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PROJECT AQUARIUM: LABORATORY AND FIELD CORROSION TESTS FOR THE GENEVA CONFERENCE REACTOR

J. L. English
A. R. Olsen
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J. L. English, A. R. Olsen, and E. G. Bohlmann

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ABSTRACT

The unfavorable corrosion behavior of a group of Geneva Conference Reactor fuel elements during criticality tests in the Bulk Shielding Facility prompted a laboratory and field investigation to determine the cause or causes for the observed behavior. The laboratory tests were conducted in distilled water with source materials of 1100 aluminum used in the fabrication of Geneva and other types of fuel elements. The field tests were run in demineralized cooling water at the Bulk Shielding Facility with dimensionally rejected Geneva elements.

Relatively brief exposure periods in the laboratory tests resulted in an average corrosion rate of 0.6 mpy for 1100 aluminum; the rate decreased with time. In one case, severe pitting attack was traced to iron contamination on the surface of the aluminum. An extended pickling time with sulfuric-chromic acid solution to remove the contamination was effective in eliminating the attack. There was an indication that the nitric-hydrofluoric acid pickling solution used during the fabrication of Geneva elements instigated pitting attack on aluminum. The silicon-aluminum alloy used to braze the fuel plates to the aluminum side plates was found to be highly susceptible to pitting attack in distilled water.

In the field tests, during exposure periods of several months in demineralized cooling water, numerous pits penetrating 50% of the 17.5-mil-thick aluminum cladding on Geneva elements were observed; in one case, a 62% penetration occurred in 45 days. Some evidence was obtained that the effect of water flow was to minimize pitting attack and staining on an irradiated fuel element exposed in demineralized water.

SUMMARY

The results of laboratory and field tests concerned with the corrosion behavior of Geneva Conference Reactor fuel elements are summarized as follows:

1. The short-term corrosion behavior of 1100 aluminum in distilled water at room temperature was characterized by corrosion rates between 0.5 and 0.7 mpy. The rates decreased with time. With one exception, the attack was uniform.

2. An extreme sensitivity to pitting attack was experienced by 0.091-in.-thick 1100 aluminum sheet used for cover plates on MTR elements. The cause of the attack was attributed to surface contamination by iron. The removal of 0.15 mil of metal by pickling in sulfuric-chromic acid solution eliminated the pitting.

3. No conclusive evidence was obtained that the halide-containing flux used in the brazing process increased the susceptibility of aluminum to pitting attack. There was some evidence, however, that the nitric-hydrofluoric acid pickling solution used during fabrication of Geneva elements did promote pitting attack.

4. The staining and pitting attack observed on side plates of exposed Geneva elements was reproduced in laboratory tests with crevice-type specimens. The pitting attack was attributed to concentration-cell corrosion.

5. The corrosion rate for the 12.5% Si-Al brazing alloy was approximately the same as that for acceptable quality 1100 aluminum; however, the former was very sensitive to incipient pitting attack.

6. The 0.220-in.-thick aluminum used for Geneva-element cover plates corroded at a rate less than 0.1 mpy in the demineralized cooling water at the BSF. A very prolific but incipient pitting attack was observed, however.

7. Corrosion products removed from a dummy 1100 aluminum element exposed in the BSF contained 540 ppm of uranium and 3500 ppm of fluoride. The presence of the fluoride was attributed to residual brazing flux on the element. The presence of uranium was attributed to contamination during rolling or to penetration of the cladding of an active element in the BSF core lattice.

8. Highly selective attack was found on the 12.5% Si-Al brazing alloy at a number of areas on the dummy 1100 element. Other areas showed no selective attack. Laboratory tests did not disclose any acceleration in corrosion attack of braze metal deposited on 1100 aluminum.

9. Field tests with dimensionally rejected Geneva elements in the BSF pool water showed the elements to be subject to severe staining and to a moderately severe pitting attack. In one instance, a 62% penetration of the 17.5-mil-thick cladding thickness occurred by pitting during a 45-day exposure. Numerous pits penetrating 50% of the cladding thickness were observed. The use of various surface-cleaning treatments failed to eliminate the pitting susceptibility of the elements.

10. Visual examination of an irradiated Geneva element exposed in the flowing demineralized cooling water in the LITR gave evidence that the movement of water through cooling channels of the element markedly reduced staining and pitting attack, as compared with elements exposed in the quiescent BSF pool water.

INTRODUCTION

On June 20, 1955, ten fuel elements clad with 1100 aluminum were examined prior to shipment to Switzerland for use in the Geneva Conference Reactor. The elements were examined at the Bulk Shielding Facility after removal from the reactor core lattice, which is cooled by demineralized water. The elements had been in contact with water for a period of two weeks while a series of low-power criticality tests were being run. Since the reactor was not operated continuously during this period, there were frequent intervals when the core was contacted by quiescent water. When the reactor was in operation, convection currents induced some movement of cooling water through the core lattice.

Examination of the elements disclosed a form of corrosion that has been observed frequently on MTR and BSF fuel elements after extended immersion periods in quasi-stagnant cooling water.[1] The corrosion was observed on a majority of the elements and consisted primarily of pitting attack. The attack was concentrated mainly along the areas where the fuel plates were brazed to the supporting side plates, with pits extending randomly along the full length of the brazed regions. Random pits also persisted over the entire surfaces of the two outermost plates (top and bottom) of a number of the elements. Since the aluminum-cladding thickness was only 0.0175 in. (17.5 mils), the pitting on the active fuel-plate surfaces was cause for concern as to the life expectancy of the elements.

The side plates (1100 aluminum) exhibited corrosion of a type that has not been observed on BSF fuel elements. Large areas were covered with heavy, dark gray-black stains, and the periphery of the stains was defined by a narrow band of white corrosion products and shallow pits. It was not expected that the pitting would reduce the useful life of the elements, since the side plates were 0.110 in. thick. As to the staining, Sawyer and Brown have reported that the staining of aluminum, in boiling water particularly, is usually attributed to an optical effect produced by slight etching and is not generally caused by the deposition of colored corrosion products.[2]

As a result of the corrosion of the Geneva elements, a two-phase study was undertaken to determine possible causes for the observed behavior. The first phase dealt with laboratory tests to (1) attempt to reproduce the observed effects and (2) examine various surface treatments as a possible method for eliminating or reducing the attack. The second phase was a study of the corrosion behavior of dimensionally rejected Geneva fuel elements that were exposed in the cooling water of the BSF.

EXPERIMENTAL STUDIES

Test Materials and Environment. The 1100 aluminum materials used in the laboratory corrosion studies were, with one exception, selected randomly from existing supplies at the Rolling Mill building where the Geneva and other elements are fabricated. The exception was 1100 aluminum obtained from X-10 Material Stores, which was used in a few tests.

Three different thicknesses of aluminum sheet, generally used in the fabrication of fuel elements, were selected: (1) 0.091-in.-thick sheet, used for the cover plates on the inner fuel plates of MTR elements; (2) 0.125-in.-thick sheet, used for cover plates on the two outermost fuel plates of MTR elements; and (3) 0.220-in.-thick sheet, used for cover plates on all fuel plates in the Geneva elements.

Corrosion specimens 1 x 4 in. in size were sheared from 4 x 12 in. rectangles of the source materials. No attempt was made to remove the sheared edges since these areas were not considered in the evaluation of pitting attack. A silicon-aluminum alloy, used for brazing the fuel plates to the side plates, was procured from the Rolling Mill as 0.063-in.-thick sheet and was also sheared into 1 x 4 in. specimens.

Chemical compositions of the test materials are given in Table 1. The four 1100 aluminum alloys were within the chemical composition limits for the commercial-grade alloy.

Table 1. Chemical Composition of 1100 Aluminum* and Brazing Alloy

Element	Composition (wt %)				
	0.091-in.	0.125-in.	0.125-in.**	0.220-in.	Brazing Alloy
Cu	0.10	0.13	0.14	0.13	< 0.01
Fe	0.50	0.51	0.62	0.51	0.19
Si	0.17	0.13	0.10	0.05	12.50
Mn	< 0.05	< 0.05	< 0.05	< 0.05	-
Zn	< 0.01	< 0.01	< 0.01	< 0.01	-
Al	Balance	Balance	Balance	Balance	Balance

* Nominal chemical composition ranges for 1100 aluminum alloy include: Al, 99.0 min.; Fe plus Si, 1.0 max.; Mn, 0.05 max.; Zn, 0.10 max.; and Cu, 0.20 max.

** Material from X-10 Material Stores; identified as Lot 1.

The laboratory corrosion tests were conducted in a single environment, nonaerated distilled water at room temperature. During the corrosion study, which covered the period between June and November, 1955, the distilled-water supply was analyzed at biweekly intervals. Complete water analyses were not obtained, but rather the analyses were restricted to certain ionic species, such as iron, copper, fluoride, etc., which under certain conditions are capable of interfering with the continuity of the protective hydrated oxide film formed on aluminum. A summary of the water composition over the above period is shown in Table 2.

Table 2. Composition of Distilled Water Used for Corrosion Tests

Resistivity at 25 ± 10°C, ohm-cm	$2.0\text{-}3.5 \times 10^5$
pH	5.8-6.9
SO_4, ppm	0.5-1.0
F, ppm	< 0.2
Cl, ppm	< 0.2
Fe, ppm	< 0.1
Cu, ppm	0.1-0.5
Total dissolved solids, ppm	1-2

No attempt was made to control the water temperature during the corrosion tests; the ambient temperature varied between 15 and 35°C. The test containers were 4-liter Pyrex glass beakers covered with several layers of cheesecloth to prevent accumulation of dust particles in the container and to permit solution access to air. Distilled water was added periodically to replace evaporation losses. The ratio of solution volume to specimen surface area in all tests was between 35 and 60 ml/cm^2.

Test specimens were removed after various exposure intervals for examination and for weighing to the nearest 0.1 ± 0.2 mg. Generally, in order to preserve the growth of corrosion products at localized areas, the specimens were not scrubbed at these times. The specimens were chemically cleaned at the end of the tests.

The cleaning or defilming treatment consisted of placing specimens in 5% H_3PO_4-2% CrO_3 solution (by weight) for 45 min at 80 ± 2°C. The treatment removed all voluminous deposits of corrosion products but did not remove the last traces of deposits in the deeper pits even after several cycles. The defilming treatment was repeated two and three times on all specimens to insure as complete removal of corrosion products as possible. The attack by the defilming solution on unexposed aluminum specimens was 0.03 mg/cm^2 (0.005-mil penetration) in a 45-min period.

General Corrosion Studies. The short-term corrosion behavior of the 0.091-, 0.125-, and 0.220-in.-thick 1100 aluminum source materials was first examined. The results of the tests with sets of duplicate specimens appear in Table 3.

Table 3. Corrosion of 1100 Aluminum Sheet by Nonaerated Distilled Water at Room Temperature

Thickness (in.)	Exposure Time (days)	Corrosion Rate (mpy)	Deepest Pit-Depth Range (mils)	Average Number of Pits per cm^2
0.091	28	0.6*	3.0-6.1	1.4-1.7
0.125	7	0.7	Negligible	Negligible
0.220	7	0.5	Negligible	Negligible

* Prolific pitting attack observed during the first 7 days of exposure.

The most significant feature of the experimental data was the prolific pitting on the 0.091-in.-thick aluminum, which manifested itself during the first 7 days of a 28-day test. The deepest pit-depth range was 3.0 to 6.1 mils, based on microscopic measurement of five of the

deepest-appearing pits. (The deepest pit-depth range was determined in a similar manner for all tests subsequently reported.) Pitting frequency on the specimens varied between 1.4 and 1.7 pits/cm^2 (edges excluded). Many of the pits contained bulky deposits of white, hydrated aluminum oxide. The centers of the larger-sized deposits also contained a black-colored crystalline-appearing constituent. A few of the black particles were carefully removed for examination and were found to be magnetic, indicating the presence of magnetic iron oxide, Fe_3O_4. Spectrographic analysis showed the particles to be rich in iron. It was postulated that the surfaces of the 1100 aluminum sheet as supplied were contaminated with metallic iron which underwent oxidation to magnetite during exposure in distilled water. The contaminated sites thus served as pit promoters in the aluminum. The corrosion rate, based upon total attack due to pitting and uniform corrosion, was 0.6 mpy. Figure 1 shows the development of pitting attack on the 0.091-in.-thick aluminum. The black centers of magnetite are clearly visible in the larger deposits.

No pitting attack was found on the 0.125- and 0.220-in.-thick specimens, which corroded at average rates of 0.7 and 0.5 mpy, respectively, during 7-day tests. The corrosion rates were of a decreasing order. Figures 2 and 3 show the initial and final condition of the 0.125- and 0.220-in.-thick specimens, respectively.

All specimens showed weight gains during the tests, the largest gain, 0.7 mg/cm^2, occurring on 0.091-in.-thick specimens during a 28-day test. Defilmed weight losses ranged from less than 0.1 to 0.3 mg/cm^2.

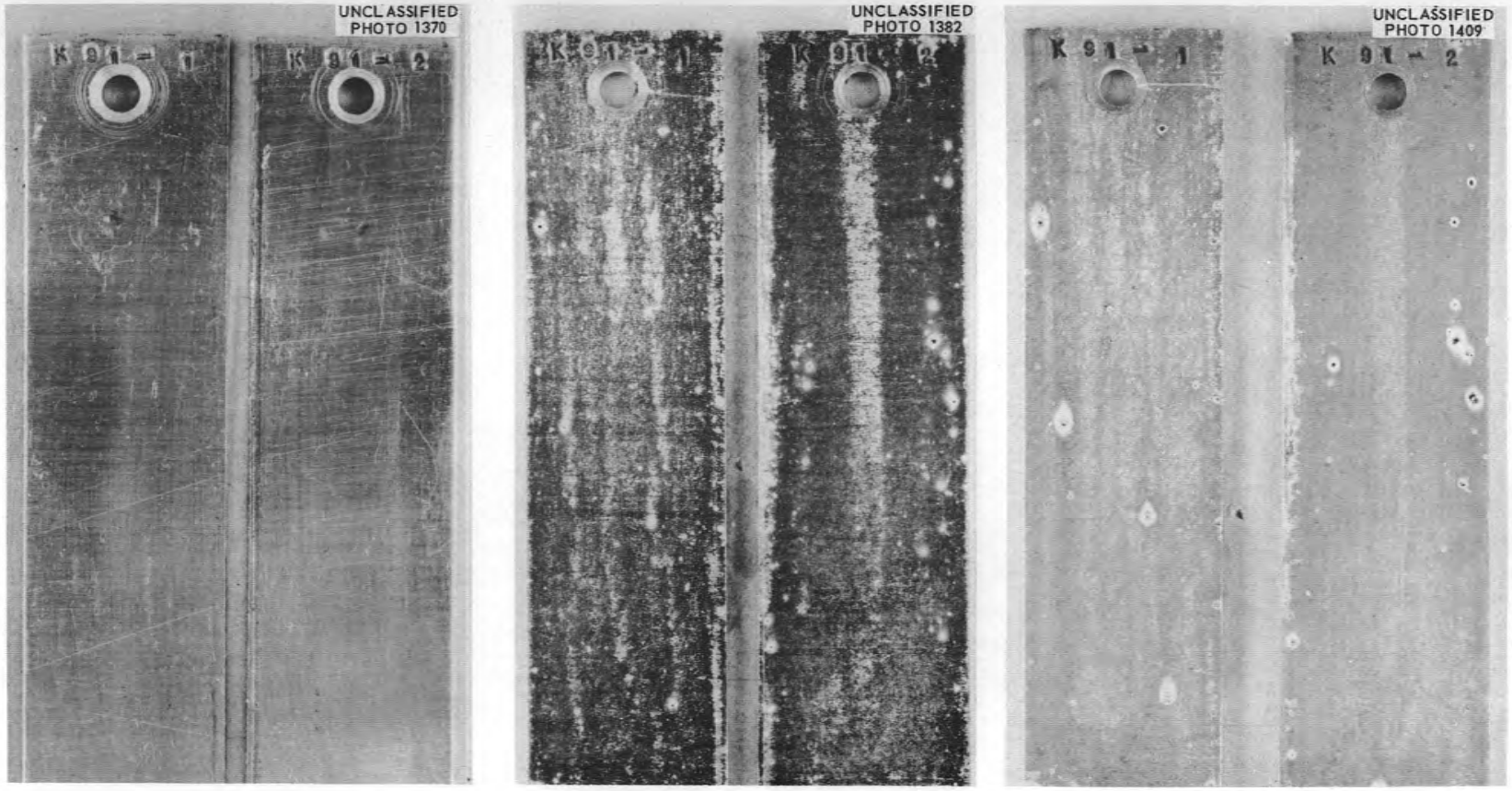
There was little change in the water chemistry during the tests. The resistivity decreased slightly to values of approximately 2×10^5 ohm-cm from an initial value of 3×10^5 ohm-cm. In the 7-day tests, the water pH decreased from 6.0 to 5.2; in the 28-day test the pH increased from 6.0 to 7.7.

Effect of Surface Condition. In additional tests with the 0.091-in.-thick aluminum, the effects of various surface treatments on the pitting susceptibility of the material were studied. The treatments included: (1) vapor degreasing with benzene, (2) vapor degreasing with trichloroethylene, and (3) pickling with a sulfuric-chromic acid solution.

The first treatment consisted of exposing specimens for 30 min in the vapors above chemically pure benzene. The purpose of the treatment was to remove any organic surface contamination that conceivably could initiate pitting attack.

The second treatment consisted of exposing specimens for 30 min in the vapors above boiling trichloroethylene. This treatment was used to determine whether residual amounts of the chlorinated solvent remaining on the surface would tend to promote pitting attack. Trichloroethylene is the solvent employed for vapor degreasing Geneva and other types of elements during fabrication.

