the mean temperature of the corrosion-product film on the surface,⁴ it is necessary to minimize corrosion-product formation. In a reactor such as the HFIR, which utilizes thin aluminum fuel plates, high temperature can lead to buckling and creep of the plates with very low pressure differences across the plates.

This report describes the results of several experiments conducted with 1100 and 6061 aluminum test specimens. Data were obtained on the effect of pH, flow rate, and temperature of the cooling water on the formation of corrosion-product films on aluminum at a heat flux of 1.5×10^6 Btu/hr·ft² and on corrosion of aluminum.

EXPERIMENTAL

The equipment and test specimens used to carry out the experiments reported here have been described in detail in a previous report.³ Briefly, the aluminum specimens were prepared by pressing an aluminum tube 8.5 in. long with a 0.100-in.-thick wall onto a mandrel to form a rectangular channel of 0.050- by 0.500-in. cross section through which the coolant flowed. The corners and narrow edges of the center 6.5-in. portion of the specimen were then machined to a wall thickness of 0.025 in. to reduce the heat generation in that region where it was expected that heat-transfer coefficients might be low. Figure 1 is a photograph of a specimen and a schematic of the cross sections. The 1-in. length at each end was welded into large aluminum electrodes to which electrical leads from the transformer were attached, and by means of which the specimen was flanged into a bypass line of the 100-gpm pump loop which provided the flow of water through the specimen. After welding to the electrodes, the specimen was the center, 6.5-in. machined section. In all tests the specimen was mounted vertically with water entering at the bottom.

Heat was generated within a specimen by passing 60-cycle current through the specimen. The electrical resistance of the 1100 aluminum specimens was approximately 10^{-4} ohm at room temperature; the resistance of the 6061 specimens was about 40% greater. With 1100 aluminum specimens

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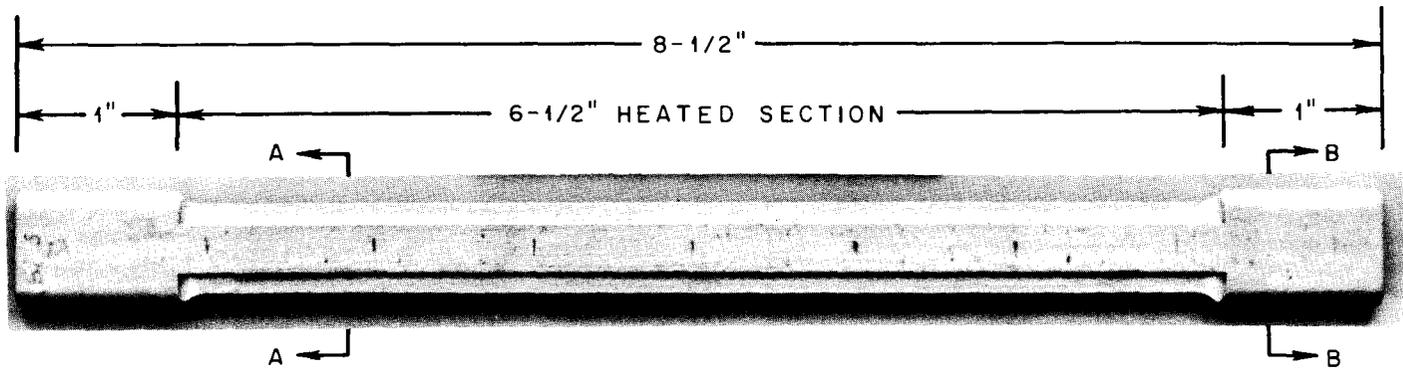
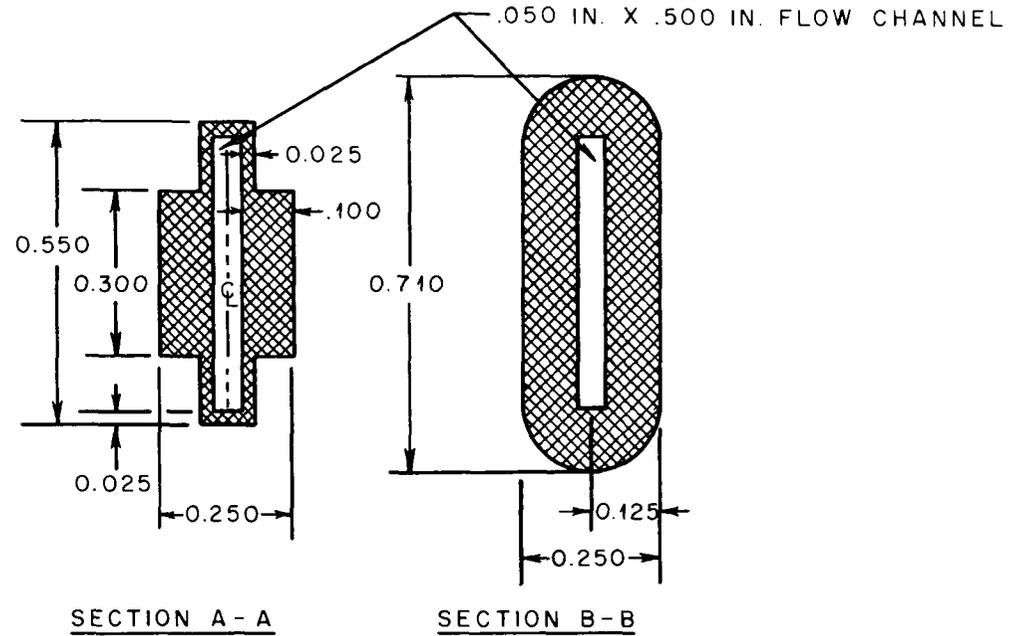


Fig. 1. Aluminum Corrosion Test Specimen.

at the temperature of a test, a current of 10,000 amp generated about 16 kw in the 6.5-in.-long test specimen; with 6061 specimens a current of 8,500 amp generated the same power. For the specimen geometry this power generation corresponded to a nominal heat flux of 1.5×10^6 Btu/ft²·hr across the water-aluminum interface under the 0.100-in.-thick part of the specimen and 0.5×10^6 Btu/ft²·hr across the rest of the surface. In all tests described in this report the heat fluxes were held constant at the above values within +5%. (In test A-2 the heat flux was as high as 1.66×10^6 Btu/ft²·hr on one side of the specimen.³)

Thermocouples were spot-welded to the outside of the specimen, and close-fitting Mycalex, which served as thermal and electrical insulation, surrounded the specimen. The Mycalex was backed up with heavy stainless steel plates so that the thin specimen could withstand the internal pressure of 900 psi used in all tests except A-2, where the pressure was 300 psi.

The quality of the cooling water in the loop was maintained as desired by use of bypass deionizers. If high-purity water was used, a bypass stream from the loop was passed through a mixed-bed demineralizer. If the water was to be kept at a pH less than 7, a cation exchanger was used.

In all tests except one, the inlet and outlet water temperatures, flow rate, heat flux, and system pressure were constant throughout a given test. The temperatures at various locations on the specimen and of the inlet and outlet water, and the flow rate of water through the specimen were recorded. The voltage drop across the specimen and the current were also recorded. The heat input to the specimen determined by heat balances and from electrical measurements always agreed within +5%. Aliquots of

water were removed from the loop periodically for determination of water quality. When the mixed-bed ion exchanger was used, the pH of the water varied between 6.0 and 6.5, and the resistivity of the water in the loop varied between 1 and 2×10^6 ohm-cm. The low pH values were probably due to dissolved carbon dioxide since the water was exposed to the atmosphere during sampling and before the pH was determined. Control of the pH of the water at values less than 7 by means of the cation exchanger was usually good to ± 0.1 pH unit. With the water at a pH of 5, the resistivity of the water was approximately 2×10^5 ohm-cm.

In the later tests the copper concentration of some of the water samples was determined. Although deionized water was used throughout, the copper content of the water in the loop at the start of a test was usually about 100 ppb. During a test this concentration decreased and after about 100 hr of operation, the copper content was usually 10 to 20 ppb. The source of the copper was not determined.

RESULTS

A number of tests run under a variety of conditions are described in this report. In all but one case the operating conditions during a given test were held constant and are summarized in Table 1. The results of test A-2 were previously reported,³ but data from this test are correlated with those from the other tests. It should be noted from Table 1 that inlet water temperatures between 131 and 186°F and flow rates between 32 and 48 fps were investigated. Three tests utilized 6061 aluminum specimens, and the other tests were conducted with 1100 aluminum specimens. Specimens were cooled either with high-purity water or with water adjusted to pH 5 with nitric acid. All tests lasted 240 hr except A-3 and A-5, which

were terminated prematurely because of mechanical failures. One additional test (A-10) not shown in Table 1, in which the operating conditions were changed several times during the test, will be discussed separately.

Table 1. Test Conditions

Test Designation	Water Temperature (°F)		Water Condition	Flow Rate (fps)	Alloy Type	Time (hr)
	Inlet	Outlet				
A-2*	149	190	Deionized	32	1100	240
A-3	149	190	Deionized	32	1100	129
A-4	149	190	Deionized	33	1100	240
A-5	149	190	Deionized	37	1100	42
A-6	149	190	Deionized	33	1100	240
A-7	156	193	pH 5	36	1100	240
A-8	156	195	pH 5	35	1100	240
A-9	186	223	pH 5	33	1100	240
A-11	152	196	pH 5	34	6061	240
A-12	166	192	pH 5	48	6061	240
A-13	131	176	pH 5	34	6061	240

*300 psi; all others, 900 psi.