The third treatment consisted of immersing specimens at 70 ± 3°C in a solution containing 10% H_2SO_4, 3% CrO_3, and balance water (by weight); after pickling, specimens were washed 15 min in flowing distilled water. Since the presence of magnetic iron oxide in the corrosion products formed

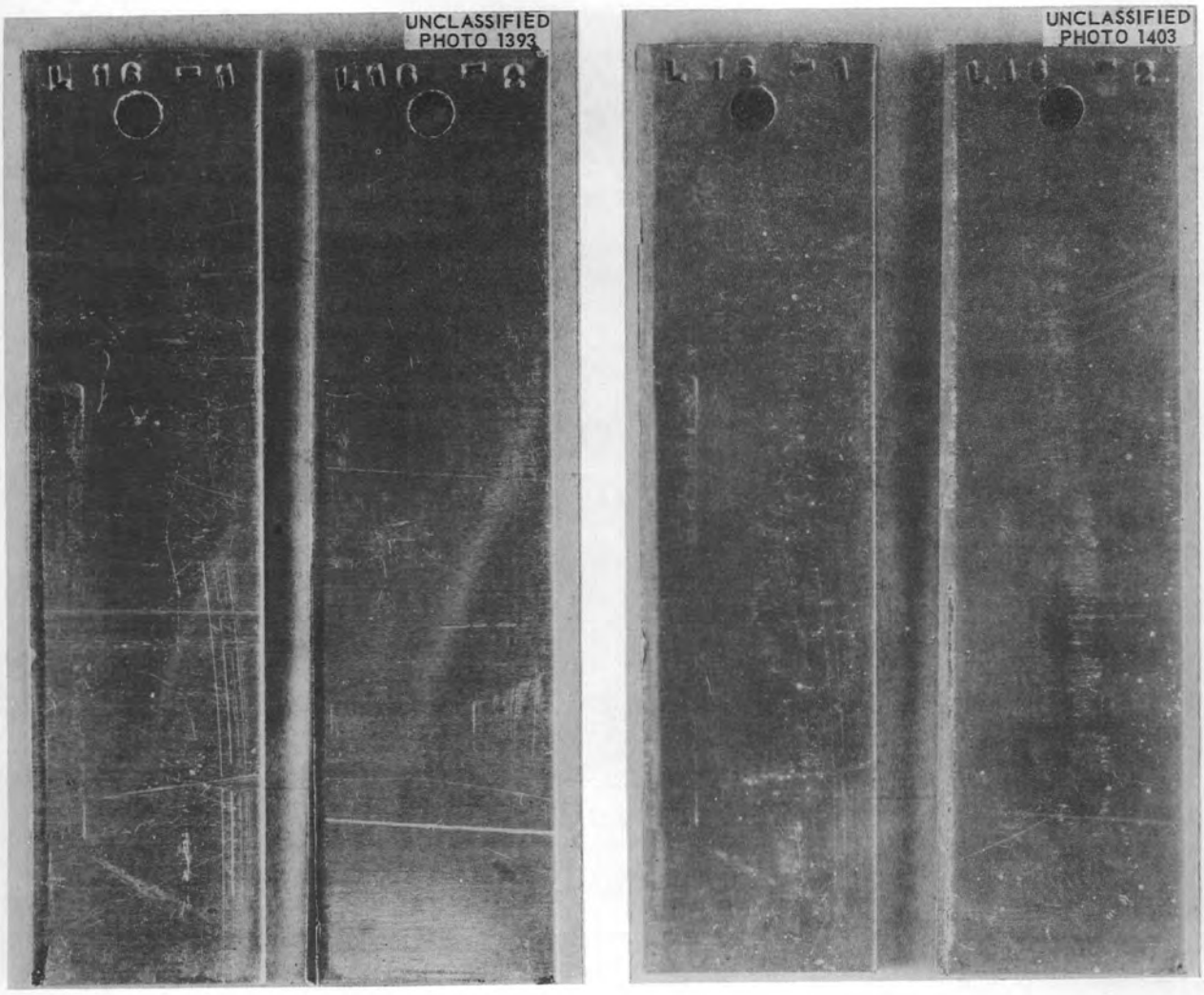


BEFORE TEST

7 DAYS

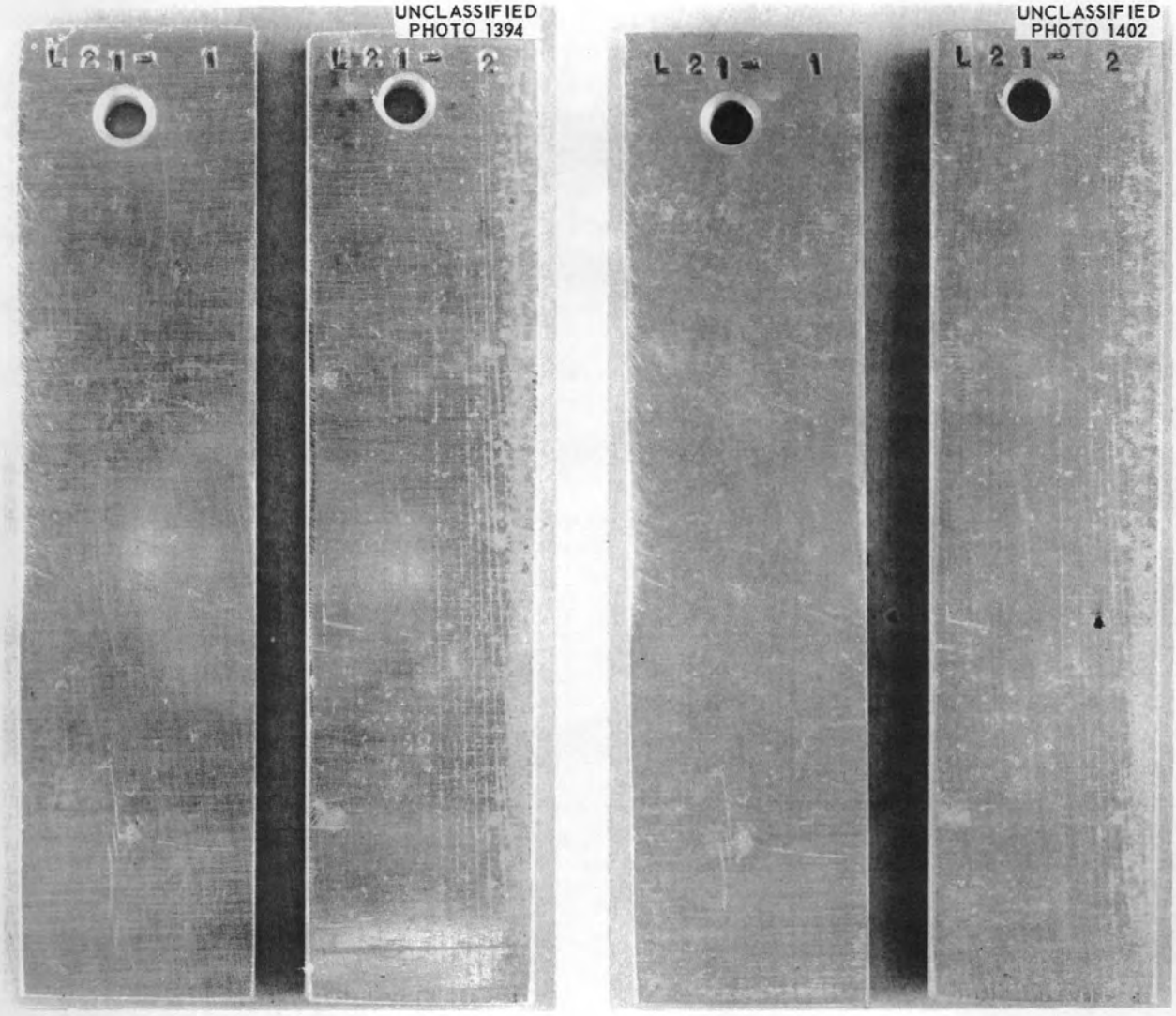
28 DAYS

Fig. 1. Development of Pitting Attack on 0.091-in.-Thick 1100 Aluminum in Distilled Water at Room Temperature. Specimen condition: degreased. Test K-91. 1.3X. Reduced 13%.



BEFORE TEST 7 DAYS

Fig. 2. Appearance of 0.125-in.-Thick 1100 Aluminum After Exposure in Distilled Water at Room Temperature. Specimen condition: degreased. Test L-16. 1.3X.



BEFORE TEST

7 DAYS

Fig. 3. Appearance of 0.220-in.-Thick 1100 Aluminum After Exposure in Distilled Water at Room Temperature. Specimen condition: degreased. Test L-21. 1.3X.

on the aluminum during the short-term tests indicated contamination of the surfaces with iron, it was felt that a pickling treatment to remove the contamination would also eliminate the susceptibility of the aluminum to pitting attack.

The metal loss on 1100 aluminum exposed in the pickling solution was determined for periods of 10, 20, 30 and 60 min. The results expressed as thickness loss vs time appear in Fig. 4. Each point represents the average of duplicate specimens, which agreed closely. The relationship between thickness loss and time was linear; the slope of the line was equivalent to a thickness loss of 0.005 mil/min. The 0.091-in.-thick specimens for the present study were pickled for 10 min; the metal removal, therefore, was 0.05 mil.

Duplicate specimens treated by each of the above methods were exposed in distilled water in separate flasks at room temperature for 28 days. A summary of the corrosion data appears in Table 4.

Table 4. Effect of Surface Treatment on the Corrosion of 0.091-in.-Thick 1100 Aluminum by Distilled Water at Room Temperature (Exposure Time: 28 Days)

Surface Treatment	Corrosion Rate (mpy)	Deepest Pit-Depth Range (mils)	Average Number of Pits per cm^2
Vapor degreased 30 min in benzene	0.7	3.8-6.7	1.1-1.2
Vapor degreased 30 min in trichloroethylene	0.7	4.0-5.7	1.6-2.5
Pickled 10 min at 70°C in 10% H_2SO_4-3% CrO_3	0.7	3.3-10.2	< 0.1-0.1

All specimens exhibited weight gains ranging from 0.7 to 1.0 mg/cm^2 upon completion of the tests; defilmed weight losses were between 0.3 and 0.4 mg/cm^2. Pitting attack in varying degrees of intensity and frequency was observed on all specimens. Pitting was first visible within 3 to 4 days from the start of the tests. The specimens also acquired a darkly stained appearance.

The pitting behavior of specimens that were vapor-degreased with either benzene or with trichloroethylene agreed closely with that of the 0.091-in.-thick acetone-degreased specimens reported in Table 3. The

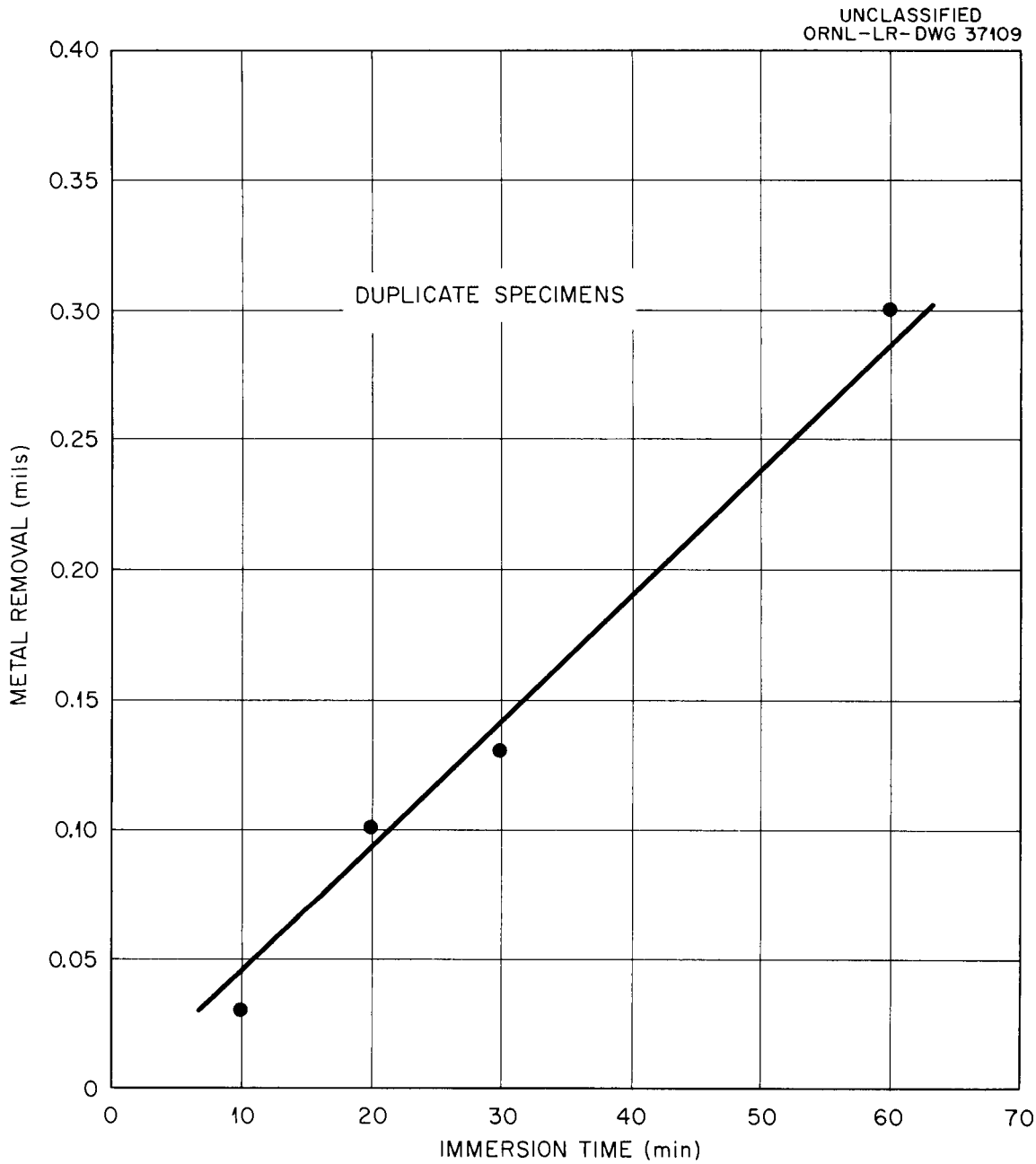


Fig. 4. Metal Removal Rate on 1100 Aluminum Immersed at 70°C in 10% H_2SO_4–3% CrO_3 Solution.

frequency of pitting in the present two tests varied from 1.1 to 2.5 pits/cm^2, and the deepest pit-depth range was 3.8 to 6.7 mils. The corrosion rate for both types of degreased specimens was 0.7 mpy. There was no indication that vapor degreasing with benzene reduced the pitting susceptibility of the specimens, nor was there any particular indication that vapor degreasing with trichloroethylene promoted the frequency of pitting.

The frequency of pitting on the pickled specimens was extremely low, 0.1 pit/cm^2 or less. The intensity of the attack was not reduced, however. The deepest pit-depth range was 3.3 to 10.2 mils. Generally, the pits were surrounded by far more voluminous deposits of corrosion products than were observed around pits on the benzene- or trichloroethylene-degreased specimens.

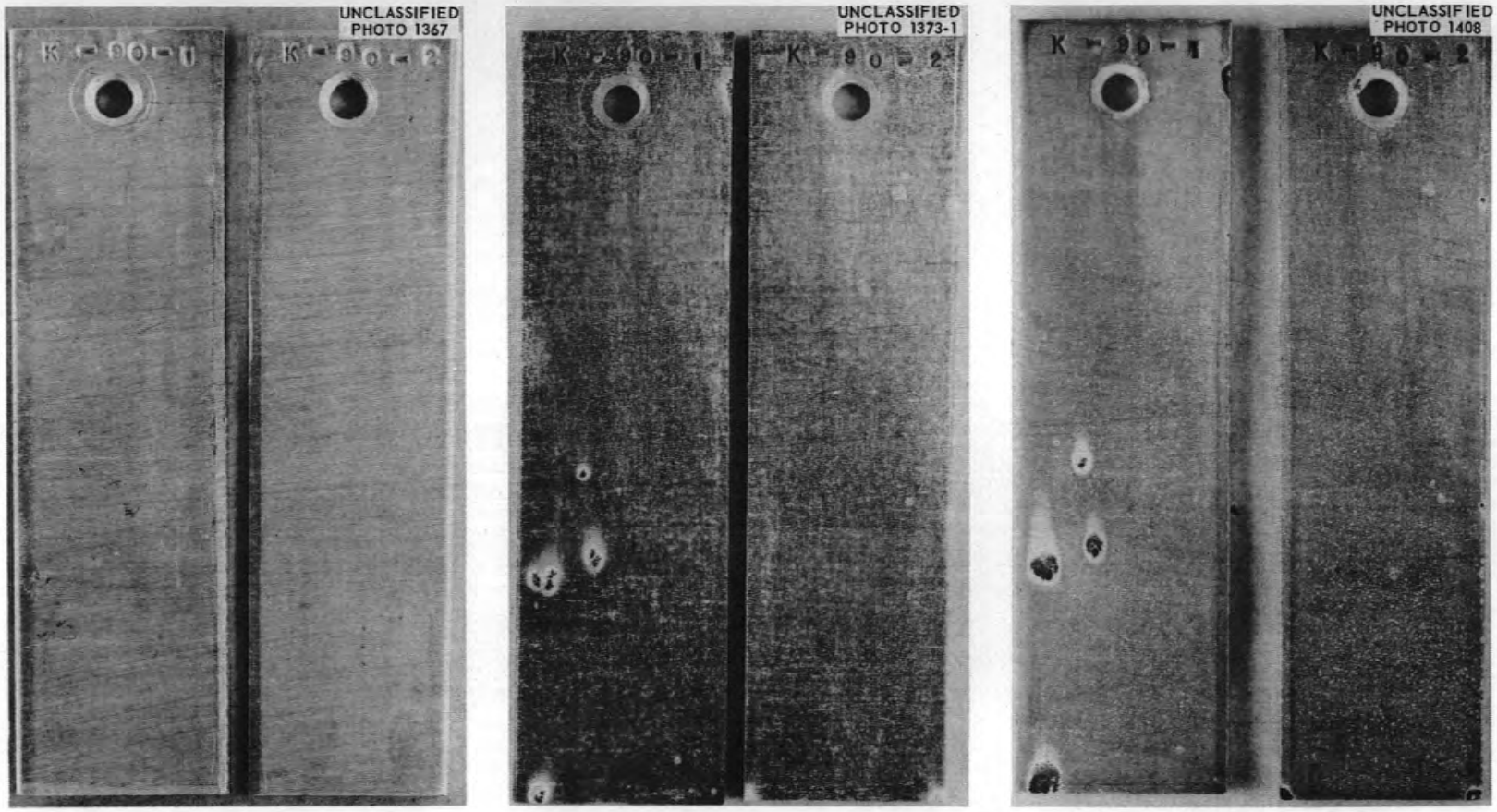
It was concluded that the removal of approximately 0.05 mil of metal by pickling in sulfuric-chromic acid solution was decidedly beneficial in reducing the frequency of pitting by eliminating the sites of iron-containing contamination. The amount of metal removed, however, was not sufficient to remove all the contamination, as evidenced by the fact that some pitting did occur. An extended pickling time to permit removal of several tenths of a mil of metal thickness may have completely eliminated the surface contamination.

Figure 5 shows the marked reduction in the incidences of pitting effected by the pickling treatment as compared with that on unpickled specimens of the 0.091-in.-thick aluminum in Fig. 1. An enlarged view of a pitted area is shown in Fig. 6. The black-colored areas are the particles of magnetic iron oxide.

The final water composition for the three tests showed a decrease in resistivity from 3×10^5 ohm-cm to approximately 1×10^5 ohm-cm. The pH in every case increased from an initial value of 6.3 to values between 7.3 and 7.7.

Brazed 1100 Aluminum. Specimens of 0.125-in.-thick aluminum from the Rolling Mill were brazed in the laboratory and subjected to various surface conditioning treatments prior to corrosion testing. The purpose of the tests was to determine whether the halide-containing flux used in the brazing operation was a source of surface contamination which increased the susceptibility to pitting attack in distilled water. Other objectives of the tests were to examine the possibility of galvanic corrosion between the brazing alloy-1100 aluminum couple and to study the efficiency of several cleaning methods for removing possible halide contamination from the aluminum surfaces.

The specimens were brazed in the laboratory under conditions approximating those employed in the Rolling Mill during fabrication of fuel elements. The sequence of operations for brazing the specimens was as follows:



BEFORE TEST 7 DAYS 28 DAYS

Fig. 5. Development of Pitting Attack on 0.091-in.-Thick 1100 Aluminum in Distilled Water at Room Temperature. Specimen condition: pickled 10 min at 70°C in 10% H_2SO_4–3% CrO_3 solution. Test K-90. 1.3X. Reduced 12%.

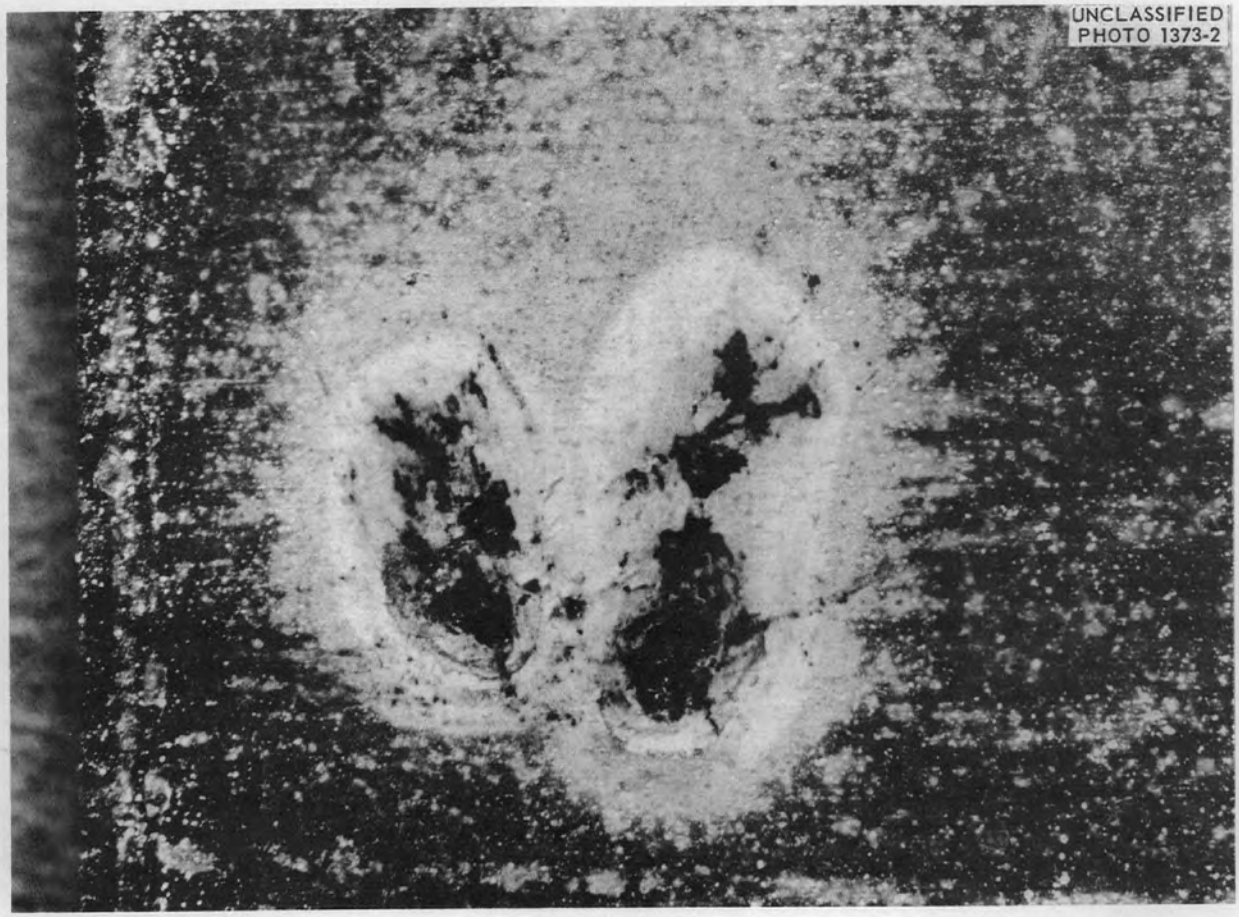


Fig. 6. Enlarged View of Pitted Area on 0.091-in.-Thick 1100 Aluminum After 28 Days in Distilled Water at Room Temperature. Black deposits in center of pits are magnetic iron oxide. Test K-90. 20X.

1. 1 x 4 in. test strips were sheared from 0.125-in.-thick 1100 aluminum. The 0.063-in.-thick brazing alloy was sheared into 1/2 x 1 in. pieces.

2. After degreasing in acetone, a 1-in.^{2} area near each end on one side of the 1 x 4 in. strips was painted with Eutector No. 190 brazing flux. The flux was prepared by mixing 3 g of dry flux with 2 ml of methyl alcohol.

3. A single piece of the 1/2 x 1 in. brazing alloy was placed on the fluxed area. The top side of the brazing alloy was then painted with flux.

4. The specimens were furnace-brazed in air for 1 hr at 607 $\pm$ 9°C (1125 $\pm$ 15°F).

5. The specimens were air-cooled to room temperature and washed for 1/2 hr in hot potable water.

Single brazed specimens were subjected to each of three surface conditioning treatments as follows:

1. Pickled 5 min at room temperature in 10% HNO_3-0.5% HF; washed 30 min in flowing distilled water.

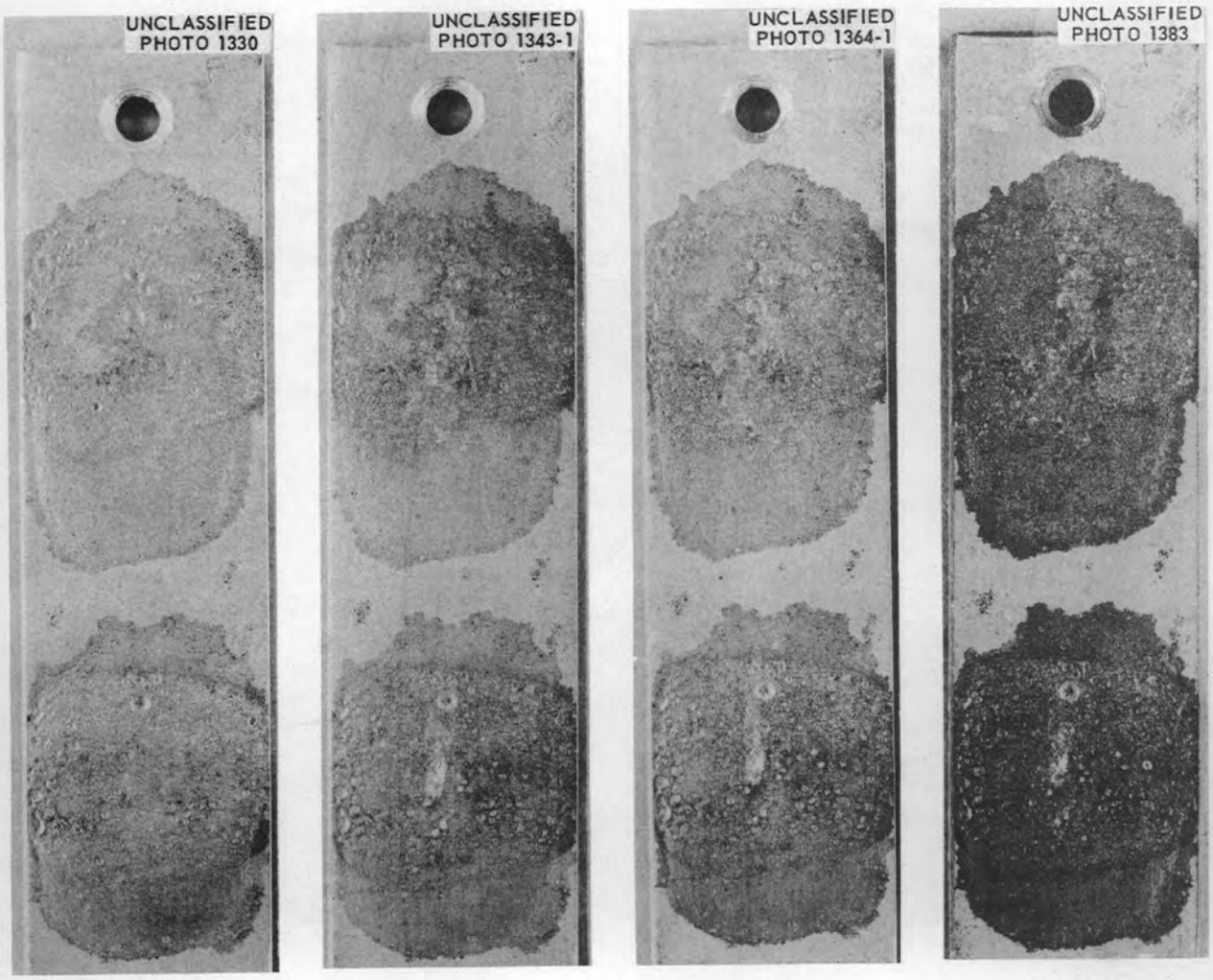
2. Pickled 15 min at 70°C in 10% H_2SO_4-3% CrO_3; washed 30 min in flowing distilled water.

3. Pickled 5 min at room temperature in 10% HNO_3-0.5% HF; washed 10 min in distilled water; immersed 3 min at 80°C in Ridoline No. 3192 alkaline cleaner (4 oz per gallon of water); washed 30 min in flowing distilled water.

The treated specimens and an as-brazed and washed control specimen were exposed in separate containers for 49 days in distilled water at room temperature. Specimens were not scrubbed prior to examination and weighing at numerous intervals during the tests. A summary of the corrosion data is shown in Table 5.

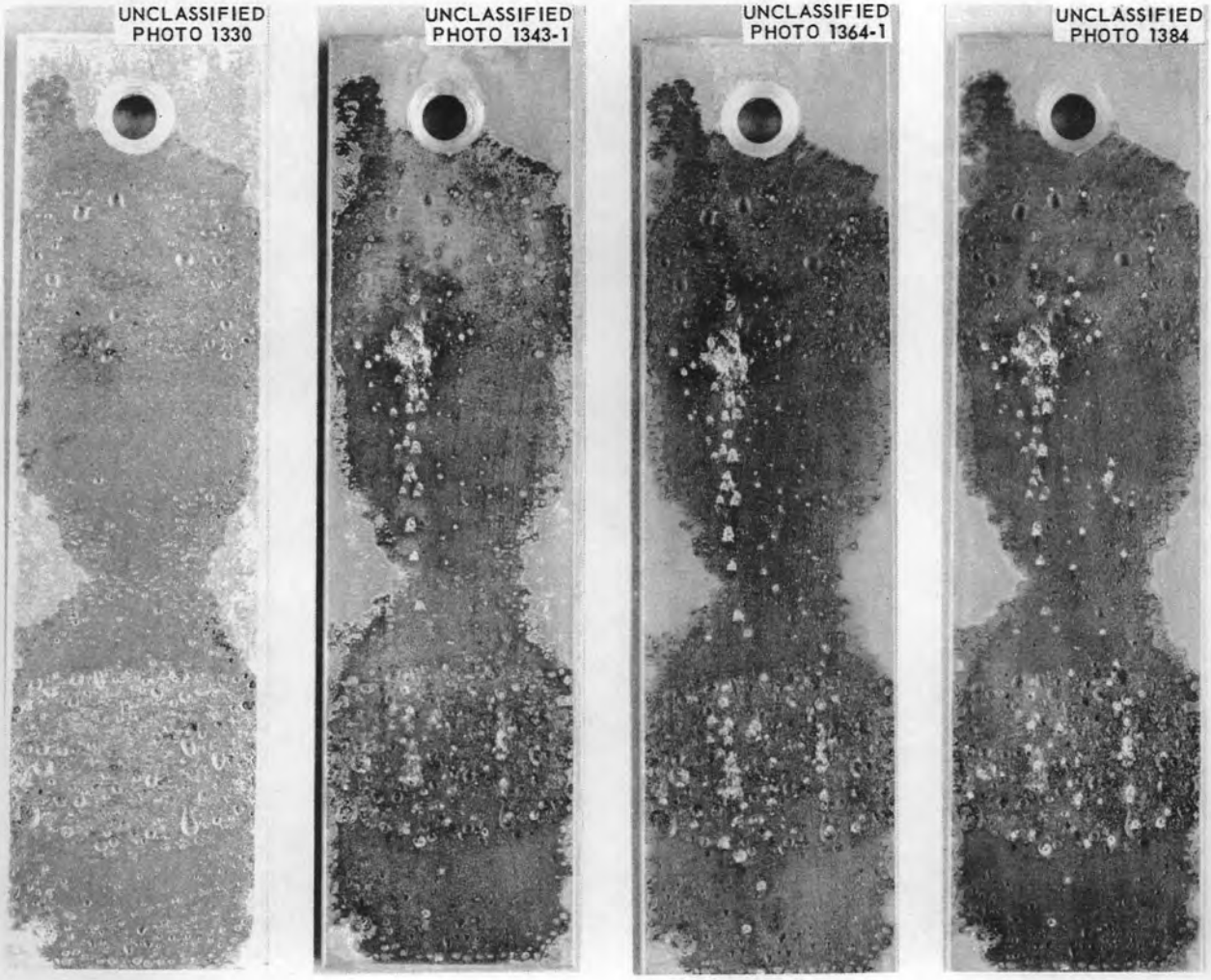
The as-brazed and washed specimen exhibited minor deposits of white corrosion products after 49 days. The deposits originated in the small smooth-faced pockets produced in the brazing alloy during heating. No active pitting was observed; the defilmed corrosion rate was 0.2 mpy. A photographic record of the specimen appearance during test is shown in Fig. 7.

Fairly voluminous deposits of corrosion products appeared on the nitric-hydrofluoric acid pickled specimen as shown in Fig. 8. Active pitting was observed; the deepest pit range was 2.1 to 9.2 mils. The pits developed during the first 7 days. The corrosion rate was 0.4 mpy.



BEFORE TEST 7 DAYS 14 DAYS 28 DAYS

Fig. 7. Appearance of As-Brazed 0.125-in.-Thick 1100 Aluminum During Exposure in Distilled Water at Room Temperature. Test J-98. 1.3X.



BEFORE TEST 7 DAYS 14 DAYS 28 DAYS

Fig. 8. Pitting Attack on Brazed 0.125-in.-Thick 1100 Aluminum by Distilled Water at Room Temperature. Specimen condition: pickled 5 min at 25°C in 10% HNO_3–0.5% HF solution. Test J-99. 1.3X.

Table 5. Effect of Surface Treatment on the Corrosion of Brazed 0.125-in.-Thick 1100 Aluminum After 49 Days in Distilled Water at Room Temperature

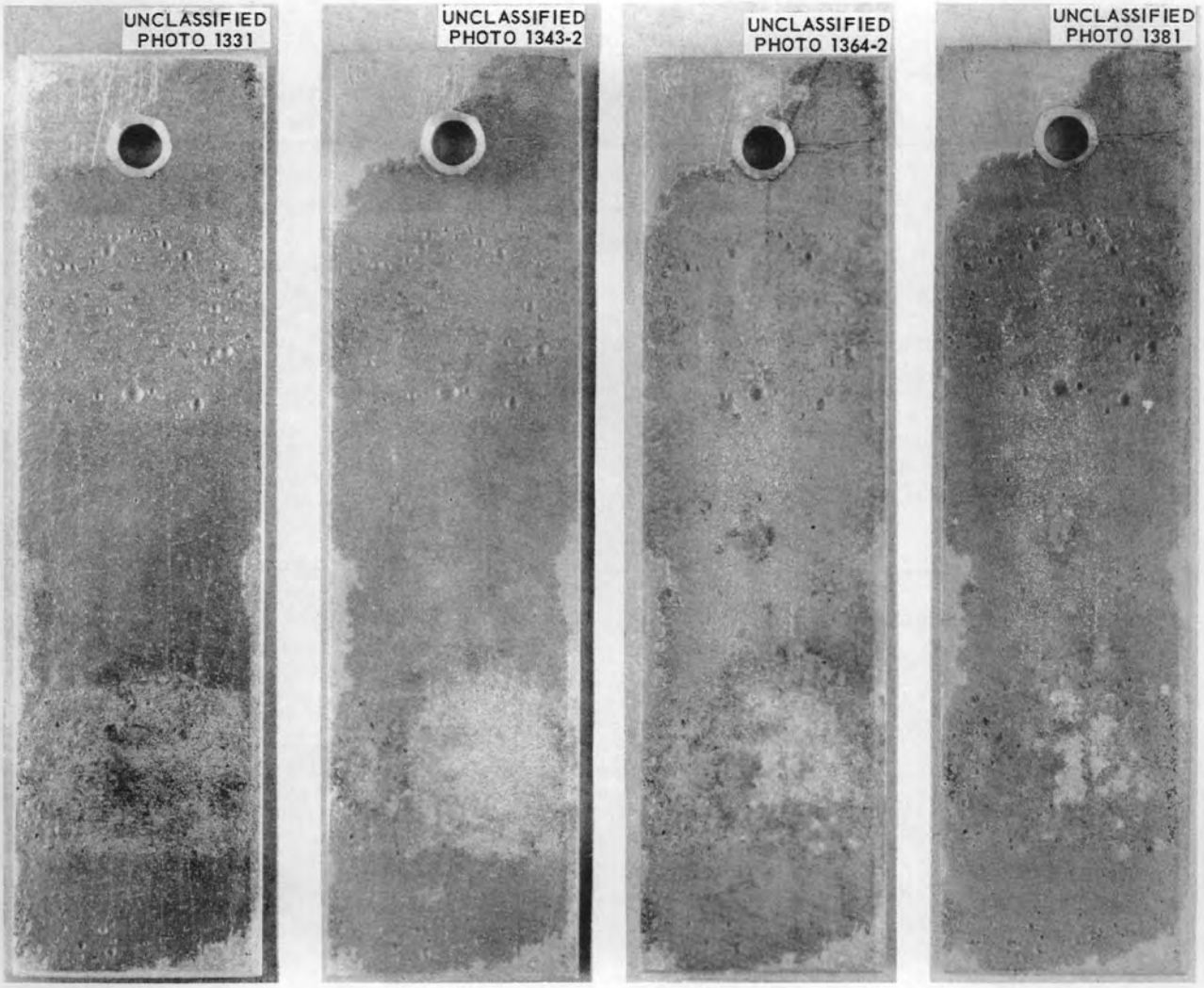
Surface Treatment*	Corrosion Rate (mpy)	Deepest Pit-Depth Range (mils)	Average Number of Pits per cm^2
As brazed	0.2	Negligible	Negligible
Pickled 5 min in 10% HNO_3-0.5% HF	0.4	2.1-9.2	0.3
Pickled 15 min at 70°C in 10% H_2SO_4-3% CrO_3	0.2	Negligible	Negligible
Pickled 5 min in 10% HNO_3 0.5% HF; washed, cleaned 3 min at 80°C in Ridoline 3192	0.5	1.9-7.9	0.5

* All surface treatments followed by washing for 1/2 hr in flowing distilled water.

The cleanest surface after 49 days was on the sulfuric-chromic acid pickled specimen. Not a single deposit of corrosion products was found; the defilmed corrosion rate was 0.2 mpy. Figure 9 shows the condition of the specimen during test.

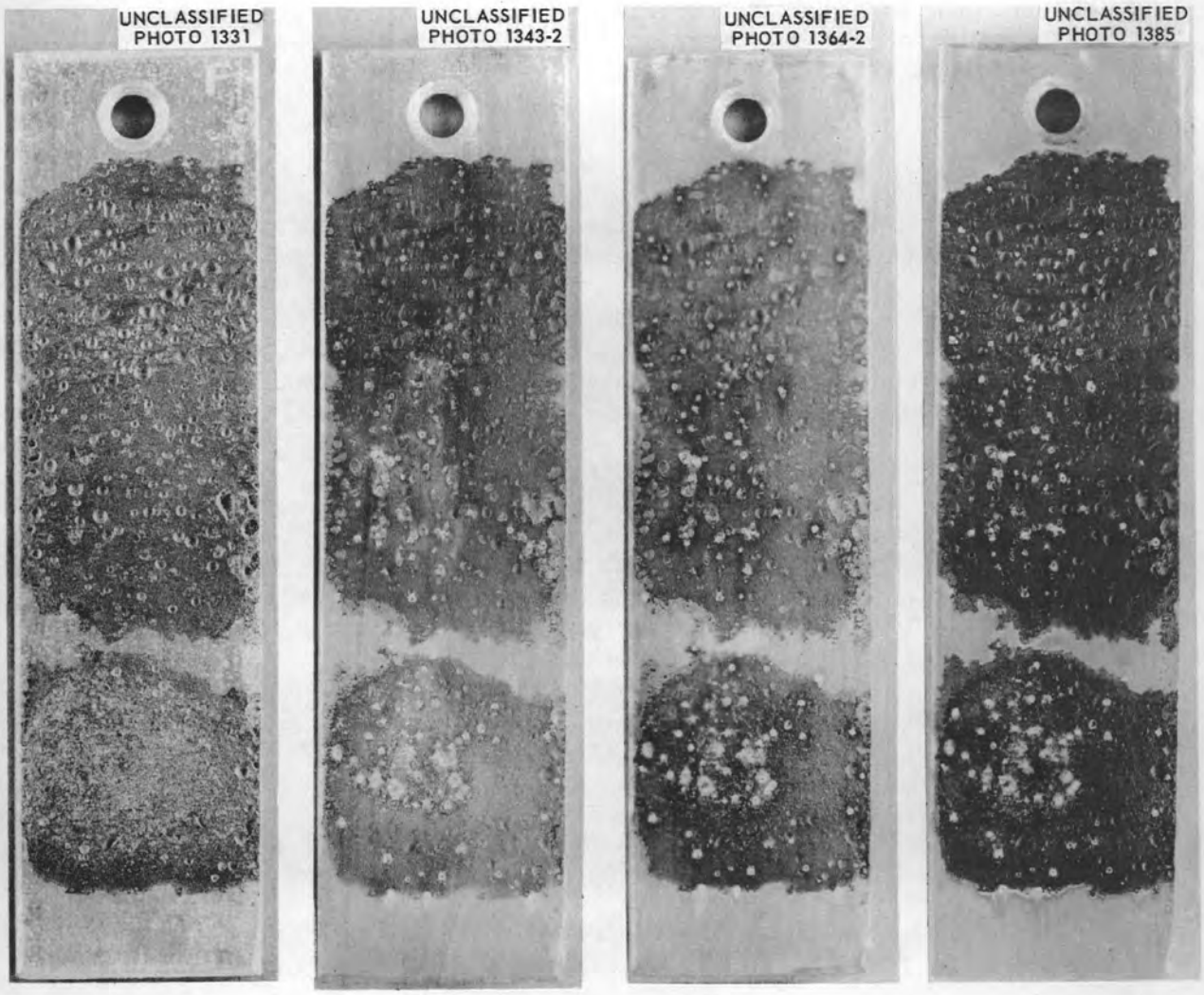
As shown in Fig. 10, bulky deposits of white corrosion products accumulated on the surfaces of the specimen that was pickled in nitric-hydrofluoric acid solution followed by alkaline cleaning in Ridoline 3192. Pitting attack occurred during the first 7 days; the range of the deepest pits was 1.9 to 7.9 mils. The defilmed corrosion rate was 0.5 mpy.