Temperature Measurements

During all tests the temperatures at several locations on the outside of the specimen were continuously recorded. Figure 2 shows the thermocouple locations. Except for thermocouple locations 7 and 8, 1/4 in. from each end, the indicated temperatures at the start of a test were usually within 5 to 10% of that expected using the Sieder-Tate equation to calculate the water-film coefficient and calculating the temperature drop through the metal, considering uniform heat generation and heat removal from one side. The temperature at thermocouple No. 7 was always much lower than calculated, whereas that at thermocouple No. 8 was usually only 5 to 10% lower than expected. The indications were that unusual flow conditions in the entrance

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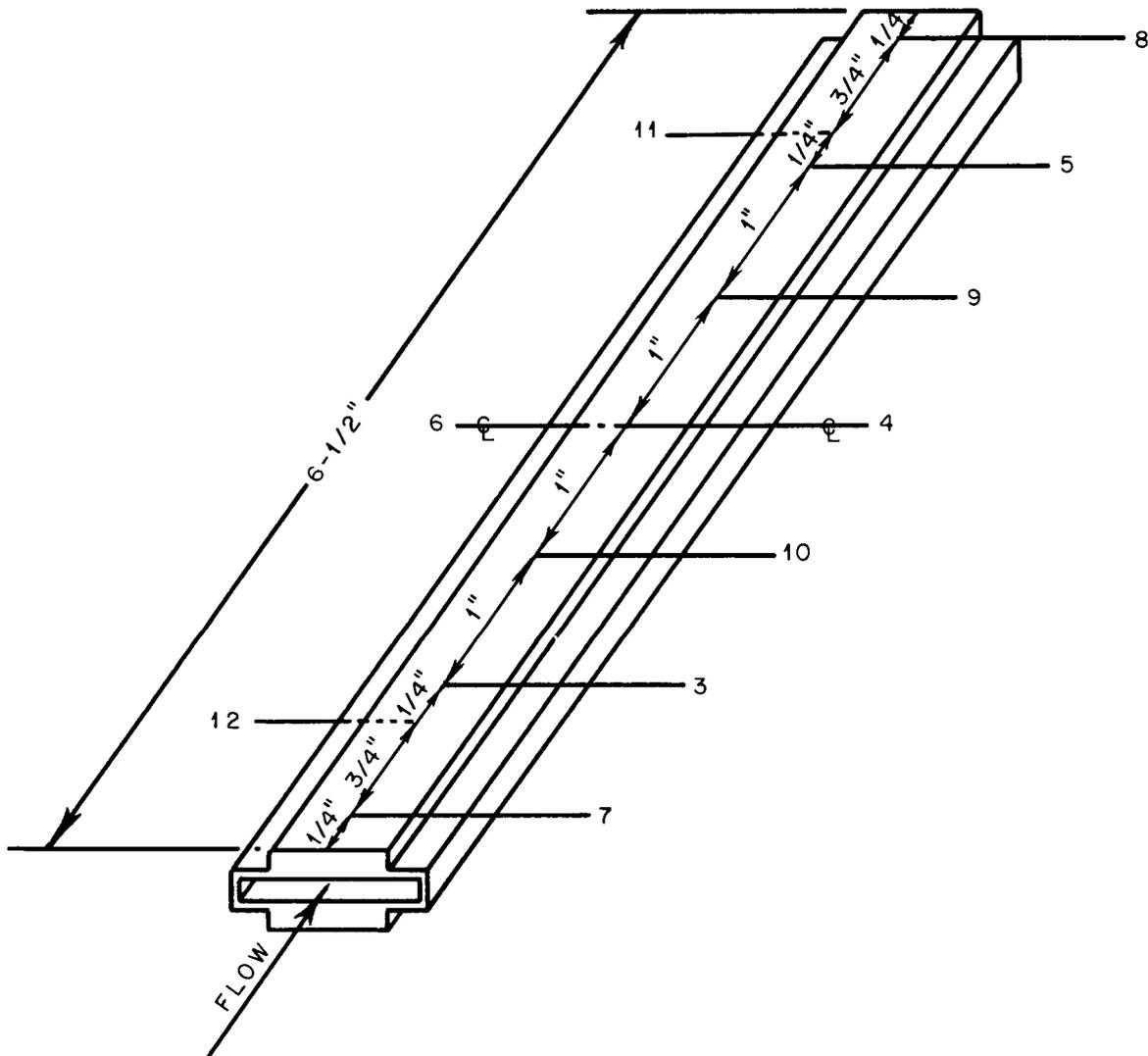


Fig. 2. Location of Thermocouples on Outside of Test Specimens.

region were primarily responsible for the lower temperature at thermocouple No. 7, and to a lesser extent, heat loss to the large, cool aluminum electrode. On the other hand, the slightly lower value at thermocouple No. 8 at the start of the test was probably the result of heat loss to the electrode.

Figures 3 and 4 show how the temperature increased during a typical test, A-6, in which the coolant was high-purity water. It should be noted that at all locations the temperature increased linearly with time and that the rate of temperature increase was greater, the closer the thermocouple was to the exit end of the specimen where the bulk cooling-water temperature was higher. The irregularities in the temperature curves were due to two causes: slight variations in the power supply and in the cooling-water inlet temperature.

Figures 5 and 6 show the temperature of the aluminum specimen during test A-8, in which the conditions were the same as those during test A-6 except the pH of the water had been adjusted to 5 with nitric acid. The very large effect of the small addition of nitric acid is readily apparent. The highest measured temperature increase in test A-8 was only 41°F, compared to 220°F in test A-6.

In all tests except A-4, which will be discussed later, specimen temperature increased linearly with time. Table 2 shows the rate at which the temperature increased at all thermocouple locations in all tests.

Test A-5 is not included in Table 2 because the test was too short to allow a reasonable estimate of the rate of temperature increase. However, during this brief test it appeared that at most locations the temperature was increasing at a rate similar to that in tests A-2, A-3, and A-6.

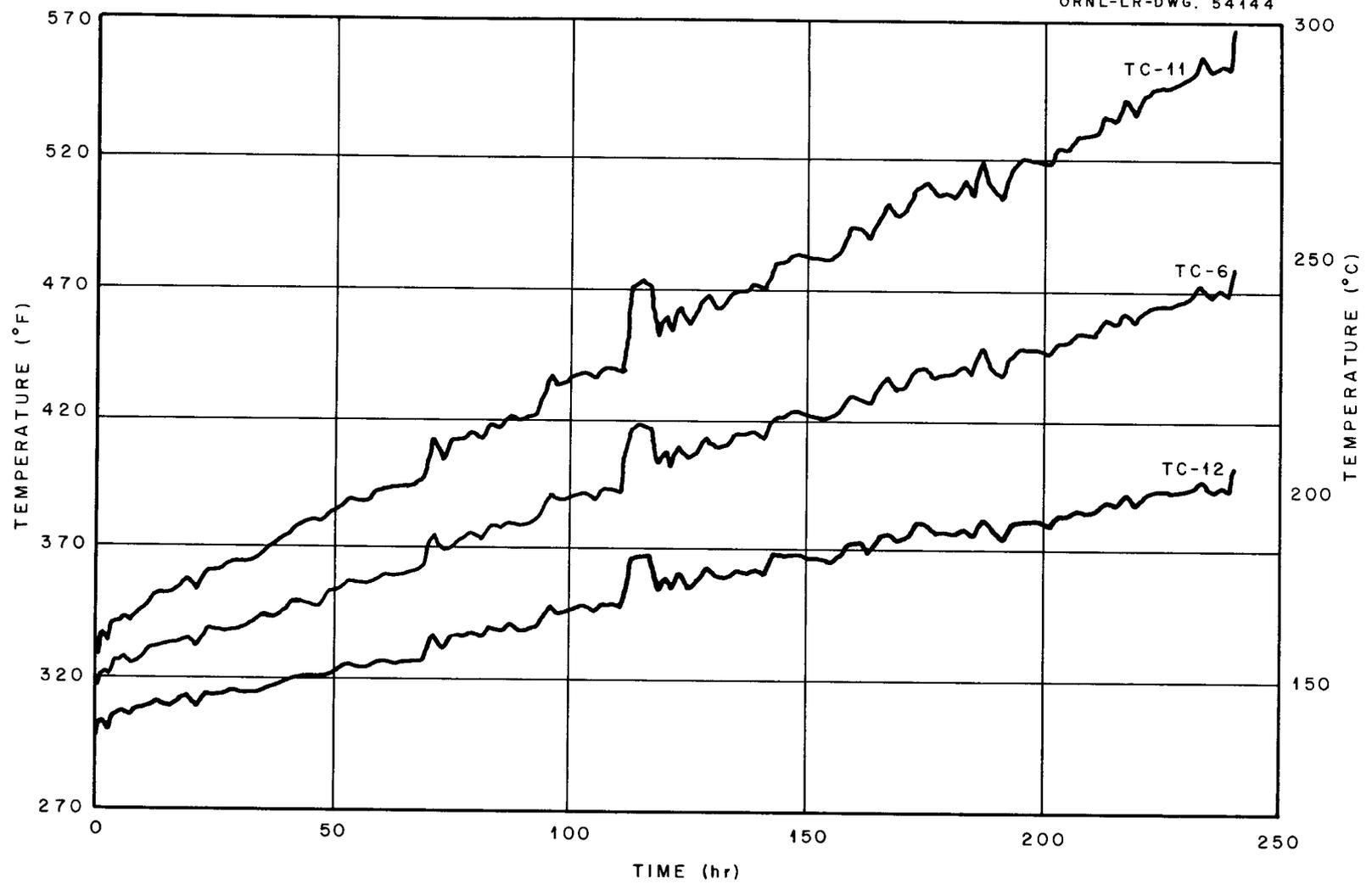


Fig. 3. Temperature on the Outside of Specimens During Test A-6. Thermocouples 12, 6, and 11.