Although it has been suspected for some time that pitting observed on fuel elements was in part, at least, due to surface contamination with the fluoride- and chloride-containing brazing flux, the results of the present tests did not confirm this possibility. In fact, the experimental data indicated that the nitric-hydrofluoric acid pickling treatment (used during fuel element processing) is more apt to promote pitting upon subsequent exposure in water than is surface contamination from the halide-containing brazing flux. In both tests involving the use of the pickle, substantial pitting was experienced, with pits ranging up to 9 mils in depth. No pitting was encountered on the as-brazed specimen nor on the sulfuric-chromic acid pickled specimen. The latter specimen was completely



BEFORE TEST 7 DAYS 14 DAYS 28 DAYS

Fig. 9. Appearance of Brazed 0.125-in.-Thick 1100 Aluminum During Exposure in Distilled Water at Room Temperature. Specimen condition: pickled 15 min at 70°C in 10% H_2SO_4–3% CrO_3 solution. Test K-1. 1.3X.



BEFORE TEST 7 DAYS 14 DAYS 28 DAYS

Fig. 10. Pitting Attack on Brazed 0.125-in.-Thick 1100 Aluminum by Distilled Water at Room Temperature. Specimen condition: pickled 5 min at 25°C in 10% HNO_3–0.5% HF solution; washed 10 min in distilled water; cleaned 3 min at 80°C in Ridoline 3192. Test K-2. 1.3X.

free of visible corrosion products. One possible explanation for its behavior, other than the removal of surface nonhomogeneities which could induce pitting, was the presence of adsorbed chromate from the pickling solution which served as an inhibitor for suppressing attack. The protective nature of the chromate ion for controlling corrosion of aluminum by water is well known.

Careful examination of the braze metal and adjacent areas on the specimens disclosed no evidence of corrosion attack due to a galvanic couple between the silicon-aluminum brazing alloy and the 1100 aluminum. The observed over-all corrosion rates were similar to those that have been reported previously for 1100 aluminum (Tables 3 and 4).

Other than a decrease in resistivity and a slight increase in pH, the final water compositions for the four tests were little changed from the initial composition. There was no detectable increase in chloride and fluoride contents from the initial values of less than 0.2 ppm.

Crevice Tests with 1100 Aluminum. Mention was made in the Introduction of staining on the side plates of the Geneva elements as a result of exposure in the BSF pool. These black stains covered massive elongated-shaped areas which extended nearly the full length of the side plates. The periphery of a stained area generally consisted of a narrow band of white corrosion products and shallow pits, estimated visually to be 1 mil or less in depth.

The clearance between the vertically loaded Geneva elements in the BSF core lattice was approximately 1/32 in., and there was a definite possibility that "swaying" of the elements occurred in the loaded position so that some side plates on adjacent elements were in contact. Furthermore, when staining occurred on the side plate of an element, the side plate of the adjacent facing element was stained similarly.

One possible explanation was offered for the staining and pitting attack. During the criticality tests, there were numerous periods of reactor shutdown when the elements were contacted by quiescent water. Swaying of the elements to permit contact may have resulted in entrapment of a thin layer of water between side plates, thereby creating a condition favorable for the initiation of pitting and probably staining. For example, localized depletion of the dissolved oxygen in the water layer could lead to differential aeration cells which in turn cause pitting. Pitting attack could also be produced by metal-ion concentration cells under these conditions.

An attempt was made in the laboratory to reproduce the conditions that caused the staining and pitting. The specimen consisted of two pieces of 1 x 4 in. aluminum sheet, one placed on top of the other, with a 1/32-in.-thick polythene spacer between each of the two ends. The result was a "crevice," 1/32 x 1 x 3 in.

Five crevice-type specimens were prepared from 0.125-in.-thick aluminum. A sixth specimen was prepared from the 0.091-in.-thick aluminum that was so highly susceptible to pitting attack. Before testing, several of the specimens were subjected to various treatments similar to those given the Geneva elements during fabrication. Other specimens were treated by different chemical cleaning methods to remove any existing surface contamination or nonhomogeneities. A detailed description of the six surface treatments for the specimens follows:

1. Degreased in acetone and alcohol.

2. Pickled 15 min at 30°C in 7.5% HNO_3-0.5% HF; washed 10 min in hot potable water; washed 3 min in cold potable water (Geneva element treatment).

3. Washed 30 min in hot potable water (Geneva element treatment after one of the pickling operations).

4. Pickled 5 min at 30°C in 10% HNO_3-0.5% HF; washed 30 min in hot potable water; cathodically defilmed in inhibited 5% H_2SO_4 at 75°C; washed in distilled water.

5. Pickled 5 min at 30°C in 10% HNO_3-0.5% HF; washed 30 min in hot potable water; cleaned 10 min at 80°C in 10% Na_2CO_3-0.5% Na_2SiO_3; washed in distilled water.

6. Pickled 25 min at 70°C in 10% H_2SO_4-3% CrO_3; washed in distilled water.

A summary of the corrosion data for the above specimens is presented in Table 6. Tests were run for 28 to 78 days, with frequent examinations of specimens.

A pronounced staining, remarkably similar to that observed on the Geneva elements, appeared on the inner surfaces of all the specimens except the one which received the final cleaning in sodium carbonate-sodium silicate solution. Staining of the latter specimen was considerably less intense and had no particular orientation. The pitting information reported in Table 6 relates to the inner faces only; pitting was rarely encountered on outer faces of the specimens.

All specimens exhibited weight gains, ranging from 0.2 to 0.6 mg/cm^2; defilmed weight losses varied from less than 0.1 mg/cm^2 to 0.2 mg/cm^2. The observed corrosion rates were 0.5 mpy or less.

Staining and pitting on the specimen that had been degreased in acetone and alcohol are shown in Fig. 11 for three exposure intervals in a 64-day test. The stained area increased in size with increased exposure time. The deepest pit measured 10.7 mils, and the number of pits on the two inner faces averaged 1.2 per cm^2 of surface. A specimen that had been pickled in nitric-hydrofluoric acid solution and then washed in hot and cold water exhibited similar behavior except that the

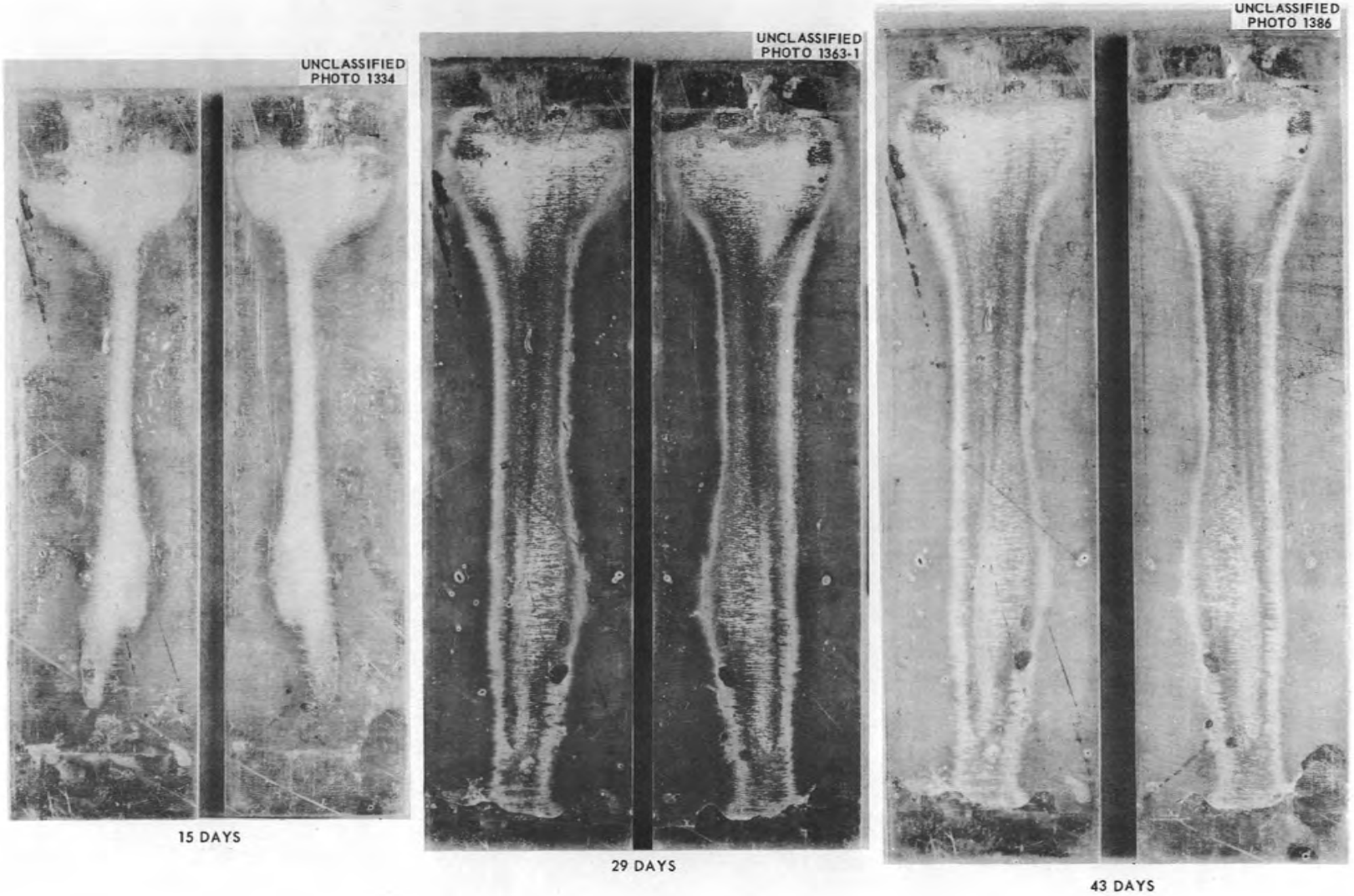


Fig. 11. Staining and Pitting on 0.125-in.-Thick 1100 Aluminum Crevice-Type Specimens by Distilled Water at Room Temperature. Specimen condition: degreased in acetone and alcohol. Test J-65. 1.2–1.5X. Reduced 17%.

pitting frequency was reduced to approximately 0.3 pits per cm^2. The latter observation indicated that, although staining still occurred, the pickling operation was at least partially successful in removing surface contamination or defects that were capable of initiating pitting attack.

Table 6. Corrosion of 0.125-in.-Thick Crevice-Type 1100 Aluminum Specimens by Distilled Water at Room Temperature

Specimen Treatment	Exposure Time (days)	Corrosion Rate (mpy)	Deepest Pit-Depth Range (mils)	Average Number of Pits per cm^2
Degreased in acetone and alcohol	64	0.2	2.6-10.7	1.1-1.3
Pickled in HNO_3-HF; washed in hot and cold potable water	64	0.2	1.8-7.9	0.2-0.3
Washed in hot potable water	78	0.2	2.3-6.2	0.7-0.8
Pickled in HNO_3-HF; washed in hot potable water; cathodically defilmed in H_2SO_4	78	0.2	Negligible	Negligible
Pickled in HNO_3-HF; washed in hot potable water; cleaned in Na_2CO_3-Na_2SiO_3	78	< 0.1	Negligible	Negligible
Pickled in H_2SO_4-CrO_3*	28	0.5	Negligible	Negligible

* 0.091-in.-thick aluminum specimen.

After a pickling operation on the Geneva elements, the practice was to wash the elements in hot and/or cold potable water. Since the water contained moderate amounts of chloride and heavy elements such as copper, iron, etc., a possibility existed that localized deposition of these elements on the aluminum surface could create sites favoring the promotion of pitting attack. To examine this possibility, one of the crevice-type specimens was exposed for 30 min in hot potable water and then immersed for 78 days in distilled water at room temperature. The condition of the inner faces after the test was much the same as shown in Fig. 11. Both

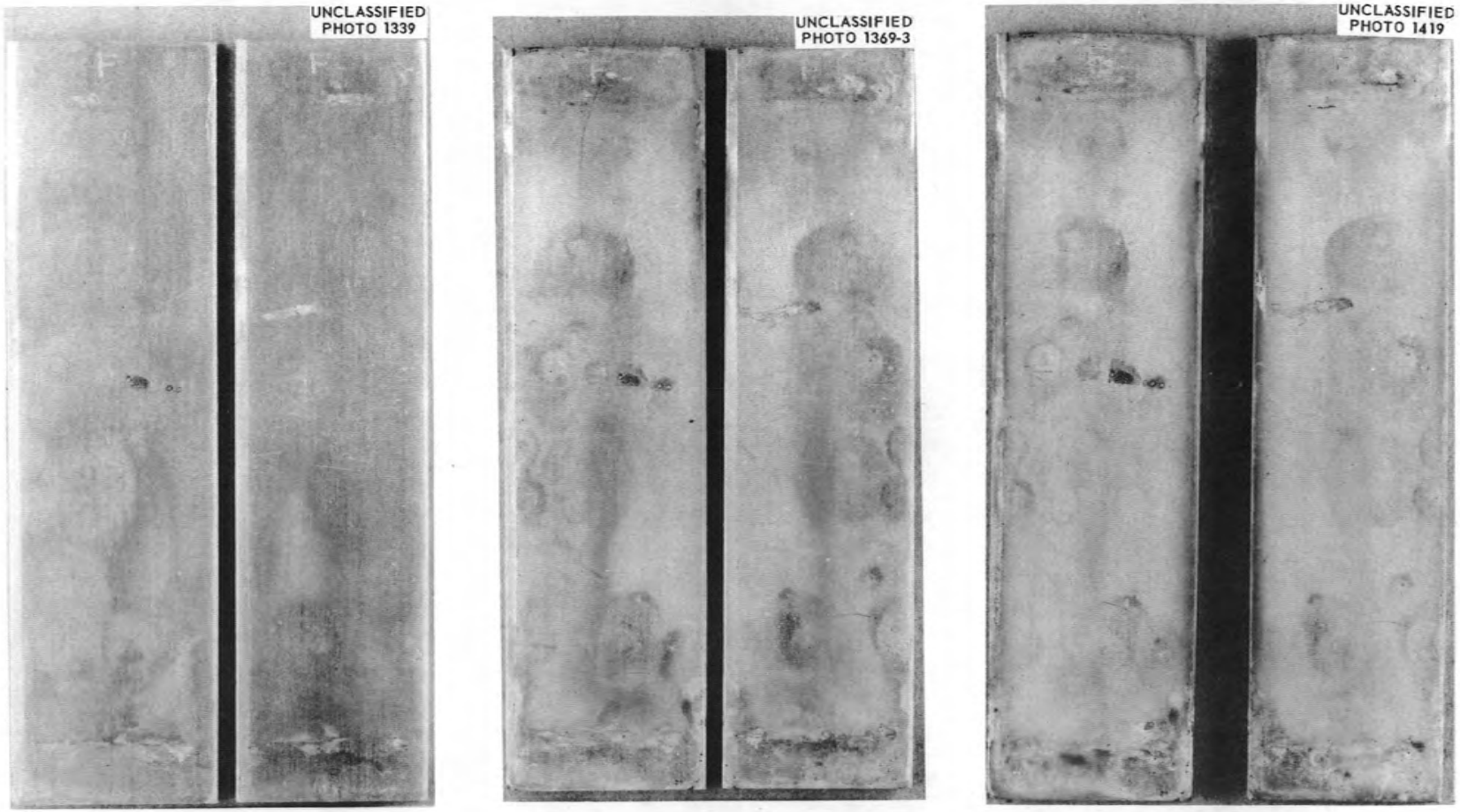
staining and pitting occurred. The frequency and intensity of pitting attack were similar to that observed on the acetone-and-alcohol degreased control specimen thereby indicating that chlorides and heavy elements in the potable wash water were not a factor in initiation of pitting.

Pitting was eliminated completely by the use of three surface treatments: (1) HNO_3-HF pickle followed by cathodic defilming, (2) HNO_3-HF pickle followed by cleaning in Na_2CO_3-Na_2SiO_3 solution, and (3) pickling in H_2SO_4-CrO_3 solution. Staining was greatly minimized in intensity by use of the second treatment but did occur with the first and third treatments. Figure 12 shows the condition of the inner faces of the sodium carbonate-sodium silicate cleaned specimen during the 78-day test.

The 25-min exposure in the sulfuric-chromic acid solution with the 0.091-in.-thick aluminum removed approximately 0.15 mil of metal. In subsequent exposure in water, no pitting occurred during a 28-day test. This material previously exhibited a marked susceptibility to pitting in the as-received condition. Staining occurred, however, during the first seven days. The fact that pitting was eliminated by a longer pickling time in the sulfuric-chromic acid solution than heretofore employed on the 0.091-in.-thick aluminum was interpreted as supporting evidence for the initial postulation that the pitting attack was due to surface contamination, principally metallic iron or an iron-containing substance. The removal of 0.15 mil of metal successfully eliminated all contaminated sites responsible for pitting. The observed behavior of the specimen also refuted the possibility of pit initiation arising from dissolved iron in the water, which, if reduced on the aluminum surface would form a nucleus for pit initiation. Were the latter mechanism operative, pitting attack would occur regardless of the initial surface treatment. As has been shown, such was not the case. Figure 13 presents the condition of the inner face of the sulfuric-chromic acid pickled 0.091-in.-thick specimens after 7 and 28 days of test.

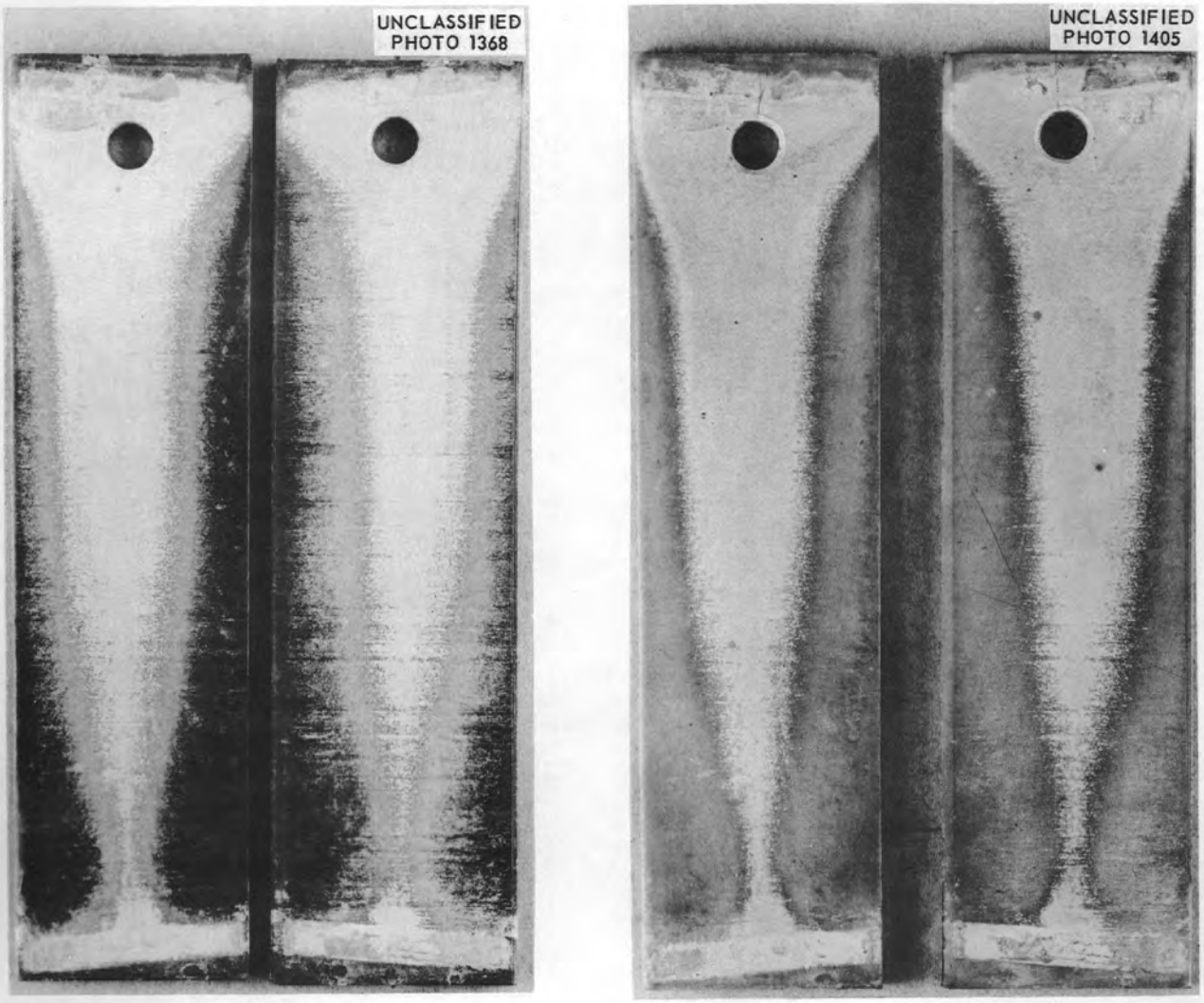
The experimental data from the six preceding tests are conclusive in demonstrating that staining and pitting of aluminum can result from the presence of a thin layer of stagnant water between aluminum surfaces. The evidence also indicated, however, that pitting attack was related to surface condition. The latter statement assumes that the freedom from pitting was not attributed to any inhibitory effects introduced by the particular surface treatments involved.

Silicon-Aluminum Brazing Alloy. The 12.5% Si-Al alloy used to braze fuel elements was corrosion tested for 47 days in the distilled-water environment. During the second week the specimens acquired a dull brown tarnish with incipient pitting. The third week produced numerous loosely adherent white tubercles and further darkening of the surfaces. After 47 days, weight gains of 0.4 mg/cm^2 were observed. The defilmed corrosion rate was 0.3 mpy.



8 DAYS 29 DAYS 78 DAYS

Fig. 12. Staining on 0.125-in.-Thick 1100 Aluminum Crevice-Type Specimens by Distilled Water at Room Temperature. Specimen condition: pickled 5 min at 30°C in 10% HNO_3–0.5% HF; cleaned 10 min at 80°C in 10% Na_2CO_3–0.5% Na_2SiO_3. Test J-97. 1.3X. Reduced 13%.



7 DAYS 28 DAYS

Fig. 13. Staining on 0.091-in.-Thick 1100 Aluminum Crevice-Type Specimens by Distilled Water at Room Temperature. Specimen condition: pickled 25 min at 70°C in 10% H_2SO_4–3% CrO_3. Test K-43. 1.3X.

By and large, the intensity of the pitting attack was not severe; the deepest pit-depth range was 0.6 to 1.1 mils. The greater portion of the pits were 0.5 mil or less in depth. The frequency of the attack was so great, however, that it was not practical to make an accurate count. The as-removed condition of the test specimens is shown in Fig. 14.

The generalized corrosion rate of 0.3 mpy for the brazing alloy was comparable to that for acceptable grades of 1100 aluminum. However, the silicon-aluminum alloy exhibited a greater sensitivity to pitting attack.

Corrosion Test at Bulk Shielding Facility. Test specimens of 1100 aluminum sheet, representative of materials used at the Rolling Mill for fabrication of Geneva and other fuel elements, were exposed in the demineralized cooling water at the BSF. The object of the test was to determine whether any particular feature of the pool water chemistry was responsible for the corrosion behavior of the 10 Geneva elements that were examined on June 20, 1955.

Duplicate sets of specimens were prepared from 0.091- and 0.220-in.-thick sheet. The latter material was used for cover plates in the Geneva elements. The 0.091-in.-thick sheet was used for cover plates on the two outermost fuel plates of MTR elements. The 0.091-in.-thick test specimens were 1 x 4 in. in size; the 0.220-in.-thick specimens were 4 1/2 x 10 7/8 in.

All specimens were degreased in acetone and alcohol. One of the 0.091-in.-thick specimens was pickled for 15 min at 70°C in 10% H_2SO_4-3% CrO_3 solution to remove surface contamination. The four specimens were then suspended with Teflon tape in the BSF pool. Concurrently exposed with the specimens were a number of dimensionally rejected Geneva elements. The behavior of the latter will be discussed in a following section.

Periodic analyses were made of the pool water during a portion of the test period; the results appear in Table 7. No analyses were made after August 15 although the test specimens and the fuel elements remained in the pool until October 20, 1955. With the exception of a lower resistivity, the quality of the BSF water approximated that of the distilled water used in the laboratory tests.

The corrosion data are included in Table 8. The observed rates were quite low, 0.1 mpy or less for 66- and 90-day immersion periods. All specimens, however, were subject to incipient pitting. The approximate pit count was in excess of 100 pits per cm^2. The pits were very shallow, 0.5 mil or less. The behavior of the specimens was appreciably different from their behavior in the laboratory tests. In the case of the 0.091-in.-thick specimens, particularly, severe pitting accompanied by voluminous corrosion-product formation was always encountered on untreated surfaces in the laboratory tests. Attack on the 0.220-in.-thick aluminum in the laboratory tests was characterized by uniform removal of metal; no pitting

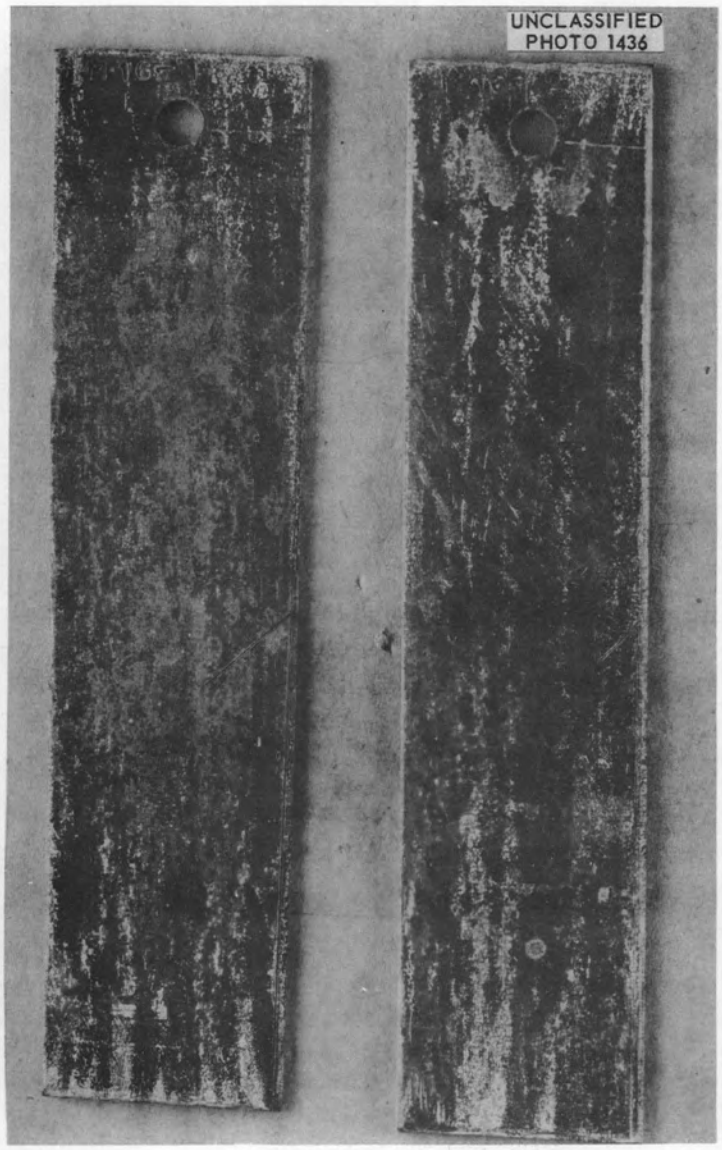


Fig. 14. Condition of 12.5% Si-Al Brazing Alloy After 47 Days in Distilled Water at Room Temperature. Test M-16. 1.5X.

was encountered. No explanation was apparent for the observed difference in behavior, since the quality of the demineralized cooling water was nearly identical to that of the distilled water used in the laboratory tests.

Table 7. Chemical Analysis of Demineralized Cooling Water at Bulk Shielding Facility

Date Sampled	Water pH	Resistivity (ohm-cm at ca 25°C)	Total Solids (ppm)	Soluble Ionic Concentration (ppm)				
				Cl	Cu	F	Fe	Zn
7-1-55	6.57	128,700	1	<1	<0.1	<1	<0.1	-
7-11-55	6.80	135,100	2	<1	<0.1	<1	<0.1	0.8
7-18-55	6.72	155,000	1	<0.2	<0.1	<0.2	<0.1	0.2
7-25-55	6.65	121,200	2	<0.2	<0.1	0.2	<0.1	<0.1
8-1-55	6.78	84,750	2.5	0.3	<0.1	<0.2	<0.1	-
8-15-55	6.99	137,750	1.5	<0.2	<0.1	<0.2	<0.1	<0.5

Table 8. Corrosion of 1100 Aluminum by Demineralized Cooling Water in the Bulk Shielding Facility

Spcm. No.	Thickness (in.)	Exposure Time (days)	Corrosion Rate (mpy)	Deepest Pit-Depth Range (mils)	Total Number of Pits per Cm^2
1	0.091	90	<0.1	0.3-0.5	>100
2	0.220	66	0.1	0.2-0.3	>100
3	0.220	66	0.1	0.2-0.3	>100
4*	0.091	90	<0.1	0.3-0.5	>100

* Pickled 15 min at 70°C in 10% H_2SO_4-3% CrO_3 solution before test; other specimens tested in as-received and degreased condition.

Chemical Analysis of Aluminum Sheet. The marked susceptibility of the 0.091-in.-thick aluminum sheet to pitting attack was of sufficient interest to warrant closer examination of the composition of the metal layer subject to attack. Since the cause for the pitting was attributed to surface contamination by metallic iron or an iron-rich substance, a

chemical analysis for iron was made of a thin surface layer of metal and compared with an analysis of the bulk metal after removal of the surface layer. Weighed specimens of the 0.091-in.-thick sheet and also of 0.125-in.-thick sheet (as a control) were exposed to boiling 2 *M* HNO_3 solution for 1.5 hr in separate containers equipped with condensers. The calculated metal removal by this treatment was between 0.7 and 0.9 mil. This amount of metal removal was considered more than sufficient to remove all surface contamination since previous work demonstrated that the removal of slightly less than 0.2 mil by pickling completely eliminated the susceptibility of the 0.091-in.-thick material to pitting attack.

The specimens were removed from the 2 *M* HNO_3 solution and placed in boiling 5 *M* HNO_3 solution containing a small amount of mercury to catalyze the aluminum-nitric acid reaction. The specimens were completely dissolved within 6 hr. Both the 2 *M* and the 5 *M* HNO_3 solutions were analyzed for iron; chloride and fluoride analyses were run on the 5 *M* solution but not on the 2 *M* solution. A summary of the analytical data appears in Table 9.

Table 9. Iron, Chloride, and Fluoride Contents of 0.091- and 0.125-in.-Thick 1100 Aluminum Dissolving Solutions

Sheet Thickness (in.)	Constituent	Concentration (ppm)	
		Outer 1-mil-Thick Metal Layer	Bulk Metal
0.091	Iron	3700	5200
	Chloride	N.D.*	14
	Fluoride	N.D.	< 1
0.125	Iron	3800	3500
	Chloride	N.D.	< 1
	Fluoride	N.D.	4

* N.D. (not determined).

The iron content of the outer 1-mil-thick layer of the 0.091-in. aluminum was less than that in the bulk metal, 3700 vs 5200 ppm, respectively. The outer 1-mil-thick layer of the 0.125-in. aluminum contained approximately the same iron content as the bulk metal, 3800 vs 3500 ppm, respectively. The original iron content of the 0.091-in. aluminum was reported as 5000 ppm (Table 1), whereas that for the 0.125-in. aluminum was 5100 ppm. Thus from the analytical data, if iron contamination on the surface of the 0.091-in.-thick aluminum were responsible for the severe pitting attack experienced by the material, its presence was not detected by the analytical technique employed.

A chloride content of 14 ppm was found in the bulk metal of the 0.091-in. aluminum; no chloride analysis was made on the outer 1-mil-thick layer. The chloride content of the 0.125-in. aluminum was less than 1 ppm. Some fluoride, 4 ppm, was also found in the bulk metal of this material.

BSF Dummy-Fuel-Element Test. The preliminary results from examination of a brazed 1100 aluminum dummy fuel element which had been exposed intermittently for a period of approximately two years in chromate-treated process water of the BSF have been reported.[1,3] The element was found to be subject to extensive pitting attack, particularly on and around brazed areas. Severe pitting attack was also found on the individual plates in areas that normally would encase enriched uranium-aluminum core material. Measured pit depths in the latter areas ranged from 25 to 32 mils in a number of cases (the cladding thickness on an active BSF fuel plate is 20 mils).

The dummy element as received contained voluminous deposits of white corrosion products scattered throughout the inner surface. A quantity of these products were submitted for chemical analysis; the results are shown in Table 10.

Table 10. Composition of Corrosion Products Removed from Dummy 1100 Aluminum Fuel Element Exposed in Cooling Water of Bulk Shielding Facility

Element	Concentration (mg/g)	Concentration (ppm)
Al	246.0	246,000
Cl	< 0.01	< 10
Cr	0.25	250
F	3.5	3500
Fe	1.41	1410
Si	13.9	13,900
U	0.54	540

The aluminum was assumed to be present in the corrosion products as the beta trihydrate of aluminum oxide (Bayerite), since this is the form of the oxide normally found on metal exposed in water at temperatures below 70°C.[4] The silicon was attributed to attack on the silicon-aluminum brazing alloy. Some silicon is also present in 1100 aluminum, of course.

One of the most significant features of the corrosion-product analysis was the detection of 3500 ppm of fluoride. The chemical state of the fluoride was not established, but it was thought to be present as an insoluble complex with aluminum. The presence of such a large quantity of fluoride suggested the brazing flux as a source since the brazing flux contained approximately 5% fluoride by weight. It is possible that brazing flux was trapped in voids that were formed in the side-fuel plate junctions as a result of incomplete penetration of the silicon-aluminum alloy during brazing.

Since the dummy element contained no uranium, the appearance of 540 ppm of uranium in the corrosion-product analysis was especially disturbing. Several possible sources of the uranium were considered. One source envisioned was penetration by pitting of the aluminum cladding on an active fuel element or elements immediately adjacent to the dummy element in the loaded position in the BSF core lattice. Some evidence has indicated that penetration by pitting corrosion to the uranium-alloy-core material can occur.[1] The exposed uranium-aluminum alloy would be prone to attack by water.[5] The resulting uranium-rich corrosion products conceivably could be distributed over adjacent fuel-plate surfaces by water movement during reactor operation.

A second source of the uranium contamination in the corrosion products could be from the rolling mill in which the aluminum plates for the dummy element were fabricated. The mill is used to roll both aluminum and uranium-containing materials. Improper cleaning of the rolls may have resulted in particles of a uranium-containing material becoming imbedded in the aluminum plates for the dummy element.

Additional metallographic studies on the dummy element have been completed since issuance of the preliminary results.[1] A drawing showing the location of areas that were sectioned for examination appears in Fig. 15.

One of the major reasons for undertaking further examination of the dummy element was to determine whether galvanic corrosion occurred due to the couple between the silicon-aluminum brazing alloy and the 1100 aluminum. Laboratory tests discussed earlier indicated that galvanic corrosion did not result from the couple. However, visual examination of brazed areas on the dummy element disclosed some areas of localized attack.

One area selected for metallographic examination was a brazed junction between a side plate and a dummy fuel plate (position 1 in Fig. 15). The physical condition of the braze metal in this area implied the absence of corrosion attack. Metallographic examination substantiated this observation as shown in Fig. 16. The braze metal was sound. The dark needle-like constituent in the braze metal is the silicon-aluminum eutectic; the large white-colored areas are dendrites of primary aluminum.

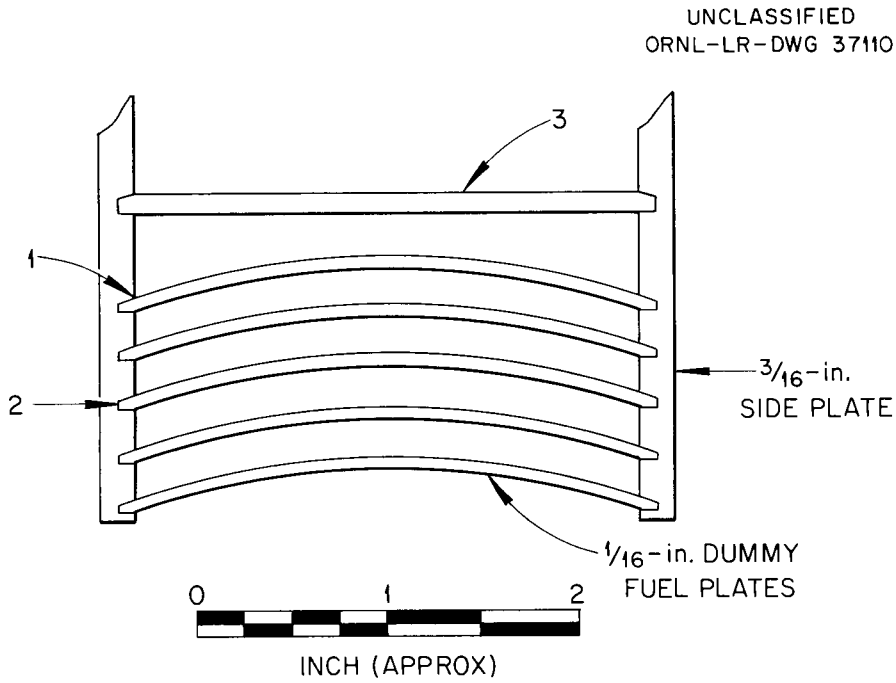


Fig. 15. Cross-Section of Dummy 1100 Aluminum Fuel Element Showing General Location of Areas of Metallographic Examination.

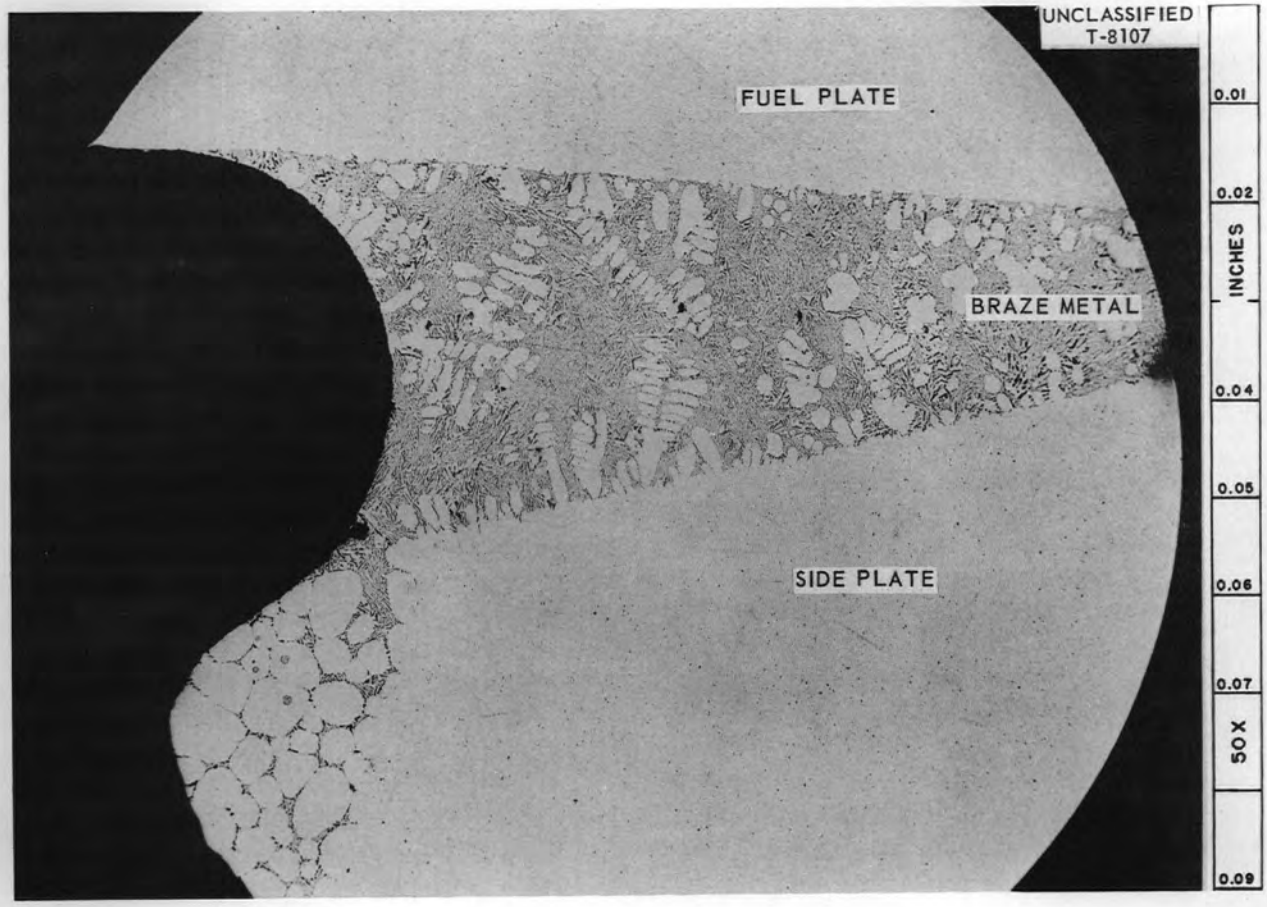


Fig. 16. Brazed Junction of Dummy 1100 Aluminum Fuel Plate with 1100 Aluminum Side Plate. No sign of selective corrosion attack on 12.5% Si-Al braze metal. Water-contact side on left in photograph. As-polished surface. 50X.