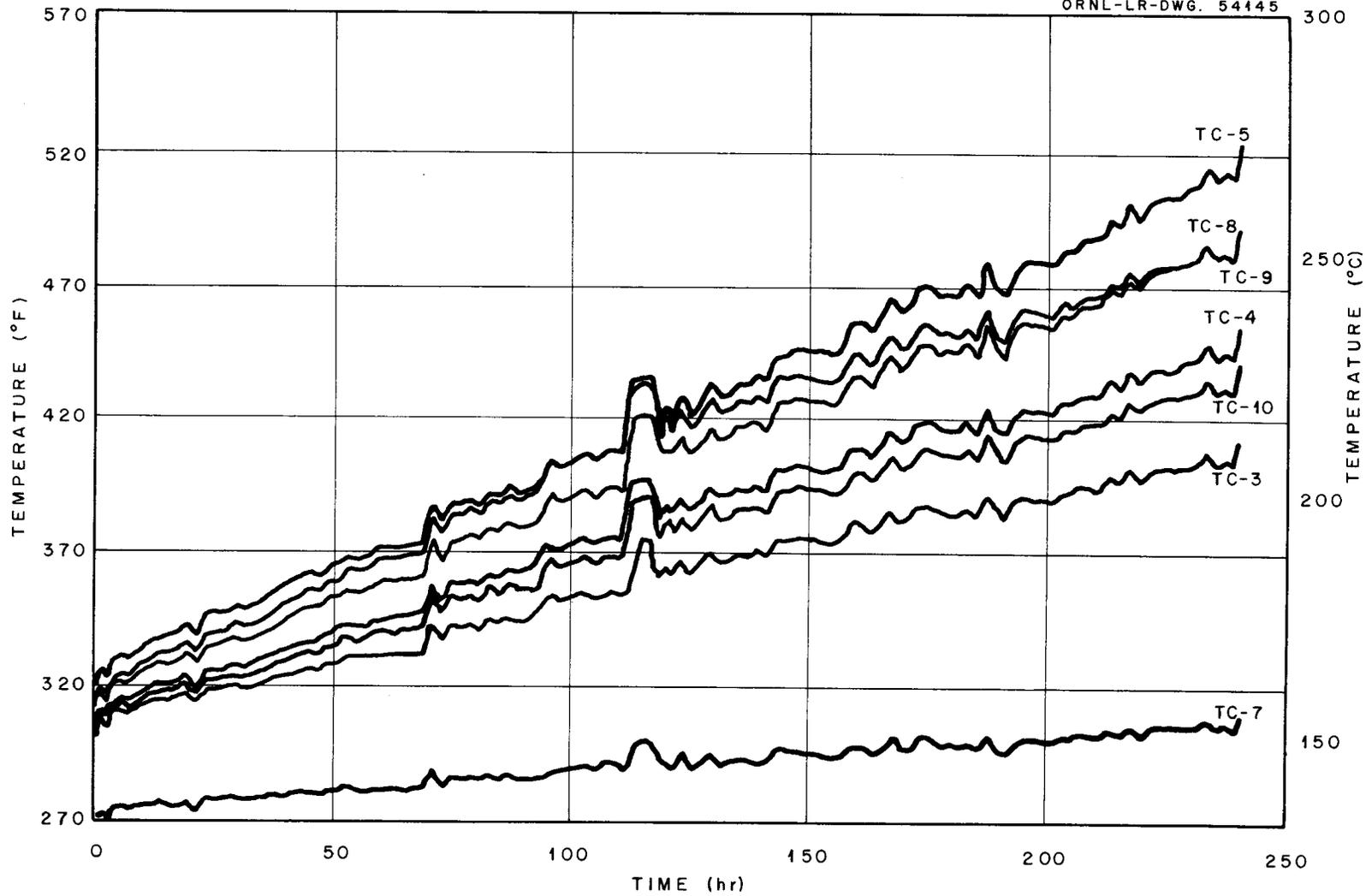


Fig. 4. Temperature on the Outside of Specimen During Test A-6. Thermocouples 7, 3, 10, 4, 9, 8, and 5.

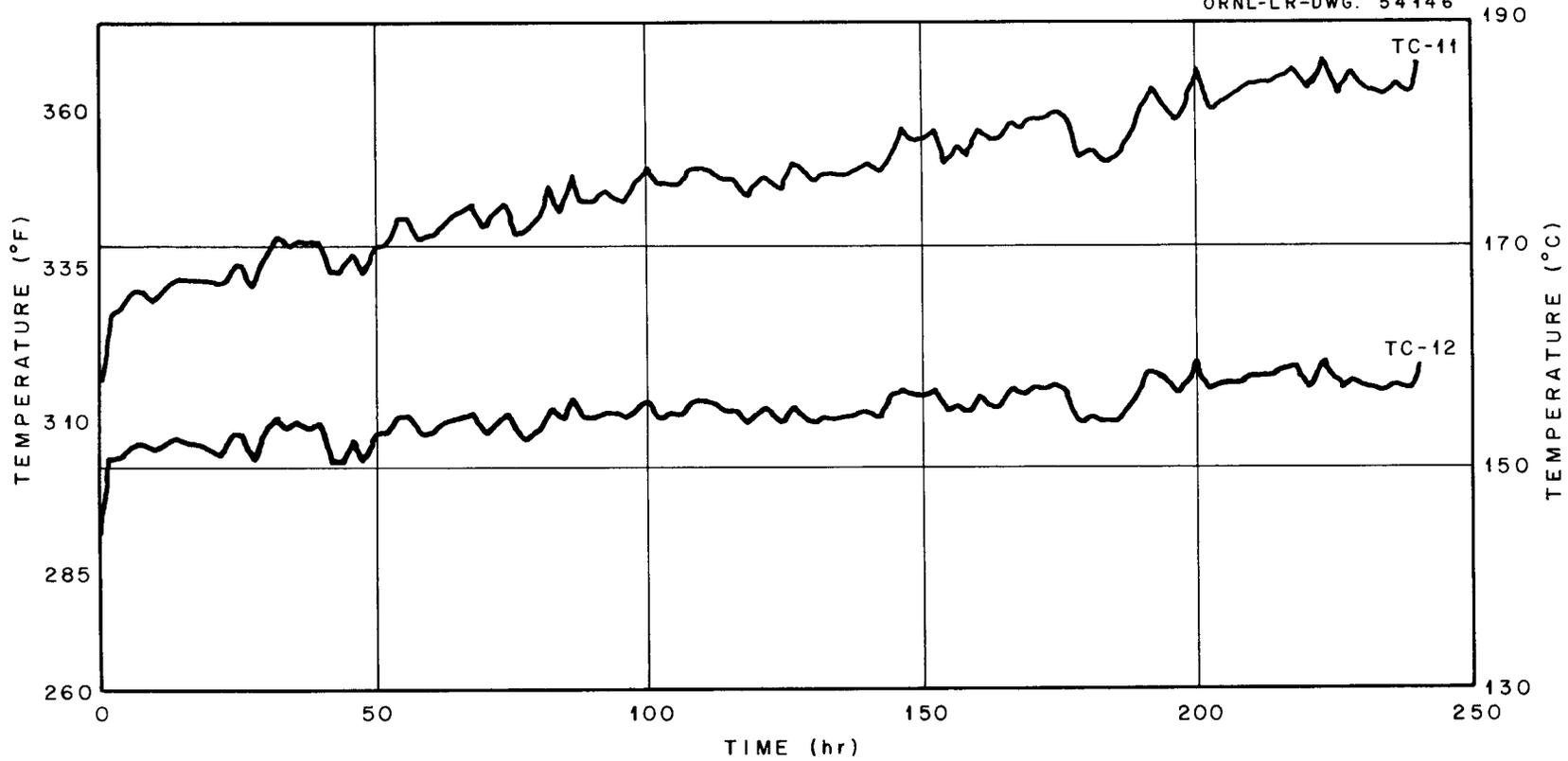


Fig. 5. Temperature on the Outside of Specimen During Test A-8. Thermocouples 12 and 11.

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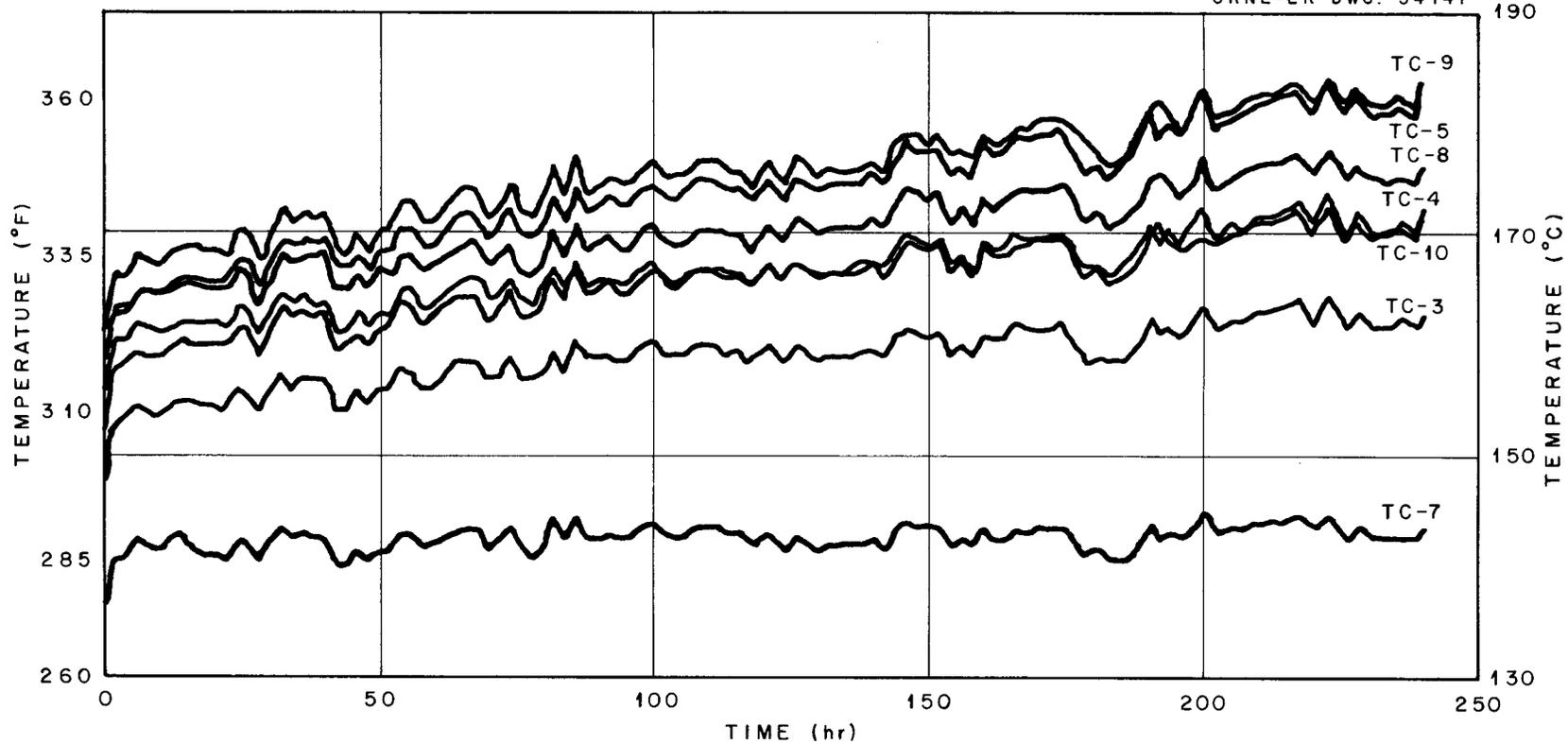


Fig. 6. Temperature on the Outside of Specimen During Test A-8. Thermocouples 7, 3, 10, 4, 8, 5, and 9.

Table 2. Increase in Aluminum Temperature During Test

Test Designation	Rate of Temperature Increase ($^{\circ}\text{F}/10$ days)									
	Thermocouple Designation*									
	7 (1/4)	12 (1)	3 (1 1/4)	10 (2 1/4)	4 (3 1/4)	6 (3 1/4)	9 (4 1/4)	5 (5 1/4)	11 (5 1/2)	8 (6 1/4)
A-2	-	49	45	59	86	99	112	-	180	124
A-3	83	148	-	173	240	240	260	290	340	240
A-6	34	94	99	130	135	148	168	190	220	162
A-7	13	22	20	25	34	34	36	52	61	50
A-8	4	13	18	22	18	-	29	41	36	22
A-9	18	32	31	40	41	43	50	59	59	56
A-11	4	13	14	18	-	18	20	34	38	31
A-12	9	13	14	20	18	18	22	29	27	18
A-13	<2	2	2	3	4	2	4	7	4	4

*The numbers under the thermocouple numbers indicate the distance of the thermocouple from the entrance end of the specimen.

It should be noted in Table 2 that the rate of temperature rise was lower than expected at thermocouples 7 and 8, located on the ends of the specimen. At thermocouple 7 unusual flow effects may have prevented retention of corrosion products on the surface. Although at thermocouple 8 heat loss by conduction to the large aluminum electrode did not appear to be large at the start of the test, it is probable that as a corrosion-product film with low thermal conductivity formed, the heat losses to the electrode increased, resulting in a temperature rise lower than would be expected if all heat were transferred through the corrosion-product film.

The first three tests in the table were conducted with high-purity water, and all others utilized water adjusted to pH 5 with nitric acid. Although the tests in each of the two groups were not exact duplicates, the effect of the nitric acid in reducing the rate of temperature rise is clearly evident.

A comparison can also be made between 1100 and 6061 aluminum. Tests A-7 and A-8 utilized 1100 aluminum specimens, whereas in test A-11 a 6061 aluminum specimen was used; all other conditions were the same in the three tests. Within the limits of reproducibility the rate of temperature rise was the same in all three tests, indicating that there was no significant difference between 1100 and 6061 aluminum with regard to the temperature increase of the aluminum during the tests.

The influence of flow rate on the rate of temperature increase was not important in the range investigated. Tests A-11 and A-12 were comparable except for flow rate (34 versus 48 fps), and from Table 2 it is apparent that the rates of temperature rise were approximately the same in the two tests.

The temperature of the bulk coolant was a significant factor in determining the rate of temperature rise. The temperature of the coolant varied from run to run, and in a given run, from inlet to outlet of the specimen. Since the temperature of the coolant increased uniformly on passage through the specimen, it was possible to determine the temperature of the coolant at all thermocouple locations in each test. Figure 7a shows how the rate of temperature rise of the aluminum varied with the temperature of the coolant in the tests conducted with water at pH 5, and Fig. 7b shows a similar plot of the data obtained in the tests with high-purity water. All the data shown in Table 2 are included except those obtained at thermocouple locations 7 and 8, which in nearly all cases gave abnormally low values. Note that the scale of the ordinate in Fig. 7b is 5 times that of Fig. 7a. At both water qualities there appeared to be an approximately linear relationship between the rate of temperature rise and the temperature of the bulk coolant, in spite of the fact that at the lower pH different flow rates and different alloys were used.

Test A-4 produced anomalous results. Figure 8 shows a plot of the temperature recorded at three locations, from which it can be seen that the temperature-time relationship was considerably different from those of other tests (see Figs. 3 through 6). The reason for the peculiar behavior in this test was not related to changes in power input or cooling-water temperature during the test. Examination of the specimen at the conclusion of the test yielded a probable explanation (discussed later).

Specimen Examination

At the conclusion of each test the specimen was cut from the electrodes and the edges were milled off so that the water-cooled surfaces could be

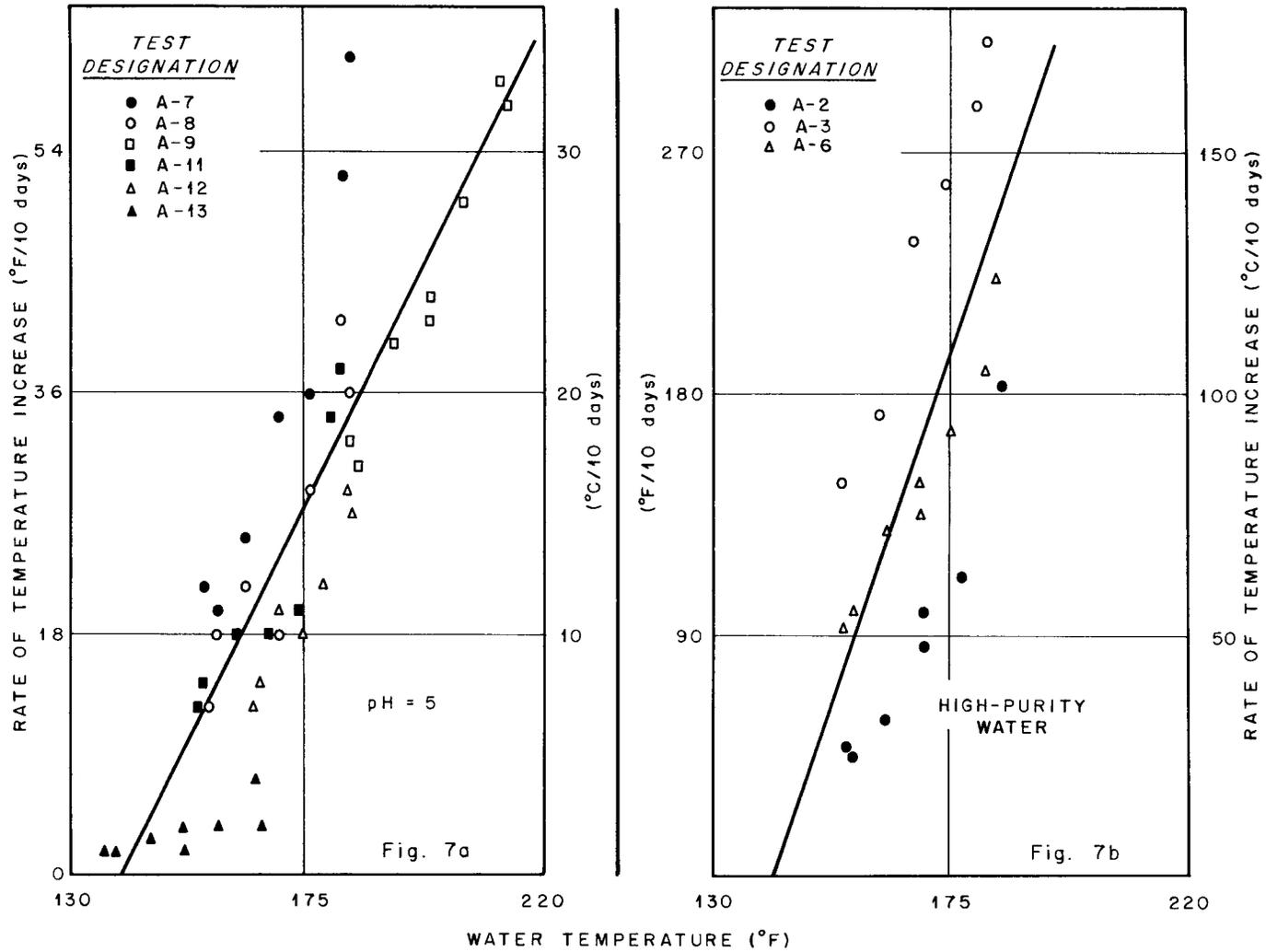


Fig. 7. Correlation of Rate of Temperature Increase and Water Temperature.

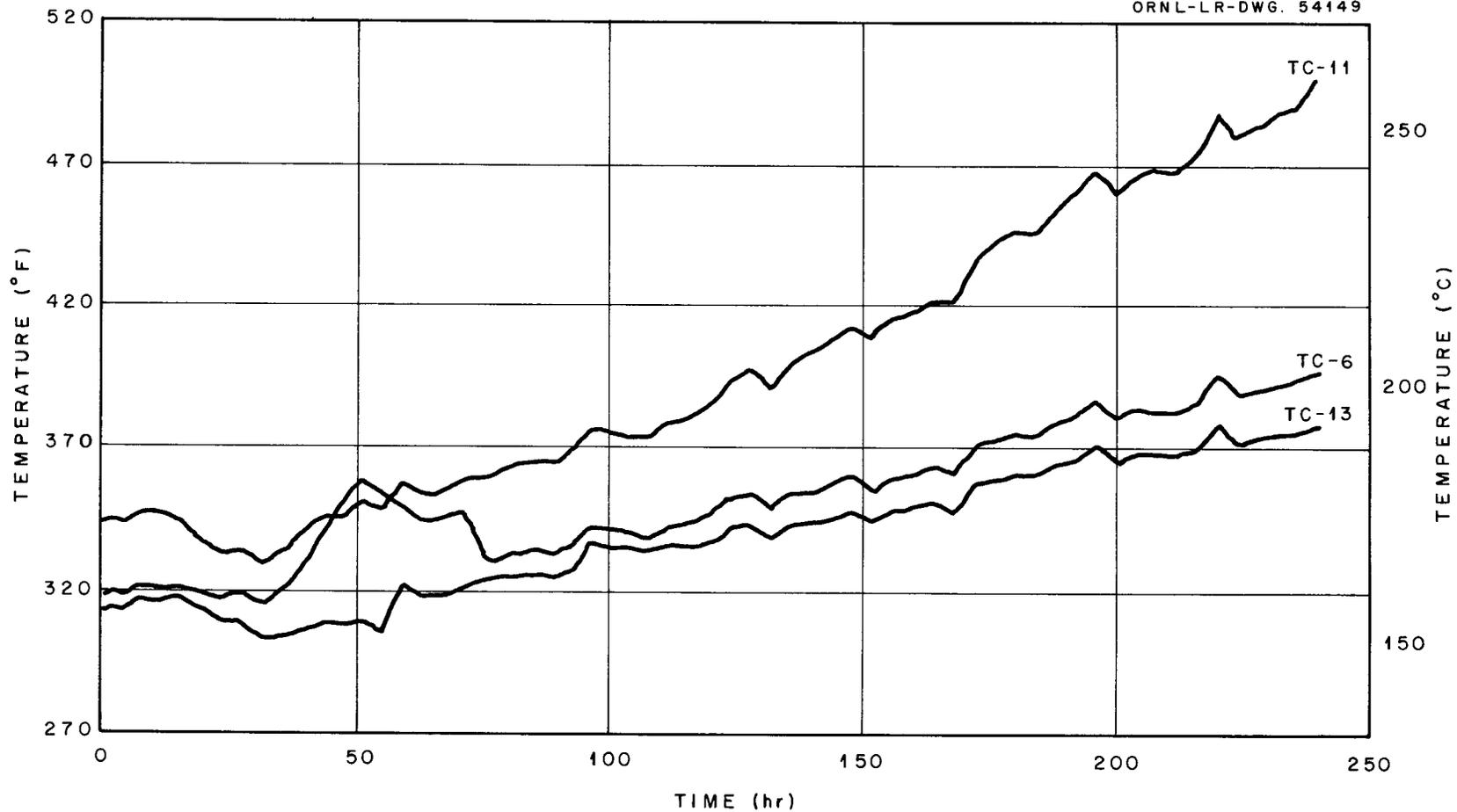


Fig. 8. Temperature on the Outside of Specimen During Test A-4. Thermocouples 13, 6, and 11.