A second metallographic section was taken in the same vicinity as shown in Fig. 15. The braze metal by visual examination appeared to have undergone attack. Figure 17 shows this to be the case; severe preferential attack was experienced by the braze alloy. The dendrites of primary aluminum in the braze alloy appeared to have undergone attack at a slower rate. Thus from a comparison of Figs. 16 and 17, it is obvious that under certain undefined conditions the silicon-aluminum brazing alloy is subject to a highly selective form of corrosion attack. The fact that the preferential attack occurred in random fashion suggested that galvanic effects were not the underlying cause.

Void formation at the junction between a "fuel" plate and a side plate is shown in Fig. 18 (position 2 in Fig. 15). The voids result from incomplete penetration by the silicon-aluminum alloy during the brazing operation. The voids, from a corrosion viewpoint, are highly undesirable since they can serve as catchment areas for the halide-containing brazing flux. Seepage of water to these areas could result in a highly aggravated corrosion condition.

During examination of the dummy element, a suspicious area was observed about 1/2 in. away from a brazed area (position 3 in Fig. 15). The area showed signs of grain-boundary attack. A section through the area was examined metallographically; results appear in Figs. 19 and 20. The attack was definitely of an intergranular nature and extended to a depth of approximately 4 mils. Most of the metal grains involved were completely encircled by the attack. Several other similar areas on the dummy-element plates were examined metallographically; all exhibited intergranular attack.

FIELD STUDIES

Four GCR fuel elements that were not acceptable for reactor use, because of failure to meet dimensional tolerances, and one MTR fuel element were corrosion tested in the cooling water of the BSF. One standard GCR fuel element was tested in the core lattice of the LITR. Results of the six tests are presented in the following sections.

Preliminary Inspection of GCR Elements. The visual appearance of the ten Geneva elements after two weeks of exposure in the demineralized pool water of the BSF was described in the introduction. The next step was the identification of the constituents in the corrosion products on the elements. The following samples were removed from the elements and submitted for spectrographic and chemical analyses:

A-1, a gray deposit removed from the fuel-plate surfaces of an exposed element;

A-2, white-colored corrosion products removed from brazed areas and from around the plug welds on the end boxes of an element that had been cleaned in Ridoline 3192 after the pool exposure;

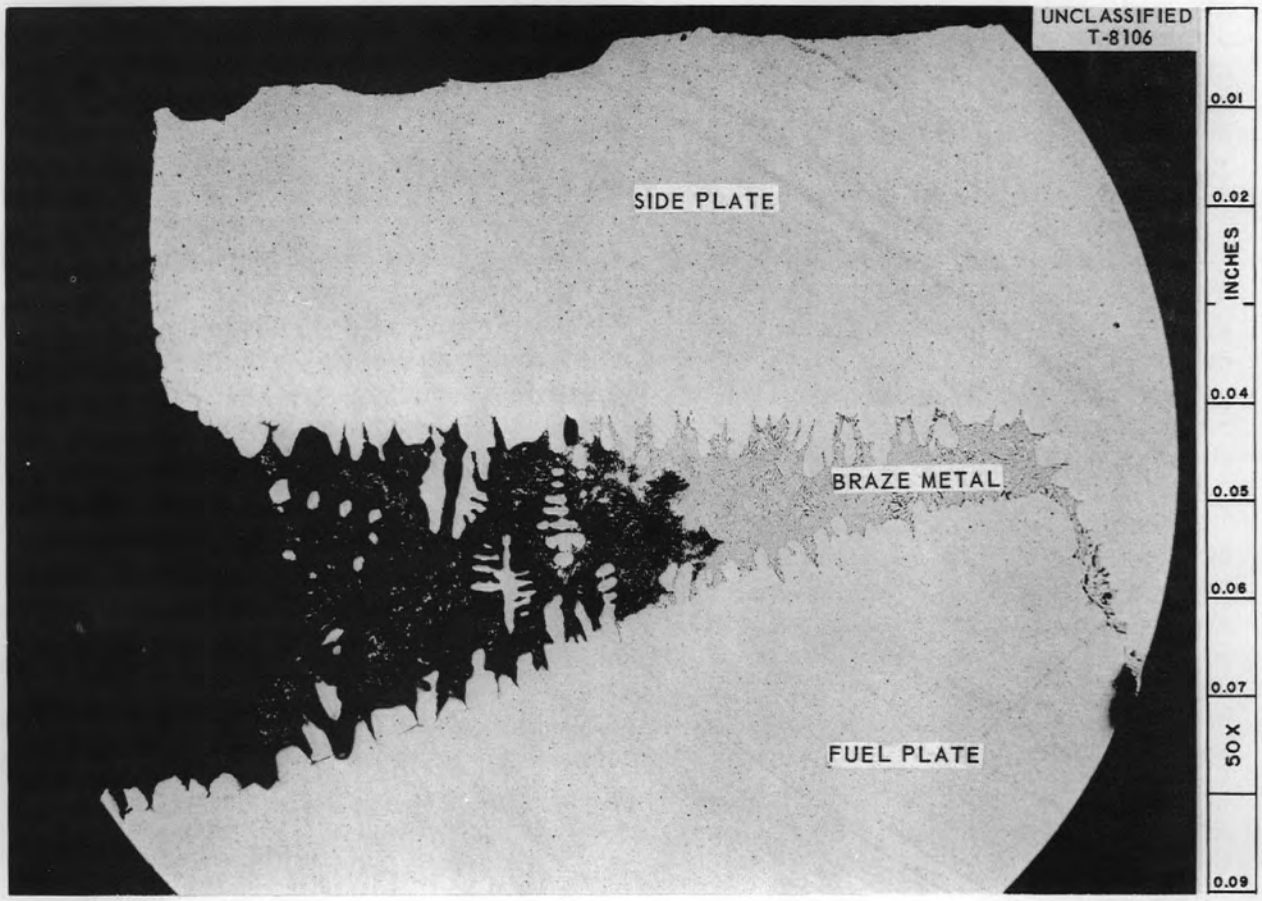


Fig. 17. Selective Corrosion Attack on 12.5% Si-Al Braze Metal by Cooling Water in the BSF. 50X.

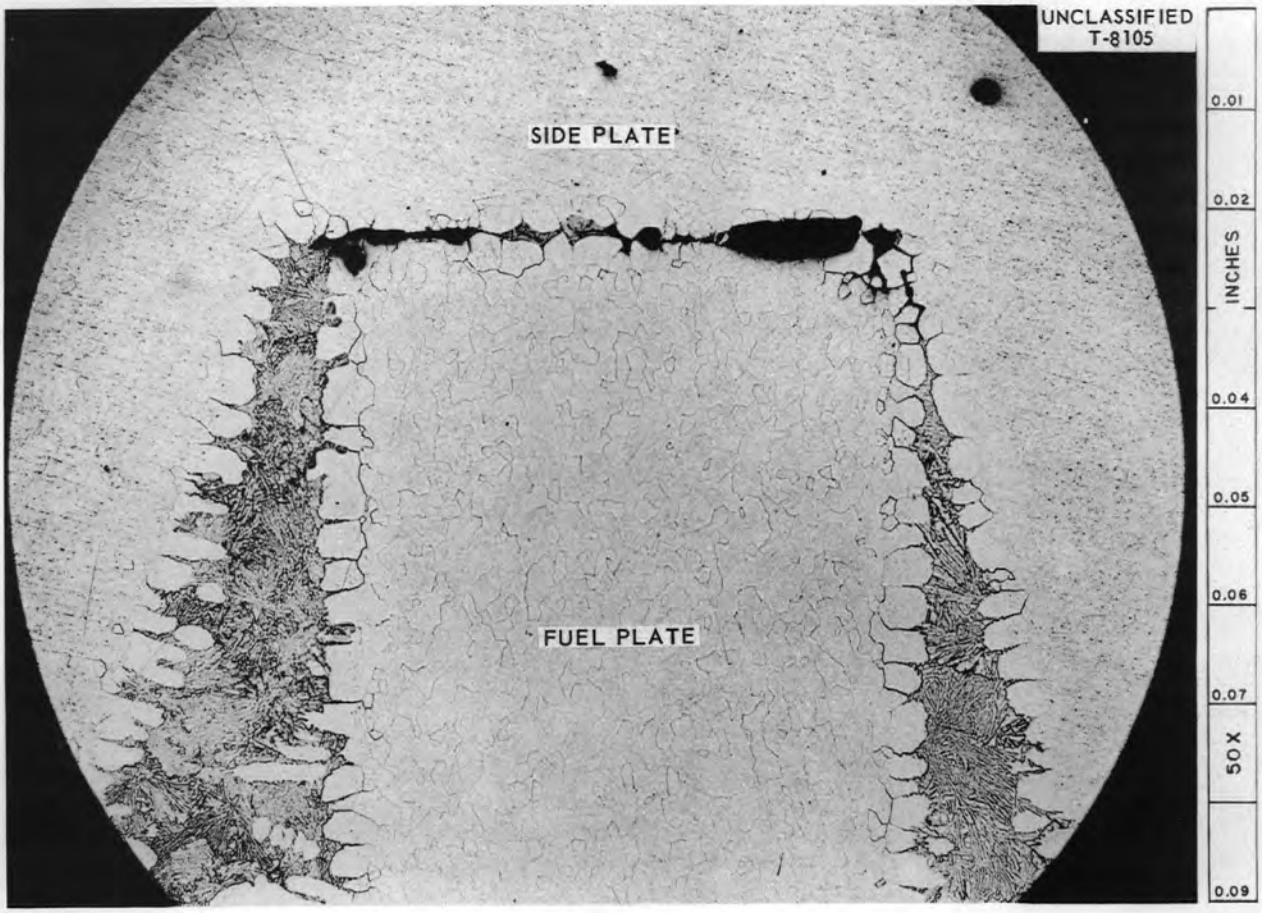


Fig. 18. Void Formation in Brazed Joint Due to Incomplete Penetration by 12.5% Si-Al Braze Metal. Keller's etch. 50X.

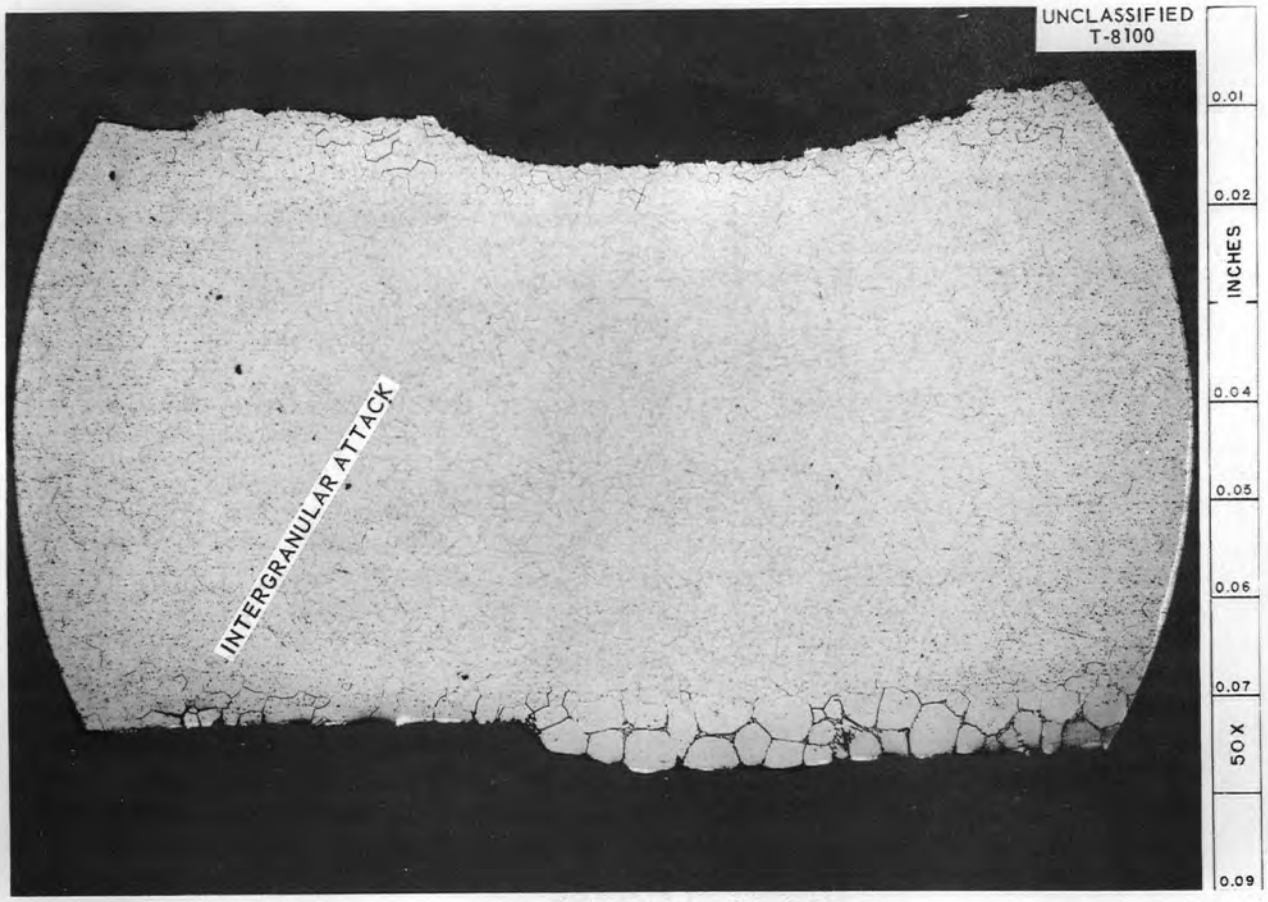


Fig. 19. Cross-Sectional View of Dummy 1100 Aluminum Fuel Plate Showing Area of Intergranular Attack. Keller's etch. 50X.

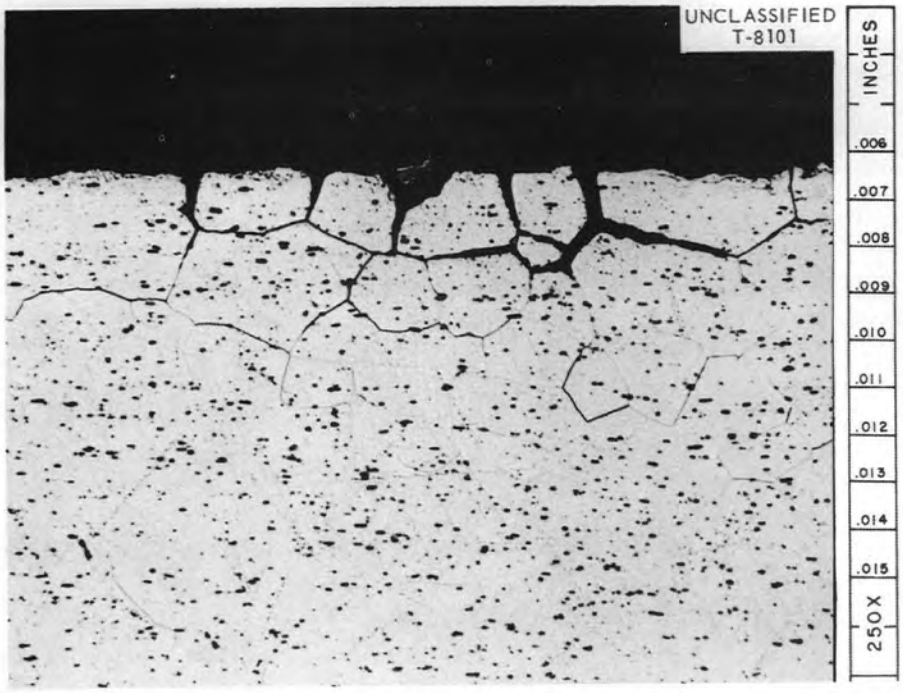


Fig. 20. Magnified View of Area in Fig. 19 Showing Intergranular Attack. Keller's etch. 50X.

A-3, brown-colored corrosion products taken from the fuel and side plates of an element that had been cleaned in Ridoline after exposure.

Spectrographic analyses disclosed that aluminum was very strong in all three samples, copper and iron varied from trace to very weak, and uranium was very weak. Since no unusual effects were disclosed by the spectrographic analyses, the chemical analyses were restricted to determinations for chloride and fluoride. The results appear in Table 11.

Table 11. Halide Content of Corrosion Products Removed from Geneva Fuel Elements

Halide	Concentration (ppm)		
	Sample A-1*	Sample A-2*	Sample A-3*
Chloride	2000	25000	Negligible
Fluoride	100	100	Negligible

* See text for description of samples.

Fabrication History for GCR Elements. The following fabrication history for GCR fuel elements has been made as definitive as possible by discussions with personnel concerned with the fabrication and by reference to reports on the subject.[6,11] The starting materials were: (1) aluminum powder of minus-100 mesh, (2) enriched UO_2 powder in the minus-100 to plus-325 mesh particle-size range, and (3) 1100 aluminum sheet for picture frames and cladding sheets. The fabrication procedure was as follows:

1. Core materials are proportioned and blended.

2. The amount of powder mixture required for each core compact is loaded into a die cavity and hydraulically pressed under a pressure of 33 tons/in.^{2}.

3. The powder core is completely enclosed by the picture frame and cladding plates.

4. The composite fuel assembly is heated at 590°C (1094°F) and hot-rolled from the starting thickness of 0.070 in. to obtain a sound metallurgical bond between the clad and core materials. The rolling schedule normally consists of six separate hot passes to yield a total reduction of 91% in thickness.

5. Flux-anneal:

   a. Surfaces of the fuel plates are coated with a slurry of Eutector 190 brazing flux and alcohol in the ratio of 3 g of flux to 2 ml of methyl alcohol.

   b. The fuel plates are annealed for 1 hr at 610°C (1130°F).

   c. The plates are scrub-washed in potable water.

   d. Plates are immersed for 3-5 min at room temperature in 10% HNO_3-0.5% HF solution, washed in hot potable water for 1/2-1 hr, and air dried.

6. The composite fuel plates are cold reduced by several passes to a final thickness of 0.060 ± 0.001 in.

7. The plates are stress-annealed for 1 hr in air at 600°C (1112°F).

8. Plates are x-rayed for core location and detection of flaws, batch-machined to final width and thickness, and vapor degreased with trichloroethylene.

9. The plates are growth-annealed for 1 hr in air at 604°C (1120°F).

10. The side plates, clad on one side with 12.5% Si-Al alloy, are machined to size with plate slots in the clad side.

11. All components of the elements are vapor degreased with trichloroethylene and are handled with cotton gloves thereafter.

12. The clad faces of the side plates are painted with brazing flux slurry and the edges of the fuel plates are also dipped in flux. The fuel plates are positioned into the slotted clad face of the side plates. The assembly is placed in a drying jig and aligned.

13. Brazing cycle for elements:

   a. Dry in an oven at 150°C (302°F) for 3-4 hr to remove alcohol and moisture from brazing flux.

   b. Transfer from the metal drying jig to a ceramic (AlSiMag) brazing jig.

   c. Heat for 1 hr at 500°C (932°F) to preheat jig and fuel element.

   d. Braze at 610°C (1130°F) for 25 min.

e. Cool to room temperature with forced air flow.

f. Wash element for 1/2-1 hr in hot potable water.

g. Immerse for 3-5 min at room temperature in 10% HNO_3-0.5% HF solution.

h. Wash 1/2-1 hr in hot potable water and air-dry.