examined. With the exception of specimens A-2 and A-4, the surfaces of the aluminum were free of localized attack and visually appeared to be free of corrosion products. Microscopic examination of the surfaces, however, revealed in all cases the presence of a thin, nearly transparent oxide film through which the surface of the metal could be clearly distinguished. In a few cases a trace of an extremely thin deposit which was black to brown was seen on the surface of the oxide. This coloration was probably due to a very small amount of mixed iron and chromium oxides from slight corrosion of the stainless steel loop. The amount of colored material was so small that it could not be isolated for identification and probably did not interfere with heat transfer. A typical example of a specimen surface at the end of a test is shown in Fig. 9.

The appearance of specimen A-2 has been described in detail.³ This specimen is the only one that showed "film-stripping" and severe intergranular attack in that region.

The appearance of specimen A-4 was distinctly different from all others. The surface of the specimen was covered with a poorly adherent, brownish-red, deposit which was shown to be metallic copper by x-ray examination. It is possible that the uneven deposition and sloughing-off of copper from the surface of the specimen caused the unusual temperature fluctuations in the aluminum during the early part of the test (see Fig. 8). The source of the copper was not determined.

One side of each specimen was examined metallographically to determine the thickness of the corrosion-product layer and to look for evidence of localized attack of the aluminum. Figure 10 is a typical photomicrograph showing the oxide film on the surface of the aluminum when high-purity

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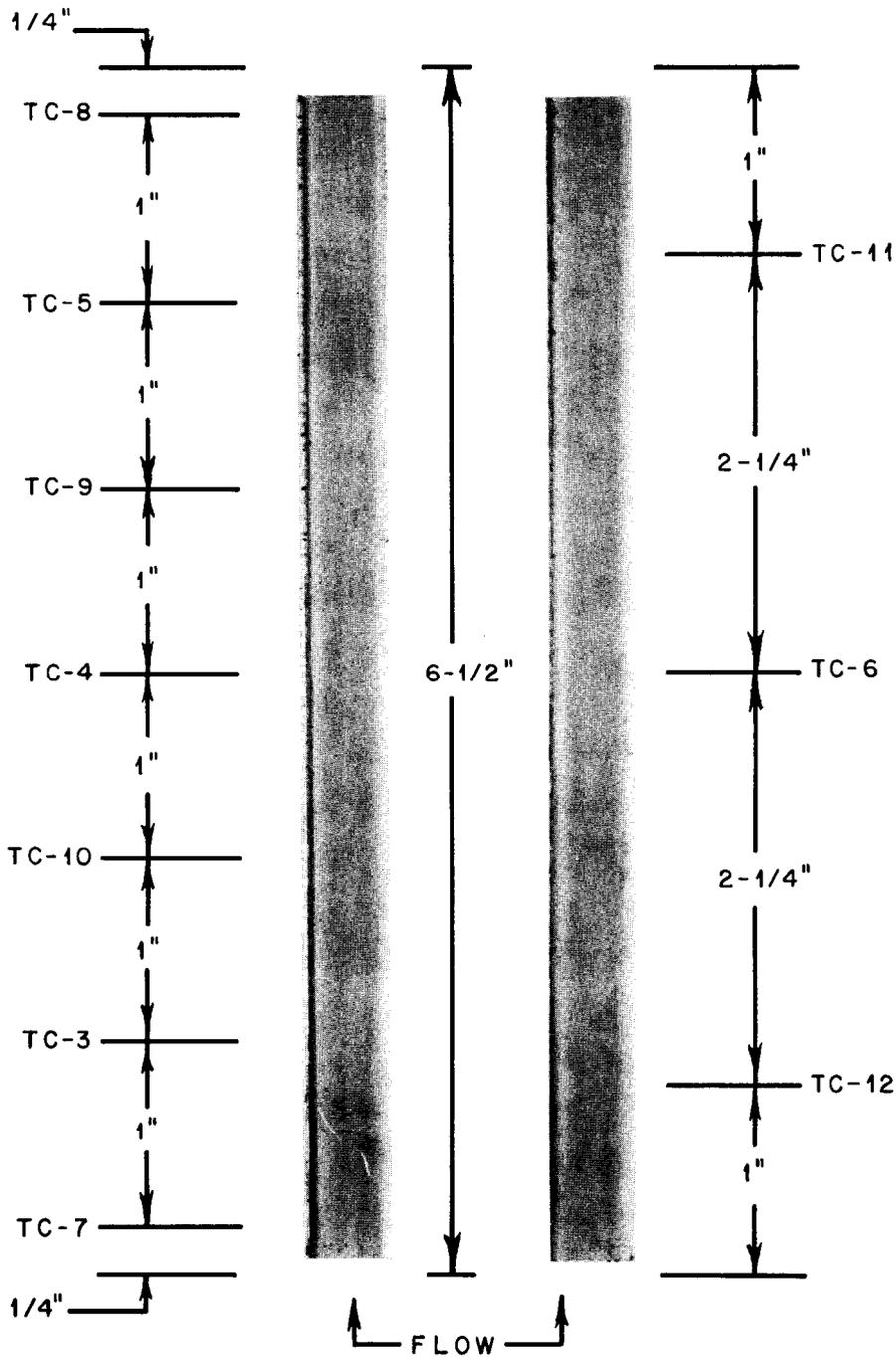


Fig. 9. Typical Appearance of Type 6061 Aluminum Water-Exposed Surfaces at Completion of 240-hr Run. Magnification 1.1X. Reduced 14%.

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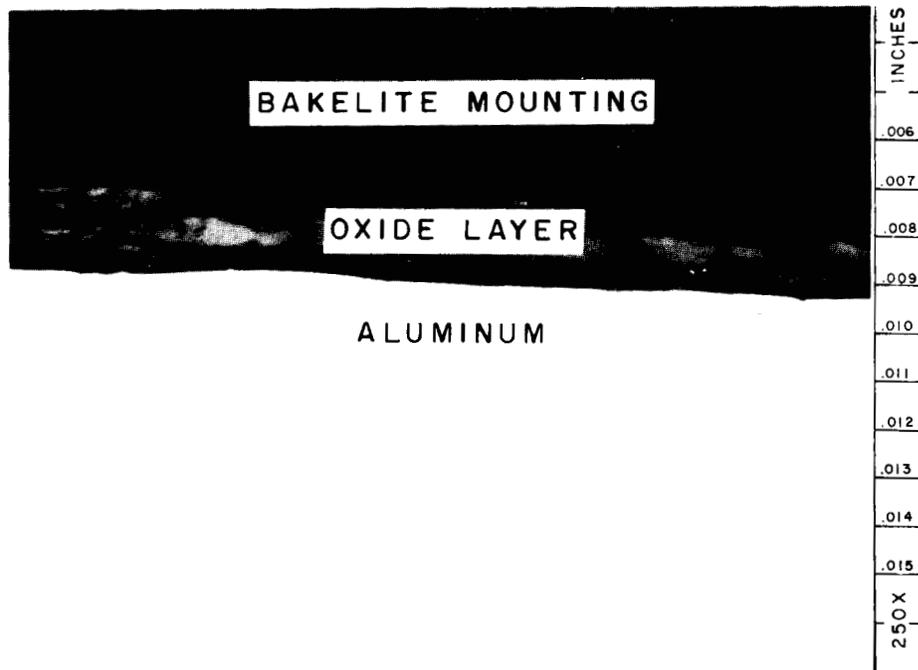


Fig. 10. Oxide Layer Found 1.5 in. from Outlet on Exposed Surface of Type 1100 Aluminum Specimen A-6 After 240 hr in Deionized Water. Magnification 250X.

water was the coolant. This particular section was taken 1 1/2 in. from the outlet of specimen A-6. Figure 11 is a similar photomicrograph of a specimen cooled with water that had a pH of 5. This latter specimen was taken 0.5 in. from the outlet of specimen A-8. Note that the magnification is 250X on the former photomicrograph and 750X on the latter. The difference in the oxide thickness on the two specimens and the absence of localized attack in both cases are readily apparent. It is also obvious from the photomicrographs that the temperature of the aluminum increased faster when pure water was the coolant than when the slightly acid water was used, because the thickness of the oxide film increased faster in the pure water.

Figure 12 is a photomicrograph of a section taken from specimen A-4 and shows the copper deposit at one location on the surface of the oxide. Similar deposits were found over the entire specimen. A small amount of copper was found at one location on specimen A-5 during metallographic examination, but no trace of copper was found on any other specimen. At the end of the test copper was found on the oxide, not directly on the aluminum. The presence of the copper produced no evidence of localized attack on either specimen. Because of the uncertainty of the effect of the copper deposit on heat transfer and because test A-5 was of such short duration, the data from tests A-4 and A-5 were of questionable validity, and no attempt was made to correlate them with those from the other tests.