14. The assemblies are examined for brazing or dimensional flaws.

15. Elements are sent to machine shop for attachment of end boxes by welding. The end boxes are machined to final tolerance.

16. The elements are vapor degreased with trichloroethylene.

The fuel elements used in the criticality tests were given a final cleaning in Ridoline 3192 cleaner at 90°C.

The aluminum cladding thickness of the fuel plates was 17.5 mils; the UO_2-Al core was 25 mils thick. Total plate thickness was 60 mils.

Geneva Fuel Element G-29. Element G-29 was one of the elements that was rejected owing to failure to meet dimensional tolerances. Figure 21 shows a view of the convex surface of the element before it was placed in a vertical position in the demineralized cooling water at the BSF. After 10 days in the pool water, the element was removed for examination. Widespread pitting was observed on all outer surfaces, especially at brazed areas. Heavy concentrations of white corrosion products were also found on the brazed areas, and by sighting through the length of the multiplate element, it was possible to see similar deposits on the inner plates. Deposits were also observed on the central portions of the convex and concave surfaces of the inner plates.

A small quantity of brown-colored corrosion products was removed from a pit in one of the side plates and submitted for spectrographic analysis. Iron, silicon, and aluminum were found to be high in concentration. Investigation as to the cause for the iron contamination disclosed that a fairly standard machine-shop practice was to hand-rub the side plates with ordinary steel wool to improve the physical appearance. Undoubtedly, during the rubbing process, particles of the steel wool became imbedded in the aluminum and became sites for pit initiation. It was immediately recommended that the practice of polishing with steel wool be stopped.

The element was returned to the pool for an additional seven-day period, making a total of 17 days. An increase in the pitting frequency was noted, particularly on the side plates. Pits in the brazed areas were relatively shallow, 1 to 2 mils in depth. Pits measured in the central portions of the fuel plates were appreciably deeper, however;

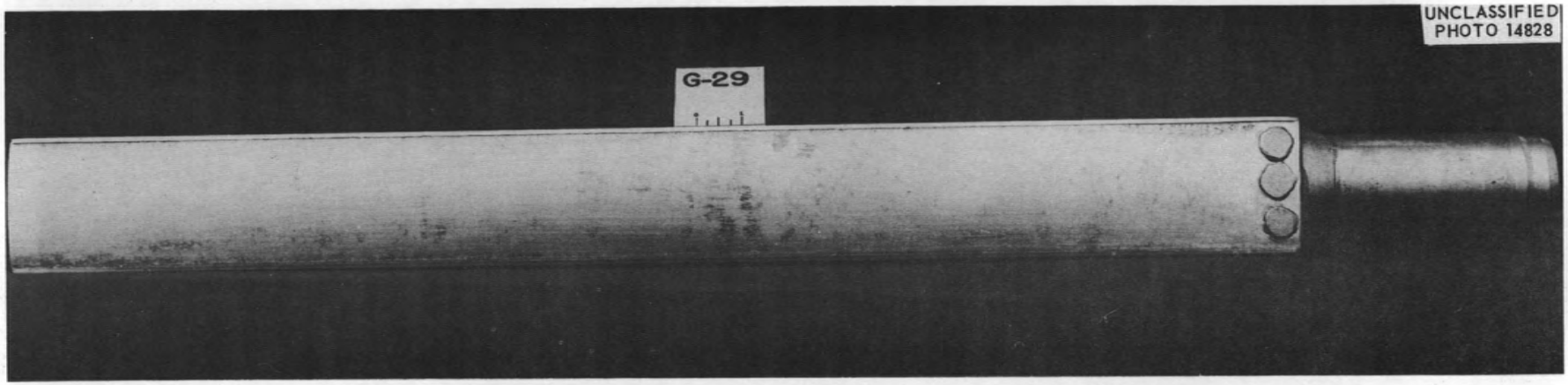


Fig. 21. Pre-exposure Appearance of Convex Surface of Geneva Element G-29.

maximum pit depths of 5.0 and 5.4 mils were found on the convex and concave fuel-plate surfaces, respectively. Figure 22 is a photograph showing the condition of the convex surface after 17 days.

A small area in the centermost portion of the convex surface had undergone intergranular corrosion attack. The area is shown by the composite photograph in Fig. 23. The preferential grain-boundary attack is clearly evident. The dark areas are voids caused by grain removal resulting from complete encirclement by the boundary attack.

After the element had been exposed for a total of 20 days, it was decided to remove the outer convex plate to permit examination of the inner fuel plates. The outer plate was removed by slitting the side plates. After examination, the newly exposed plate was also removed by the same technique.

The surfaces of the inner plates were much the same in appearance as those of the outermost plates. Considerable black staining was evident, and there were heavy, gelatinous, white deposits scattered over the surfaces. The frequency and intensity of pitting attack were about the same as on outer surfaces.

Methods of cleaning the element were tested in the laboratory. It was found, with the removed fuel plates being used as specimens, that the 10% H_2SO_4-3% CrO_3 solution at 70°C effectively removed the black stains and the corrosion products. Consequently, the remaining portion of element G-29 was pickled for 10 min in the sulfuric-chromic acid solution, followed by thorough rinsing in cold, running potable water. The aluminum surfaces were bright and shiny after pickling. The element was returned to the underwater storage rack in the BSF pool.

After four days, the surfaces were stained light gray. After 11 days, the staining intensity and the number of pits had increased. Although the brazed areas remained free of corrosion products, white deposits were present in and around the pits. Maximum pit depths of 8 and 7 mils were measured on the convex and concave surface, respectively, of the outermost plates. A fairly large number of pits were measured in the 3- to 6-mil-deep range. A few of the deepest pits were marked for identification during future examinations, and the element was returned to the BSF pool.

Twenty-five days after pickling, the element was again examined. All external surfaces were coated with gray, gelatinous corrosion products. No appreciable increase in pit depths was observed; one pit 11 mils deep was measured, however, which represented a 62% penetration of the aluminum cladding thickness after a <u>total</u> exposure period of 45 days. The element was returned to the pool water.

A thorough examination was made 67 days after the pickling treatment (87 days from the start of the test). All surfaces were mottled-black in appearance; there was no evidence of the previously observed

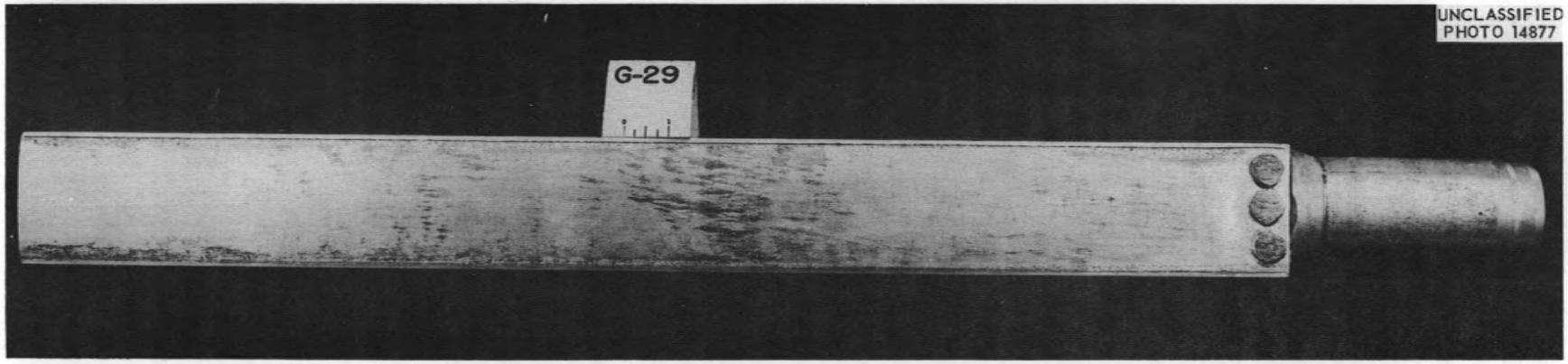


Fig. 22. Convex Surface of Geneva Element G-29 After 17 Days in Demineralized Cooling Water at the BSF.

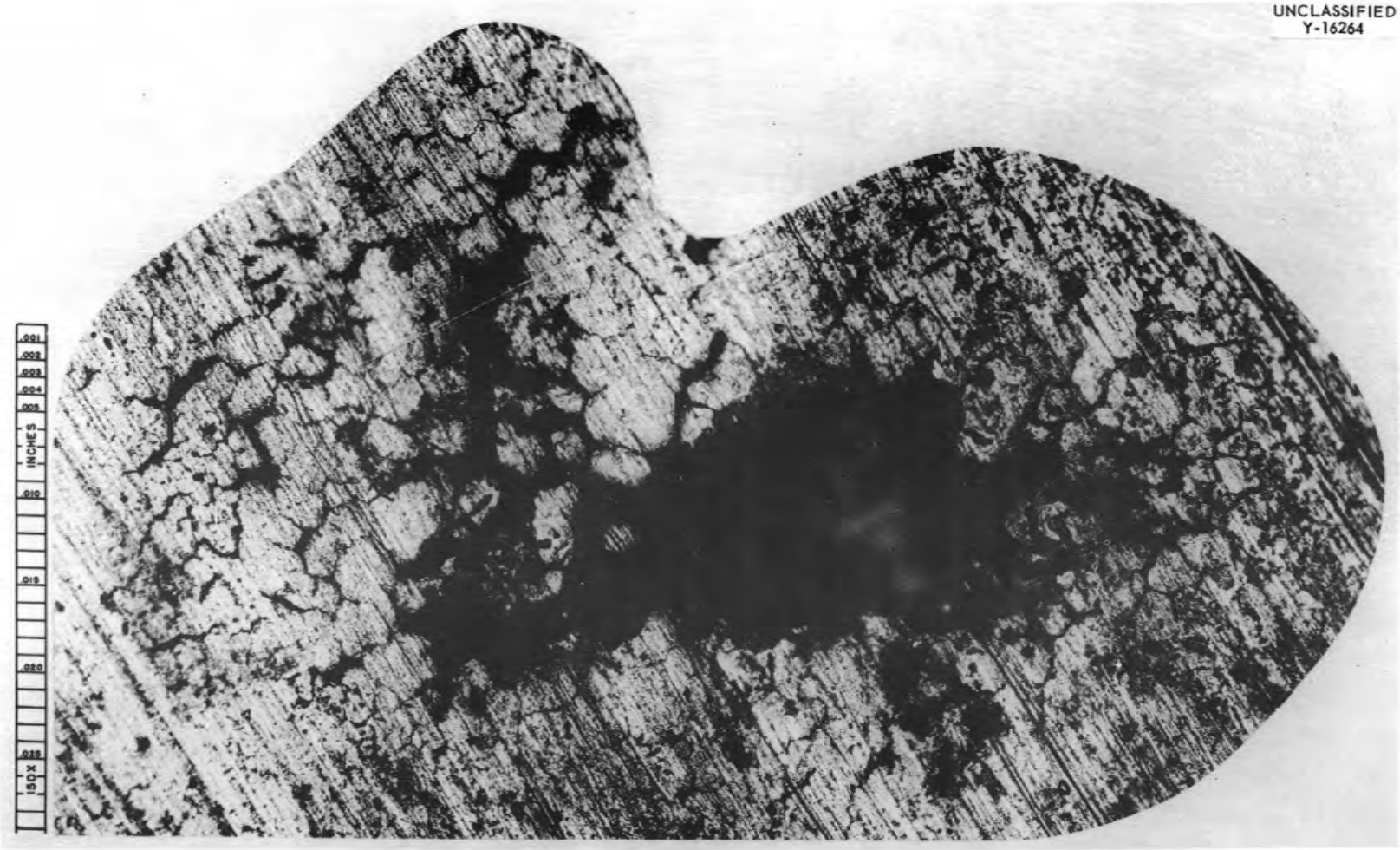


Fig. 23. Area of Intergranular Attack on Geneva Element G-29 After 17 Days in Demineralized Cooling Water at the BSF. 50X. Reduced 5%.

gelatinous corrosion products. White corrosion products were present in pits. The number of pits on the fuel plates had increased substantially from the preceding examination. The deepest pits measured between 9 and 10 mils; there were numerous pits between 5 and 9 mils in depth. It should be noted that the actual pit depths were undoubtedly greater than indicated by microscopic measurements since the bottoms of the pits contained corrosion products of unknown thickness.

The final examination of the element was made after a total exposure period of 111 days (91 days after cleaning). There was no apparent change in the condition of the element from that observed in the preceding examination. Pitting intensity and frequency remained relatively unchanged. Figure 24 shows the final appearance of the element.

Geneva Fuel Element G-30. Element G-30 was also a standard element that had been rejected for mechanical reasons. The pre-exposure condition of the element was much the same as was observed for element G-29 (Fig. 21). The element was placed in the underwater storage rack in the BSF pool.

Examinations were made after totally elapsed periods of 10, 17, 24, 31, and 45 days. The progression of corrosion attack was similar to that noted on the previous element, G-29. The surfaces of the side and fuel plates gradually acquired mottled gray-brown stains. The deepest pits on convex and concave surfaces of the fuel plates were around 8 mils, with pits being generally deeper on the concave surface than on the convex surface. Figure 25 shows the appearance of the element after 45 days.

The exposure was continued for a total of 111 days; Fig. 26 shows the final condition. The intensity of staining was considerably less than was found on the sulfuric-chromic acid pickled element, G-29. There was also a lesser accumulation of corrosion products. Nevertheless, pitting attack was much the same as experienced by G-29. The deepest pit measured 11 mils; a fair number of pits ranged from 8 to 10 mils on both concave and convex surfaces.

Geneva Fuel Element G-3. Since the sulfuric-chromic acid treatment had no effect in minimizing staining or pitting attack by the BSF pool water, an alternate cleaning procedure was used on G-3 prior to exposure. The element was immersed at 80°C in a solution of 5% H_3PO_4 and 2% CrO_3 for 10 min. Following cleaning, the element was washed in cold, flowing potable water.

The initial examination was made 10 days after exposure in the BSF pool water. No accumulations of corrosion products were found, in contrast with elements G-29 and G-30 after a comparable exposure period. However, widespread pitting was present on and around brazed areas and also on the central portions of the outermost two fuel plates.

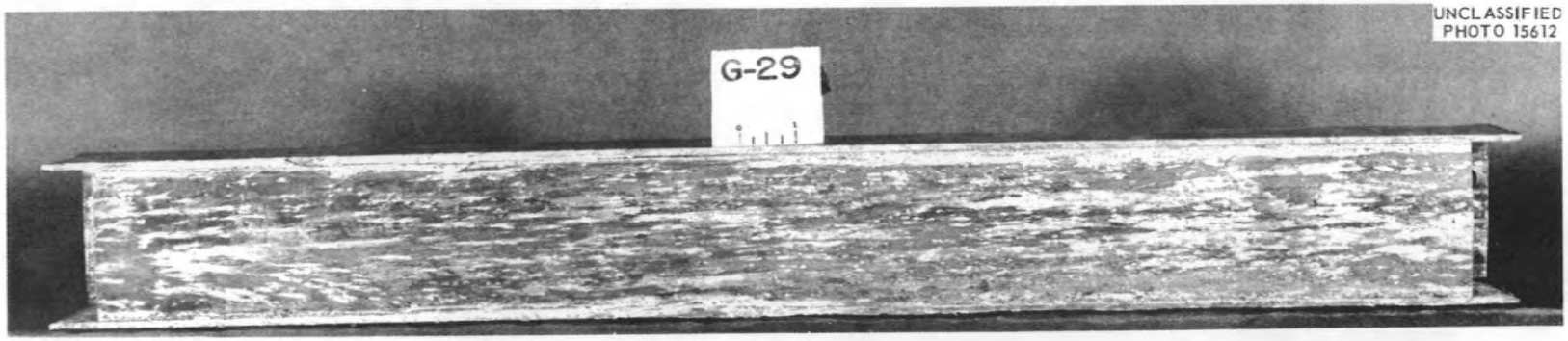


Fig. 24. Convex Surface of Inner Active Plate on Geneva Element G-29 After 111 Days in Demineralized Cooling Water at the BSF.

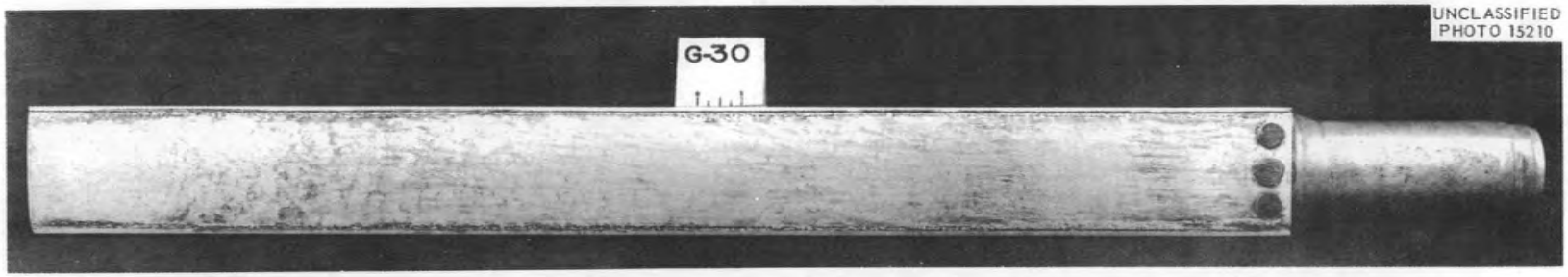


Fig. 25. Convex Surface of Geneva Element G-30 After 45 Days in Demineralized Cooling Water at the BSF.

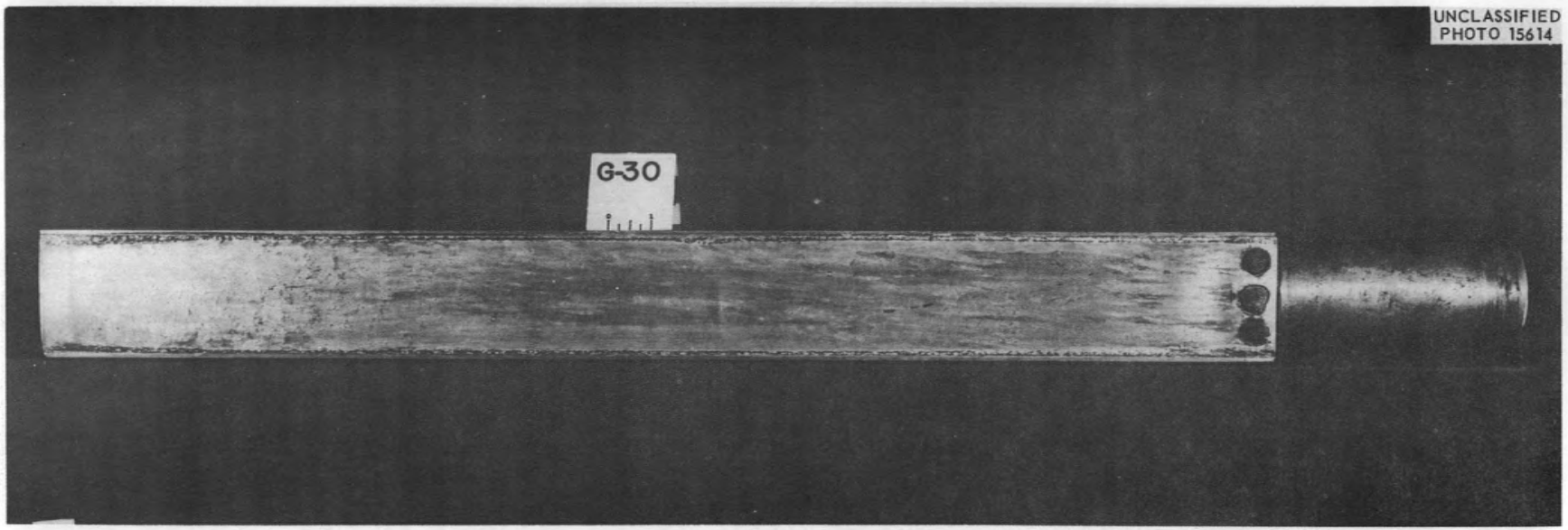


Fig. 26. Convex Surface of Geneva Element G-30 After 111 Days in Demineralized Cooling Water at the BSF.

Some staining of fuel plates was observed after 17 days. The deepest pits measured 8.0 mils on the convex plate surface and 5.8 mils on the concave plate surface.

After 20 days, when the test was terminated, the top two fuel plates from the convex side were removed by slit-sawing the side plates so that interior plate surfaces could be examined. The major difference between the condition of the inner and the outer plate surfaces was that staining was much more pronounced on the former. There was no apparent difference between pitting frequency, pit distribution, or pitting intensity of the interior and exterior surfaces.

Geneva Fuel Element G-4. Another attempt was made to utilize the sulfuric-chromic acid pickling solution for surface cleaning of a rejected Geneva element. The element available for this purpose was G-4. The sulfuric-chromic acid pickle previously used on element G-29 had been exposed in the BSF pool water for 20 days before the pickling solution was used, and it was believed that any corrosion due to surface contamination was well established during this period.

Element G-4 was pickled for 10 min at 70°C in 10% H_2SO_4-3% CrO_3 solution before exposure in the BSF pool water. The amount of metal removed during pickling was approximately 0.05 mil.

The first examination occurred four days after the element was placed in the pool. The external surfaces were shiny and unstained; there were no signs of corrosion products. Some shallow pitting was noted in the brazed areas, and a few random shallow pits appeared on the central portions of the outer plates.

At the end of 11 days, the element was again removed for examination. The surfaces were still shiny and unstained. Small deposits of white corrosion products were observed in brazed areas and around pits. The deepest pit measured on the convex surface was 5.6 mils; the deepest pit on the concave surface was 5.3 mils. In general, most of the visible pits were 4 mils or less in depth.

Staining of the element was observed after 25 days. In addition, gelatinous gray-white corrosion products were present on active-plate surfaces. Pitting on all surfaces was rather prevalent. Some of the pitted areas had also undergone intergranular attack in a manner similar to that described for element G-29.

The element was exposed for a total of 91 days; Fig. 27 shows the final appearance of the convex surface. Considerable staining was present as were heavy deposits of white corrosion products in the brazed areas and in pitted areas. Microscopic determination of pit depths was difficult because of the bulky corrosion deposits. The deepest pit found on either concave or convex surfaces of the outermost fuel plates was 6 mils. A large number of pits ranged from 4 to 5 mils in depth.

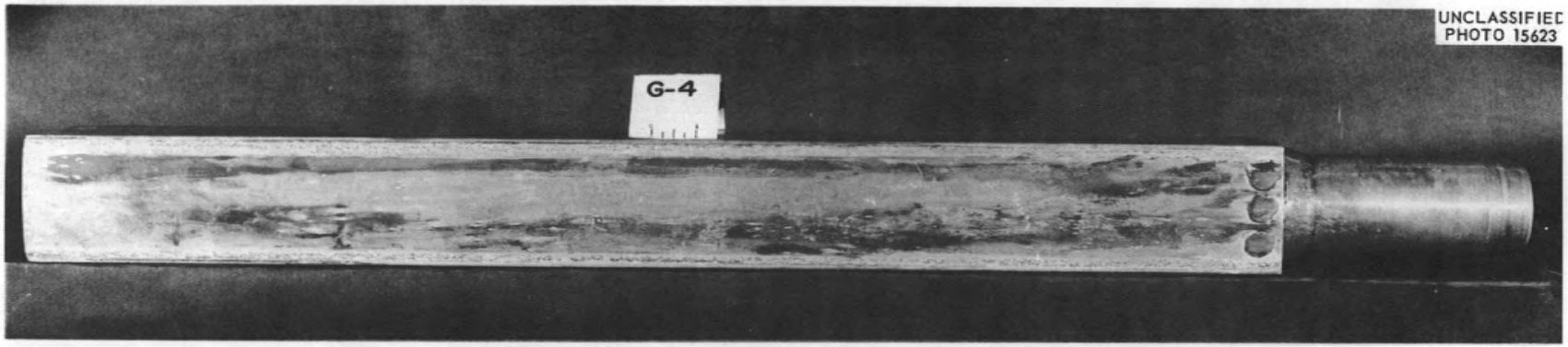


Fig. 27. Convex Surface of Geneva Element G-4 After 91 Days in Demineralized Cooling Water at the BSF.

On the basis of the behavior of the present element, coupled with the experience with element G-29, it was concluded that surface cleaning by pickling in sulfuric-chromic acid solution offered no solution to the problem of minimizing corrosion attack by the BSF demineralized cooling water.

MTR Fuel Element M-7-R. There was speculation that some operation in the fabrication process for the Geneva elements which differed from the standard processing schedule for MTR elements was responsible for their corrosion behavior. Accordingly, an MTR element was obtained for exposure in the BSF. The element was fabricated during the same period as were the Geneva elements. The only significant difference in the production cycle for the two types of elements was the growth-annealing treatment (1 hr at 604°C) given the Geneva elements; MTR elements do not receive this treatment.

After 10 days in the BSF pool water, the selected MTR element, M-7-R, was examined. All external surfaces were severely stained, and shallow pitting attack had also occurred on all surfaces. Some of the pits were surrounded by areas of intergranular attack. The deepest pit measured on the concave surface was 5.1 mils, while that on the convex surface was 6.5 mils.

Thick deposits of gelatinous gray-white corrosion products were observed on the element after 24 days. The deposit was so thick on the convex surface, shown in Fig. 28, that pit depths could not be measured. The deepest pit on the concave surface, which was not so heavily coated, was 7.5 mils.

Final examination of the element, after 90 days of exposure, revealed an appearance much the same as shown in Fig. 28 and similar to that of the exposed GCR elements. It was concluded that variations in fabrication techniques for Geneva and MTR fuel elements were not responsible for the corrosion behavior of the Geneva elements.

Geneva Fuel Element G-6. Element G-6 was a standard element that was fitted with end boxes for loading into the core lattice of the Low-Intensity Test Reactor (LITR) to examine, primarily, dimensional stability of the element under irradiation. The element was installed in the LITR early in May 1955 as part of the fuel loading. The time of contact by flowing demineralized cooling water through the core lattice was 104 days. For 83 of the 104 days, the neutron flux was approximately 1.5×10^{13} neutrons/cm^2·sec. The total exposure period for the element was estimated to be 209 megawatt-days for a burnup of 5%.[7,11]

The exterior surfaces of the element were examined twice during the exposure. During examination periods, the element was lifted vertically in the LITR water tank as high as was permitted by personnel radioactivity-exposure limits. The surfaces of the element were then viewed with binoculars and an underwater periscope. Although the examination technique was not entirely satisfactory, any gross damage

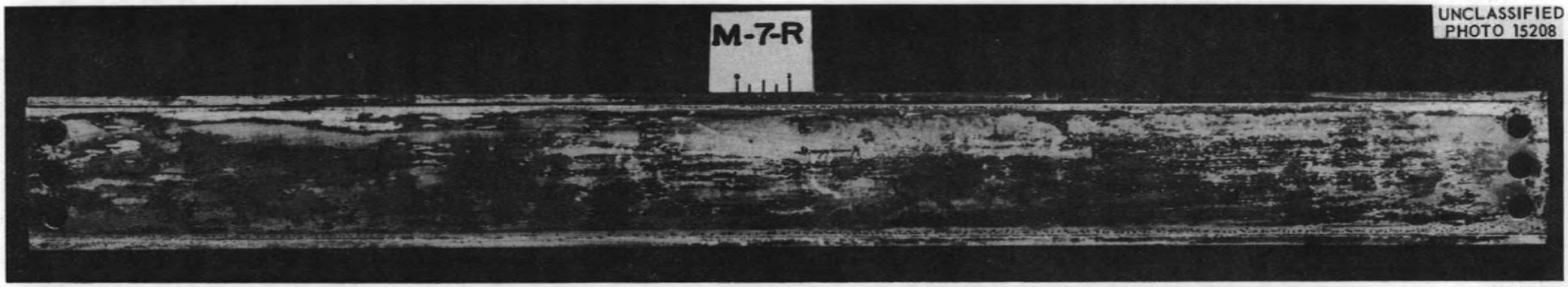


Fig. 28. Convex Surface of MTR Element M-7-R After 24 Days in Demineralized Cooling Water at the BSF.

on the element would have been observed readily. No such damage was observed during either of the examination periods.

Upon completion of the irradiation test, the element was stored in the reactor tank outside the high-flux region for an additional 21 days to allow for radioactivity decay. At the end of the cooling period, the element was removed to a hot cell in the Solid State Division. The activity level was 15-20 mr/hr through the 3-ft high-density concrete wall of the hot cell.

Figures 29 and 30 show the convex and concave surfaces, respectively, of the element after the 104-day exposure. The photographs were taken through the window of the hot cell. The wire in the center of both photographs was part of the equipment used for remote handling of the element.

There were no corrosion-product deposits observed on either the active plates or the side plates. The brazed areas were completely void of the white corrosion products generally found on the BSF-exposed elements. The entire visible surface of the element was covered uniformly with a light gray film that appeared to be very adherent.

A microscopic examination of the plate surfaces was made with equipment previously designed for similar work.[1] Viewing at 30X magnification disclosed some random pitting in the brazed areas, but the pits were too shallow for depth measurement with the available equipment. Some evidences of intergranular corrosion attack were noted also. However, the general condition of the element was considered to be extremely good as compared with that of the Geneva elements exposed in the quasi-stagnant demineralized cooling water in the BSF.

DISCUSSION OF RESULTS

The laboratory tests in distilled water at room temperature with 1100 aluminum sheet used in the fabrication of Geneva and other fuel elements produced a number of interesting observations which, although not specifically concerned in every case with the corrosion behavior of Geneva elements, were nevertheless concerned with the corrosion behavior of aluminum fuel elements in general. A discussion of several of the more pertinent observations follows:

Effect of Surface Condition. The first observation was concerned with the pitting sensitivity of 0.091-in.-thick sheet used for cladding material on the inner active plates of MTR elements. Prolific and severe pitting occurred within a few days from the start of the tests. Maximum pit depths of 6 mils were observed after 28 days. The corrosion products associated with the pits contained black deposits of magnetite, Fe_3O_4. In comparison, the short-term corrosion behavior of 0.125- and 0.220-in.-thick aluminum sheet used in the fuel plates for MTR and

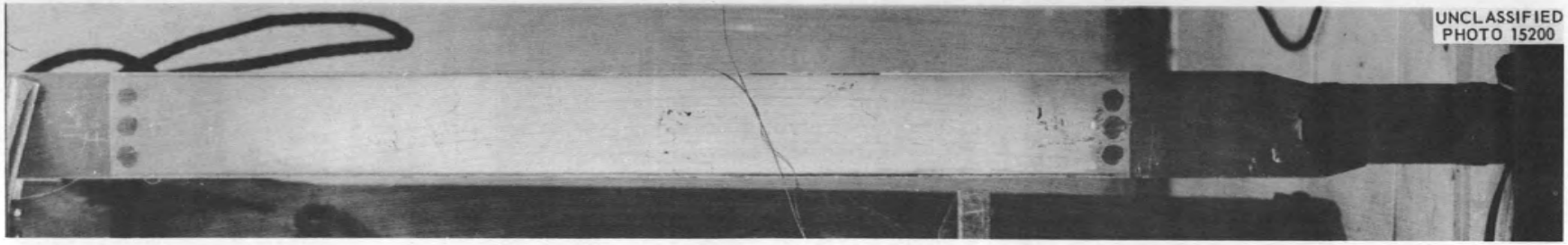


Fig. 29. Convex Surface of Irradiated Geneva Element G-6 After 104 Days in Demineralized Cooling Water at the LITR (83 of 104 Days in Flowing Water).

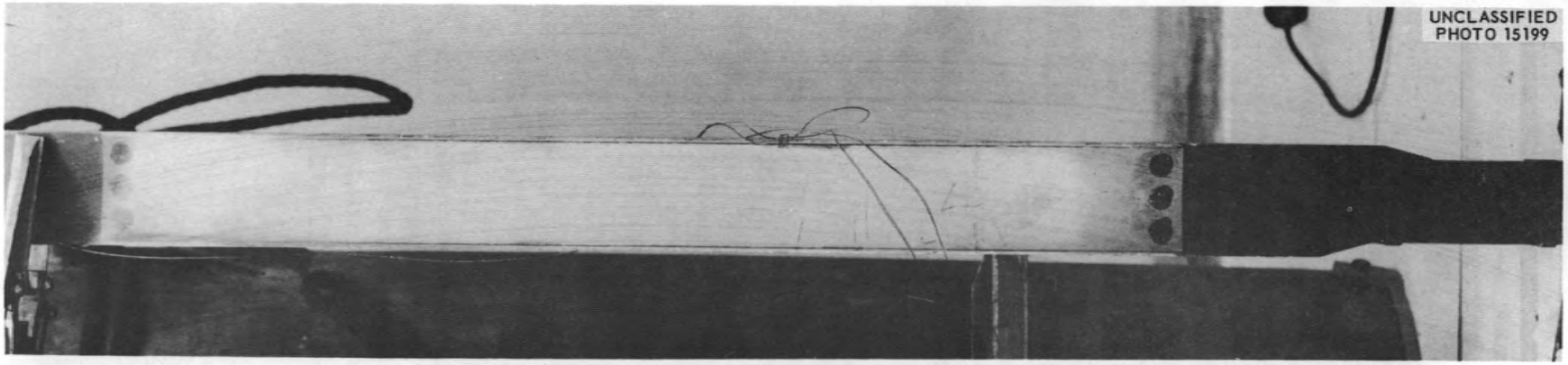


Fig. 30. Concave Surface of Irradiated Geneva Element G-6 After 104 Days in Demineralized Cooling Water at the LITR (83 of 104 Days in Flowing Water).

Geneva elements, respectively, was very satisfactory. The mode of corrosion attack was uniform removal of metal at an average rate of 0.6 mpy.

One proposed source of the iron-containing surface contamination on the 0.091-in. aluminum sheet which caused the high incidence of pitting was improperly cleaned or defective rolls at the supplier's fabrication mill. The fact that the contamination was a surface phenomenon and not inherent in the particular heat of the metal was demonstrated by the use of a sulfuric-chromic acid pickling solution to clean the surface. The removal of a 0.15-mil-thick metal layer by pickling resulted in complete immunity of the aluminum to pitting attack during subsequent exposure in water.

Further substantiation of the above-proposed cause for the pitting on the 0.091-in. aluminum was indirectly realized by corrosion tests with 0.125- and 0.220-in.-thick aluminum. It has been reported that in certain slightly acidic potable waters containing concentrations as low as 0.1 ppm or less of iron, nickel, copper, or lead, a high incidence of pitting occurred on 1100 aluminum.[2] In the absence of these constituents, no pitting occurred. The distilled water used for the present tests contained less than 0.1 ppm iron, 0.1 to 0.5 ppm copper, and probably contained trace amounts of nickel and lead. Therefore the presence of these elements was a potential source for the initiation of pitting attack. The experimental data from the tests with the 0.125-in.- and the 0.220-in.-thick aluminum, which were conducted in the same water as the test with the 0.091-in. aluminum, eliminated the possibility of the above elements as pit promoters since no pitting was found in either case.

From the observed data, it would appear that some degree of control on the quality of aluminum sheet used to fabricate fuel elements could be effected merely by use of a simple water-immersion test with representative specimens from incoming lots of source materials to the Rolling Mill building. Such a test probably need only be of short duration as evidenced by the experience with the 0.091-in.-thick aluminum. The occurrence of pitting attack should suffice for rejection of the source material for fuel-element fabrication or for the use of remedial treatment such as pickling to remove the cause of the pitting attack if attributed to surface inhomogeneities or contamination.

Effect of Brazing Process. It has been suggested that much of the pitting observed on aluminum fuel elements, particularly on brazed areas, was caused by contamination of the surfaces by residual amounts of chloride and fluoride from the brazing flux.[8] The fact that the corrosion products removed from a severely pitted dummy 1100 aluminum fuel element in the present investigation contained <10 ppm of chloride and 3500 ppm of fluoride appeared to substantiate the surface-contamination hypothesis. The present laboratory tests, however, in which an attempt was made to relate the incidence of pitting with the presence of residual halide-containing flux on the aluminum surface were not conclusive. Uncleaned brazed specimens remained free of pitting during the course of

the test. On the other hand, cleaning of a brazed surface with a nitric-hydrofluoric pickling solution -- a procedure used in the fabrication of fuel elements at the Rolling Mill building -- was observed to instigate pitting.

Another suspected cause for the pitting that has been observed in brazed areas of MTR and BSF fuel elements was an inherent sensitivity of the brazing alloy itself to this type of attack. Laboratory tests with the 12.5% Si-Al braze metal did show the alloy to be prone to pitting attack, whereas 1100 aluminum (with the exception of the 0.091-in.-thick sheet) was not. The exhibited sensitivity of the brazing alloy to pitting therefore may account, in part, for the attack observed on brazed areas.

The possibility also exists of galvanically induced corrosion between the brazing alloy and the 1100 aluminum. Certain brazed areas examined on the dummy fuel element showed instances where the brazing alloy underwent severe preferential attack, whereas the surrounding 1100 aluminum was unaffected. Laboratory tests, however, with braze metal and 1100 aluminum couples did not confirm the existence of accelerated corrosion due to galvanic effects.

Field Tests with Geneva Elements. With one exception, the results of field tests with Geneva elements and a single MTR element in quiescent demineralized cooling water were disturbing with regard to the longevity of elements of this type in "swimming-pool" reactors. The situation is not particularly critical for MTR elements since their useful life is generally 12 to 16 weeks. However, for elements used in low-power research reactors such as the BSF and the GCR, where the desired life expectancy is several years, the corrosion behavior of brazed aluminum elements assumes a much more significant role.

Four Geneva elements and the MTR element behaved similarly in the BSF cooling water regardless of the initial surface condition. Pitting, staining, and corrosion-product deposition were common features of the attack. Pitting was especially prominent at brazed areas. Fortunately, many of the pits propagated in a lateral direction rather than in a downward direction. Even so, maximum pit depths between 8 and 11 mils were observed in the 17.5-mil-thick aluminum cladding of the Geneva elements after 30 to 111 days of exposure.

Outermost surfaces of the fuel plates as well as inner surfaces on a number of plates that were mechanically removed from two of the elements were generally badly stained. A similar staining effect was produced in laboratory tests with 1/32-in. clearance between coupled specimens. The staining in itself was considered of no consequence with regard to impairing the life expectancy of the elements. However, the proximity of fuel plates to one another in a reactor loading does present a potential hazard in the form of localized corrosion attack

due to metal ion and/or oxygen concentration cells. This hazard would be appreciably greater during periods of reactor shutdown when the cooling water was not moving through the core lattice.

The encouraging information gained from the field tests was the marked improvement in appearance of the Geneva element exposed in the LITR over the appearance of the BSF-exposed elements. After 104 days, the LITR-exposed element showed no signs of gross corrosion damage such as was observed after much shorter periods on elements exposed in the BSF. In both the BSF and the LITR, the cooling medium was demineralized water of acceptable quality. The ambient temperature of the water in the core lattice of the LITR was somewhat higher than that in the lattice of the BSF because of the higher flux level. Basically, however, there were only two significant differences between the two types of exposure; namely, the neutron-flux density and the coolant velocity. Although it has been reported that the corrosion of aluminum by water may well be affected by irradiation,[9] this was not believed to be a factor responsible for the marked difference in condition between the BSF- and the LITR-exposed elements. Since the neutron flux in the LITR was approximately 15 times greater than that in the BSF (1.5×10^{13} vs 1×10^{12} neutrons/cm^2·sec), a greater corrosion attack might be expected to occur under LITR conditions. This did not appear to be the case, although admittedly it would be rather difficult to determine based upon visual examination only of the fuel element.

Therefore, the only other logical factor to explain the difference in corrosion behavior of the elements was coolant velocity. Whereas water velocity in the core lattice of the BSF could be assumed to be almost negligible during reactor operation, the water velocity in the lattice of the LITR was 25 to 30 ft/sec. In the latter case, rapid replacement of the water in the cooling channels of the element would have the effect of minimizing the formation of concentration cells (metal ion or oxygen) and thereby greatly reduce the sensitivity of the aluminum to pitting attack. It has been reported by Wright and Godard[10] that the number of pits and the maximum pit depth on 1100 aluminum exposed in Kingston, Ontario, potable water at 20°C decreased with increased water velocity until at a flow of 8 ft/min, no pitting was observed.

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