Figure 13 shows how the oxide thickness varied from inlet to outlet in typical cases, one in which the surface was cooled with high-purity water (A-6) and the other with the water adjusted to a pH of 5 (A-8). The effect of pH on oxide thickness is clearly demonstrated by this figure. To arrive at the maximum and minimum points in Fig. 13, the maximum and

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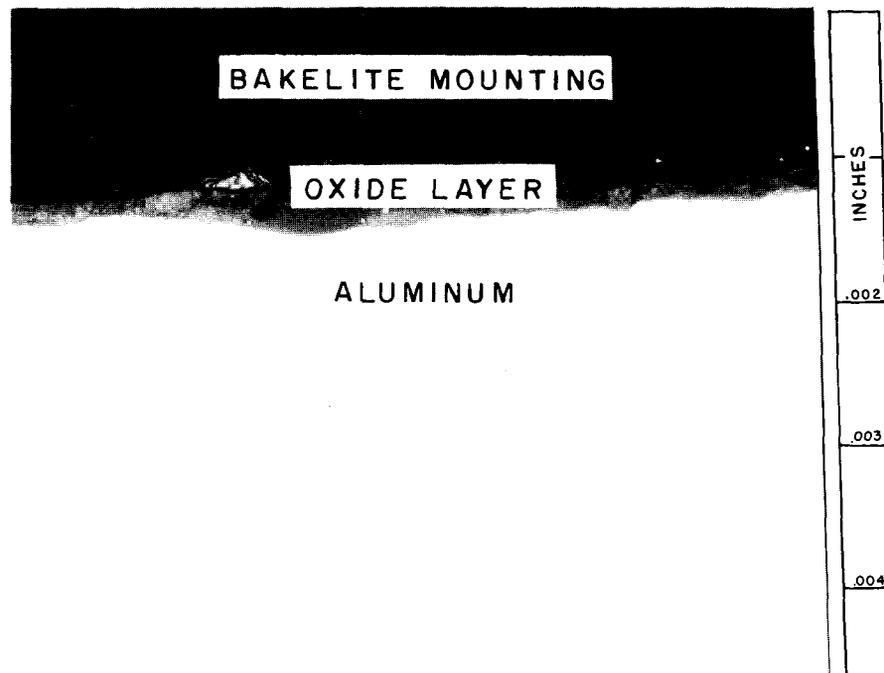


Fig. 11. Oxide Layer Found 0.5 in. from Outlet on Exposed Surface of Type 1100 Aluminum Specimen A-8 After 240 hr in pH 5 Water. Magnification 750X.

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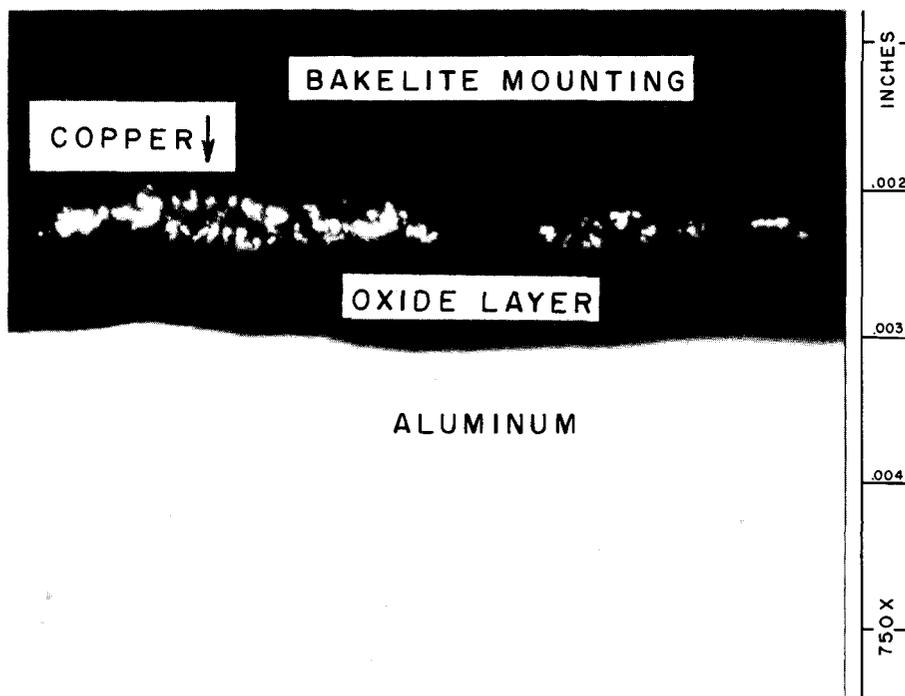


Fig. 12. Copper Deposits Found 2.5 in. from Outlet on Exposed Surface of Type 1100 Aluminum Specimen A-4 After 240 hr in Deionized Water. Magnification 750X.

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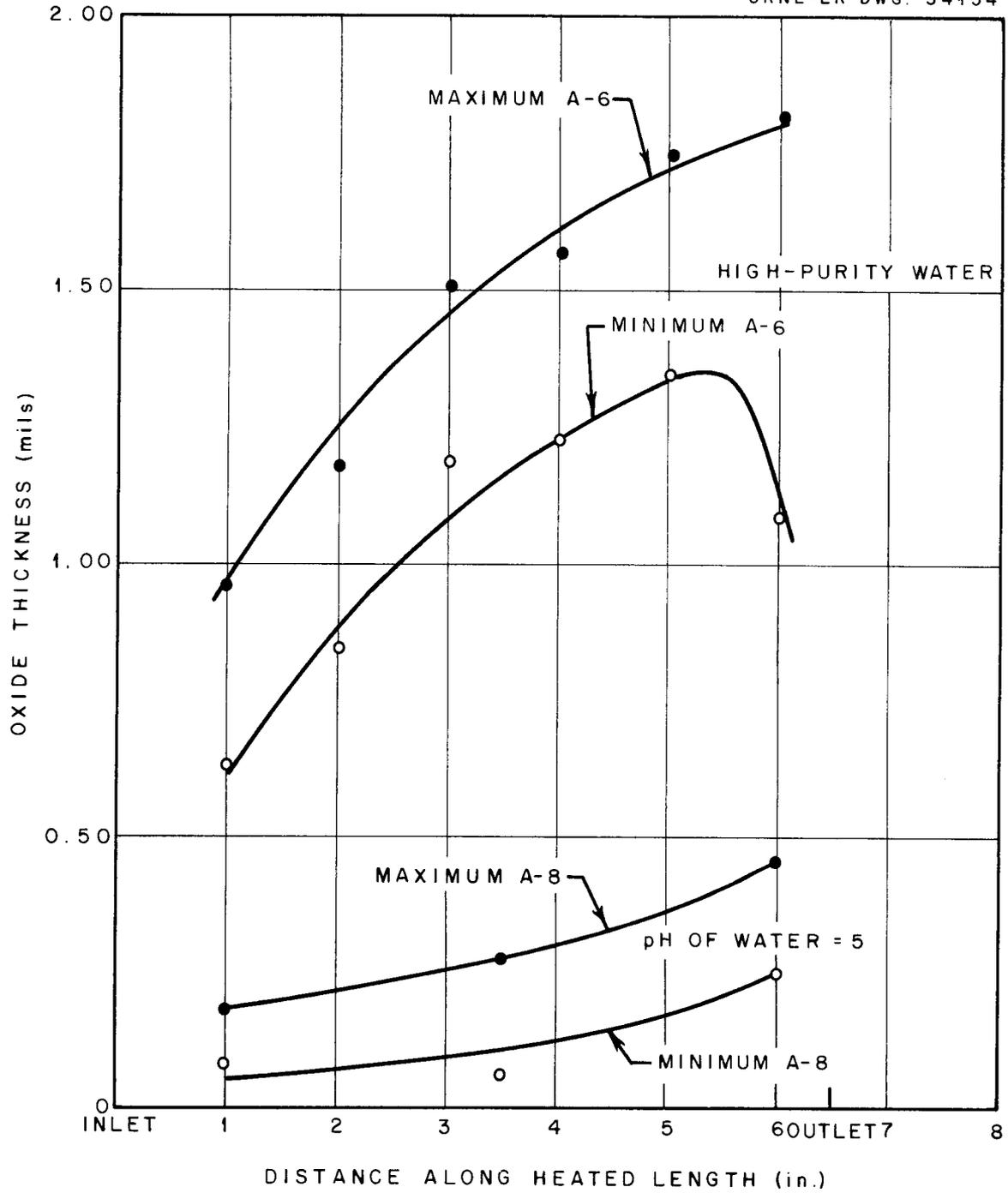


Fig. 13. Oxide Thickness on Test Specimens at the End of Tests A-6 and A-8.

minimum oxide thicknesses across the 0.500-in.-wide sections were measured microscopically at 1-mm intervals. At each location the maximum values were averaged and the minimum values were averaged to obtain the points shown on the curves.

That the temperature increase in the aluminum during a test was due to the oxide film on the surface of the aluminum is also shown by Fig. 14, in which the temperature increase observed at each thermocouple location in all tests, regardless of temperature, flow rate, pH, or alloy, is plotted against the oxide thickness at that point. The oxide thicknesses were determined from plots similar to those shown in Fig. 13, and the values plotted are the average of the maximum and minimum thicknesses. Although there is some scatter in the data, the line drawn through the points represents the data fairly well and indicates that the observed temperature rise was directly proportional to the oxide thickness. From the slope of the least-squares line fixed at the origin, a value of $1 \text{ Btu/ft}^2 \cdot \text{hr} \cdot ^\circ\text{F/ft}$ ($0.02 \text{ watts/cm}^2 \cdot ^\circ\text{C/cm}$) is calculated. This value is in reasonable agreement with the value reported by DeHalas.⁴

Experiment A-10

Experiment A-10 was conducted to determine the effect of such variables as thermal cycling, bulk coolant flow rate, and pH on the rate of oxide growth and on the stability of the oxide formed on an aluminum test specimen. The test was conducted in the same manner as all others, but during the test certain variables were changed. Twice during the experiment the test assembly (complete with electrodes, specimen, thermocouples, and back-up plates) was removed from the loop and the oxide was cleaned from the interior surfaces of the specimen. A solution containing 3% CrO_3 and

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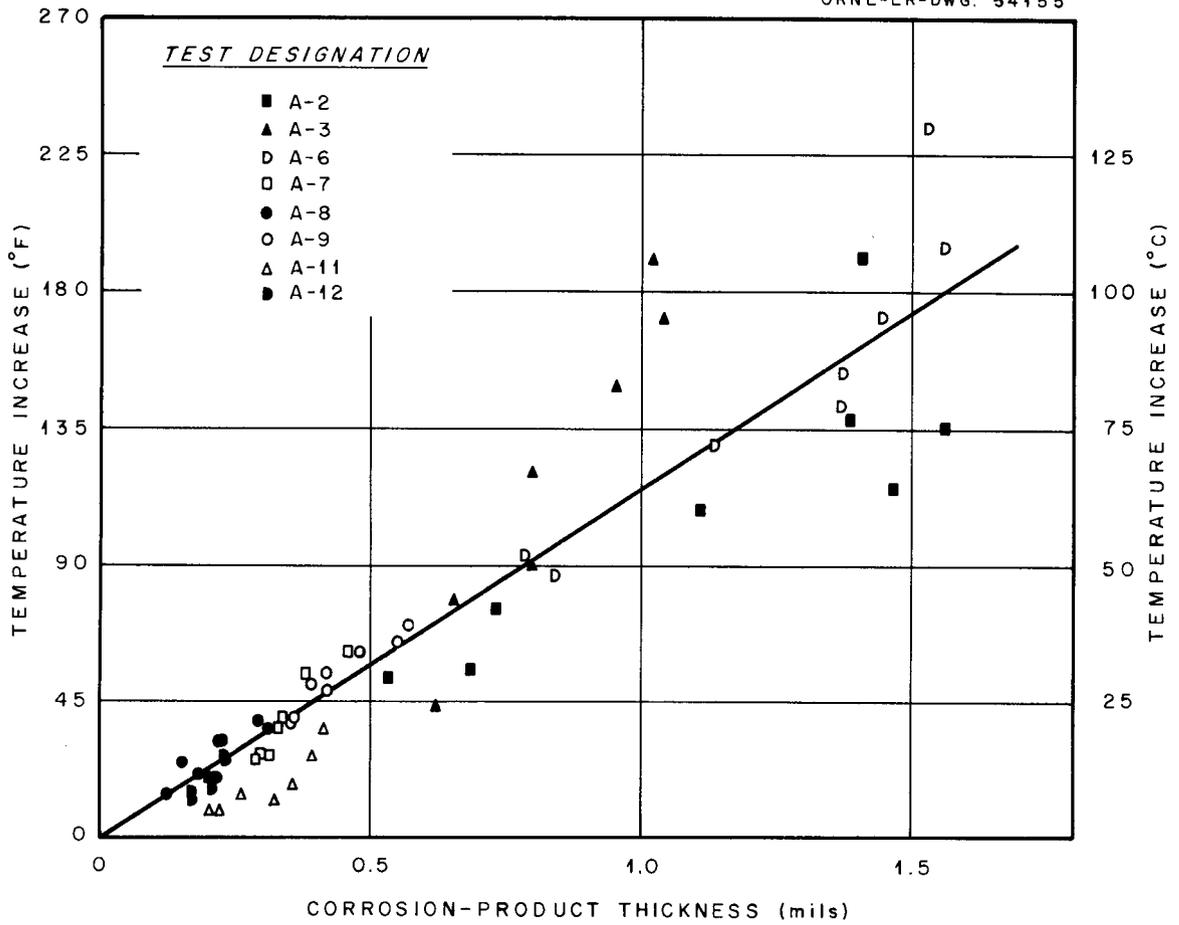


Fig. 14. Relation Between Oxide Thickness and Temperature Drop Across Oxide.

10% H_2SO_4 at 170 to 185°F appeared to remove practically all the oxide from the specimen in approximately 30 minutes.

During the first phase of the test, high-purity water flowing at 37 fps was used as coolant. The inlet and outlet water temperatures were 149 and 185°F, respectively. The heat flux was 1.5×10^6 Btu/hr·ft². During a 143-hr test the temperature increased at all thermocouple locations in a normal fashion. After 143 hr the specimen was thermally cycled by turning the power on and off at 5-second intervals for a 5-minute period. This thermal cycling did not result in changes in the temperature when normal operation was resumed, indicating that none of the oxide was removed during this cyclic treatment. Following the thermal cycling, the flow rate of the water was increased from 37 to 46 fps for a 19.5-hr period. After readjusting the flow rate to 37 fps, the temperatures at all locations returned to their extrapolated values, indicating no film removal as a result of the increased flow rate. Without interrupting the test, the pH of the water was adjusted to 5.2 with nitric acid, and the test was continued under the same conditions for the next 78-hr period, at the end of which time the nitric acid was removed from the water by means of the mixed-bed ion exchanger. The test was continued using high-purity water as coolant for the next 90 hr, at the end of which time the specimen was removed from the loop and descaled with the chromic acid - sulfuric acid solution.

The rate at which the temperature increased at all thermocouple locations during the three periods of test is shown in columns 3, 4, and 5 of Table 3. The results of the first part of the test in which the coolant was high-purity water are shown in column 3. The rate of temperature rise

was comparable to that shown in tests A-2 and A-6 (see Table 2). Lowering the pH to approximately 5 resulted in lower rates of temperature increase (column 4), rates similar to those observed in the pH-5 tests, A-7 and A-8 (see Table 2). Removal of the nitric acid from the water caused an increase in the rate of temperature rise (column 5), although the rate of rise was not as high as was observed in the first part of the test.

Table 3. The Rate of Temperature Increase at Various Locations During Parts of Test A-10

Thermocouple Number	Distance from Inlet (in.)	Rate of Temperature Rise (°F/day)			
		High-Purity	HNO ₃ *	High-Purity	CO ₂
7	0.25	4.5	0	2.9	22
12	1.00	-	-	-	-
3	1.25	7.6	2.2	4.9	11
10	2.25	8.8	2.2	4.9	50
4	3.25	10.6	3.4	5.8	94
6	3.25	10.3	2.7	4.9	104
9	4.25	12.1	4.0	8.6	40
5	5.25	15.5	4.0	10.0	142
11	5.50	15.7	5.0	11.0	230
8	6.25	9.0	2.2	11.0	200

*pH = 5.2

The second phase of test A-10 was conducted to determine if carbon dioxide dissolved in the water would produce an effect similar to that produced by nitric acid at a pH of 5. A concentration of carbon dioxide of 2000 ppm in the coolant was maintained by pressurizing the feed tank with 50 psi of carbon dioxide. Although this concentration of carbon dioxide in water produces a pH of less than 5 (approximately 4) at room temperature, it is known that the dissociation constant of the acid decreases at high temperature, and it was hoped that the pH of the solution

in contact with the heated walls would be in the range of 5. Except for the carbon dioxide, the test conditions were the same as those during the first part of the test.

When the power was turned on, all temperatures measured on the outside of the aluminum were slightly higher than those at the start of the first part of the test, indicating that most of the oxide had been removed in the cleaning process, but that a small amount still remained. This part of the test was continued for only 20 hr because the rate of temperature increase was very high. The actual values obtained are shown in column 6 of Table 3. The high metal temperature at the end of the test indicated a substantial oxide film, and for that reason the specimen was again removed from the loop and descaled in the chromic acid - sulfuric acid solution.

At the start of the third phase of test A-10, the pH of the coolant was adjusted to 4.0 with nitric acid; the other conditions were the same as in the first two parts of the test. When the power was turned on, the initial thermocouple readings were very close to the original values, indicating that practically all the oxide had been removed during the second cleaning treatment.

Figure 15 shows the temperature as indicated by two typical thermocouples and the operating variables that were changed during the course of the test. Throughout most of the test, thermocouples 6, 4, and 8 gave readings similar to thermocouple 9; that is, where sudden changes were noted in one they were usually observed in the others. Thermocouples 5 and 10 yielded temperature-time curves similar to that of thermocouple 11. Thermocouples 7, 3, and 12 apparently became detached during the cleaning

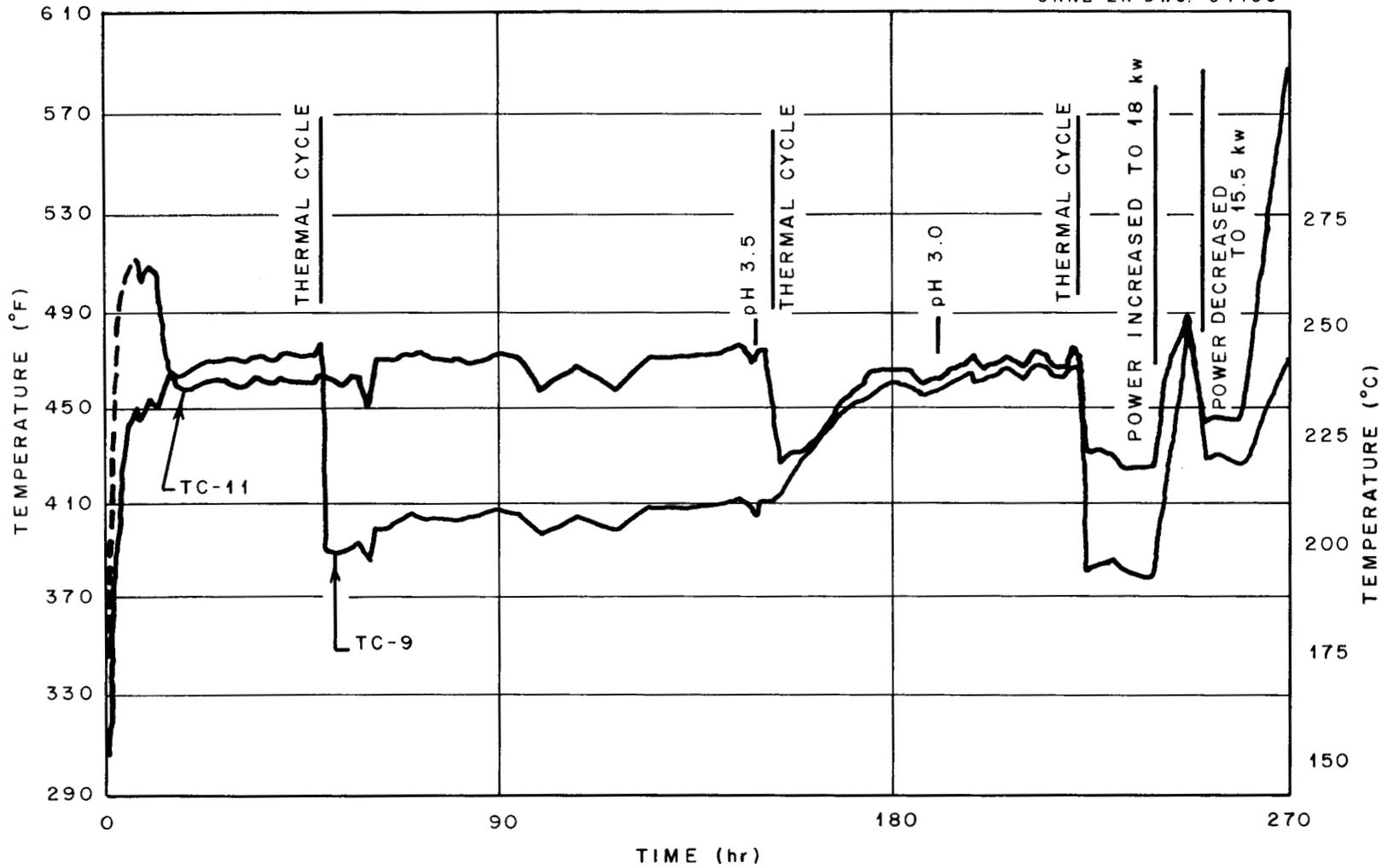


Fig. 15: Temperature of the Aluminum Test Specimen During the Third Phase of Test A-10.

of the specimen and did not give meaningful readings (see Fig. 2 for thermocouple locations).

During the first three to four hours of test at pH 4, the temperature of the specimen increased rapidly. It was interesting to note that thermocouples 9, 6, and 4 which were located in the middle part of the specimen showed greater temperature increases and reached higher temperatures than did thermocouples 11 and 5 which were located near the outlet of the specimen. As indicated in Fig. 15, the higher-reading thermocouples showed spontaneous drops in temperature, probably indicating some spalling of the oxide from the aluminum surface. After 49 hr of operation the specimen was thermally cycled by turning the power on and off at 5-second intervals for 3 minutes. At those locations with the higher temperatures, large temperature changes resulted from the cycling. At the other locations essentially no changes in temperature occurred. For the next 100 hr of test all temperatures increased uniformly at a slow rate. Changing the pH of the water gradually from 4 to 3.5 over a period of several hours appeared to have no effect on the rate of temperature change.

Thermally cycling the specimen again after 150 hr produced temperature drops of 20 to 40°F at the hotter locations but not at the other locations. However, following the thermal cycles, all temperatures increased at an appreciable rate for the next 20 hr and then continued to increase at a lower rate. As shown in Fig. 15, adjustment of the water to pH 3 seemed to have no effect on the rate of temperature change. Thermally cycling the specimen for the third time after 220 hr of the test produced marked decreases in temperature at all locations followed by a period during which all locations showed either no temperature change or very slight temperature

decreases. Increasing the power input from 15.5 to 18 kw raised the temperature of the specimen as expected. When the power was reduced to 15.5 kw, some of the temperatures returned to values nearly the same as before the power increase as typified by thermocouple 11, and others were appreciably higher as indicated by thermocouple 9. Following a 10-hr period during which temperatures changed very little, temperatures began to increase at all locations at a very high rate. After a total operating time of 269 hr, the test was terminated.

Figure 16 is a photograph of one half the specimen after it was removed from the electrodes and cut open. It can be seen that there was an appreciable and irregular oxide coating on the specimen. Large flakes of aluminum oxide had randomly spalled from the surface. Thermal cycling of the specimen apparently caused oxide to be detached in some places and not in others, a fact which accounted for temperature changes at certain locations and not at others during the cyclic treatments.

The corrosion product was scraped from one half of the specimen for identification. An examination of the x-ray diffraction pattern revealed only boehmite, $\alpha\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$. Chemical analysis of the oxide as removed from the specimen showed it to contain 39.8% aluminum, 1.1% iron, 0.1% chromium, and 0.2% nickel. Pure $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ contains 45% aluminum, a fact which indicates that the corrosion products retained some physically bound water.

The results obtained during test A-10 indicate that an optimum pH range exists where the rate of formation or deposition of oxide on the surface of an aluminum specimen subjected to a high heat flux will be at a minimum. At pH values of 3, 4, and near 7, greater rates of oxide deposition occurred than at pH 5. Further experimentation must be carried out

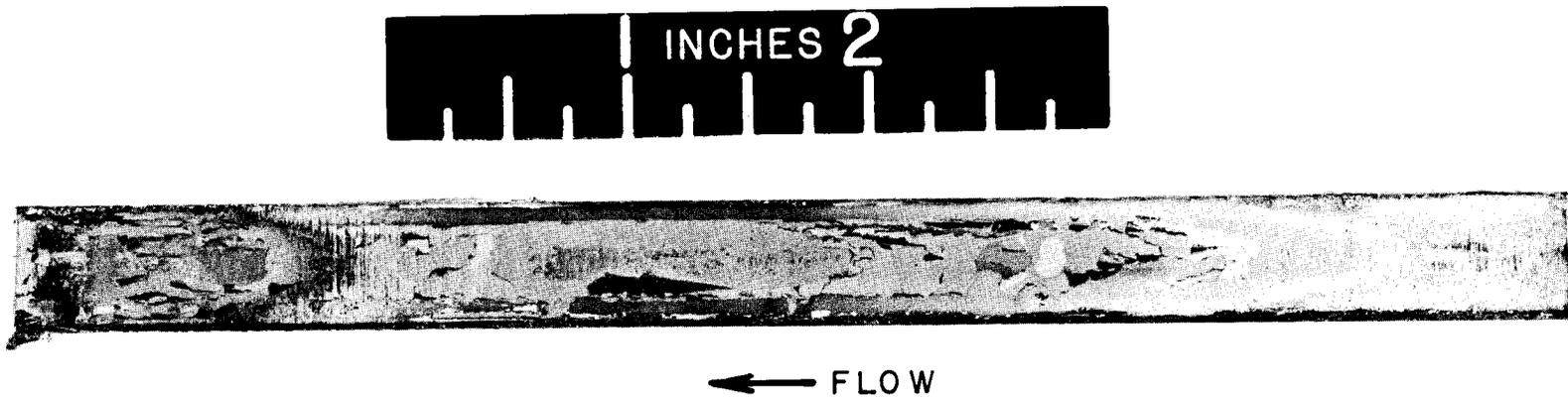


Fig. 16. Photograph of Specimen at Conclusion of Run A-10.

to determine the optimum concentration of nitric acid. Although not explored fully, it appears that carbon dioxide is not a suitable agent for lowering the pH of the coolant.

The results further indicate that if the corrosion-product oxide is sufficiently thin, probably less than 0.001 in., thermal cycling of the specimen does not result in corrosion-product removal. On the other hand, thermal cycling does remove some oxide from the surface if the oxide is sufficiently thick.

Corrosion

Since the test specimens were prepared by pressing a tube to form a very narrow channel through which the water flowed, and since the specimens were welded to electrodes, it was not possible to measure the thickness of the metal or weigh the specimens before test. It was, therefore, not possible to obtain a quantitative measure of the extent of corrosion damage. However, from the appearance of the specimens at the end of the tests, it was concluded that corrosion was not severe on any specimen except A-2, which has been described.³ Furthermore, metallographic examination of many sections through the specimens failed to show evidence of localized attack.

If one makes the assumption that all the corrosion product (boehmite) was retained on the surface of the aluminum from which it was formed and that the density of boehmite is 4 g/cm^3 (ref. 5), it is possible to calculate the thickness of the metal corroded. On the above basis 0.0010 in. of aluminum would form 0.0015 in. of boehmite. Referring to Fig. 14, it can be seen that the thickest oxide films occurred in the tests with high-purity water and averaged about 0.0015 in., which corresponds to an aluminum

penetration of approximately 0.001 in. On the same basis, the penetration of the aluminum would amount to less than one third of this value in most tests with pH-5 water.

It is implicit in the above analysis that under the conditions of the tests aluminum corroded less in the pH-5 water than in the high-purity water. Although it cannot be shown conclusively from the data in this report, others have shown that aluminum is more resistant to attack in slightly acid water than in neutral water.⁶

CONCLUSIONS

As a result of that part of the experimental program that has been completed, the following conclusions seem justified:

1. The corrosion of aluminum under conditions expected to exist in the High-Flux Isotope Reactor leads to the formation of an adherent, nearly transparent corrosion-product oxide which has a thermal conductivity of 1 Btu/ft²·hr·°F/ft. Thus as the corrosion product forms, the temperature of the aluminum increases under constant test conditions.

2. At a heat flux of 1.5×10^6 Btu/ft²·hr, the rate at which the oxide forms on aluminum surfaces is dependent on the pH of the coolant. The use of high-purity water or water adjusted to pH values of 4 or less with nitric acid or carbon dioxide causes more rapid film formation than does water adjusted to a pH of 5 with nitric acid.

3. The rate at which oxide forms on the water-cooled aluminum surface depends on the temperature of the coolant. For the coolant temperatures used, 131 to 223°F, the higher the temperature of the coolant, the greater was the rate at which the oxide film formed.

4. In the range of 34 to 48 fps there appears to be no effect of coolant velocity on the rate at which corrosion products build up on the water-cooled surfaces.

5. With sufficiently thin layers of corrosion products, usually less than 0.001 in. thick, thermally cycling the aluminum produces no apparent loss of oxide. On the other hand, the cyclic treatment usually causes the loss of some oxide from the surface when the oxide is relatively thick, probably much in excess of 0.001 in. thick.

6. Although quantitative corrosion rates of 1100 and 6061 aluminum alloys have not been determined, the appearance of the specimens at the conclusion of the tests described in this report indicated that corrosion damage was not severe. Metallographic examination of the specimens revealed no evidence of localized attack except in one case previously described.³

7. Under the conditions expected to exist during operation of the High-Flux Isotope Reactor, aluminum appears to have a high probability of being a successful cladding material. Corrosion damage does not appear to be a serious problem; and by adjusting the pH of the water to 5 with nitric acid, excessive fuel-element temperatures should not occur during the 10-day fuel cycle.

Although the results obtained to this point indicate that corrosion is not severe, it is essential that the actual extent of corrosion be determined. A new method of fabricating the specimen, which involves machining the specimen in two axial halves and joining the two by welding, is being developed. Using this method of fabrication, each half of the specimen can be measured before and after test and the extent of corrosion can be determined. Future tests will utilize such specimens to explore

the effects of pressure as related to boiling in the oxide film or at the oxide surface, pH, and alloy composition.

ACKNOWLEDGMENT

The authors wish to express their appreciation to M. T. Kegley for metallographic examination of the test specimens.

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