Conf-930318--1

WSRC-MS-92-393

CORROSION OF ALUMINUM ALLOYS IN A REACTOR DISASSEMBLY BASIN (U)

by J. P. Howell, et al.

Westinghouse Savannah River Company
Savannah River Site
Aiken, South Carolina 29808

WSRC-MS--92-393

DE93 003707

P. E. Zapp
D. Z. Nelson

A paper proposed for Presentation/Publication
at the Corrosion 93 - The NACE Conference and Corrosion Show
New Orleans, LA
03/07-12/93

This paper was prepared in connection with work done under Contract No. DE-AC09-89SR18035 with the U. S. Department of Energy.

CORROSION OF ALUMINUM ALLOYS IN A REACTOR DISASSEMBLY BASIN

J. P. Howell, P. E. Zapp, and D. Z. Nelson
Westinghouse Savannah River Co.
Savannah River Technology Center
P. O. Box 616
Aiken, SC 29808

ABSTRACT

Storage of aluminum clad fuel and target tubes of the Mark 22 assembly takes place in the concrete-lined, light-water- filled, disassembly basins located within each reactor area at the Savannah River Site (SRS). A corrosion test program has been conducted in the K-Reactor disassembly basin to assess the storage performance of the assemblies and other aluminum clad components in the current basin environment.

Aluminum clad alloys cut from the ends of actual fuel and target tubes were originally placed in the disassembly water basin in December 1991. After time intervals varying from 45 – 182 days, the components were removed from the basin, photographed, and evaluated metallographically for corrosion performance. Results indicated that pitting of the 8001 aluminum fuel clad alloy exceeded the 30-mil (0.076 cm) cladding thickness within the 45-day exposure period. Pitting of the 1100 aluminum target clad alloy exceeded the 30-mil (0.076 cm) clad thickness in 107 – 182 days exposure.

The existing basin water chemistry is within limits established during early site operations. Impurities such as Cl^-, NO_3^-, and SO_4^- are controlled to the parts per million level and basin water conductivity is currently 170 – 190 µmho/cm. The test program has demonstrated that the basin water is aggressive to the aluminum components at these levels. Other storage basins at SRS and around the U. S. have successfully stored aluminum components for greater than ten years without pitting corrosion. These basins have impurity levels controlled to the parts per billion level (1000X lower) and conductivity less than 1.0 µmho/cm.

Recommendations have been made to improve the basin chemistry using multiple deionizers down to levels at which long-term corrosion-free storage has been demonstrated. Clean-up activities are currently under way which should minimize future corrosion of the aluminum components in the storage basins at the Savannah River Site.

Keywords: Pitting corrosion, 1100 aluminum, 8001 aluminum, nuclear fuel, aluminum clad, reactor disassembly basin, Savannah River Site, SRS, Mark 22, K-Reactor

INTRODUCTION

Storage of aluminum clad fuel and target assemblies in the reactor disassembly basins at the Savannah River Site has been successful over the years of operations. However, localized or pitting corrosion has been a periodic concern in long-term storage. Fuel and target materials are stored in the water-filled basins after irradiation for typically 9 – 12 months awaiting transfer to the Separations facilities for processing under normal operations. When the Separations facilities are not processing fuel and target materials, as currently exists, the aluminum clad alloys are exposed to the basin environment for longer time periods.

General corrosion of the aluminum cladding material has never been a problem in basin storage. The thickness of the clad has ranged from 0.020 – 0.030 inches (0.05 – 0.076 cm) and was initially designed to minimize the amount of aluminum going to waste after the separation of nuclear materials, yet have a thickness which would permit basin storage without penetration. Breach of the cladding by pitting corrosion can lead to leakage of fission products and radionuclide activity to the basin. Basin water chemistry has been controlled in the past and is being controlled at this time, but the prime protection against breaching of the aluminum cladding has always been the shipment of materials to the Separations facilities for processing after the minimum required storage period.

As a result of a metallurgical examination in 1990 of the 6063 aluminum Universal Sleeve Housings which surround the fuel and target assemblies, it was found that through-wall penetration was occurring within a three-month exposure period in the basin.[1] Based on the results, the Savannah River Technology Center (SRTC) initiated a disassembly basin corrosion study designed to better understand the corrosion of the aluminum cladding alloys in the water storage environment. This paper reviews the disassembly basin storage experience and presents results from inert component immersion tests conducted in the K-Reactor disassembly basin.

ALUMINUM ALLOYS IN FUEL AND TARGET ASSEMBLIES

Three aluminum alloys are currently being used in the fabrication of fuel tubes, target tubes, and sleeve housings. The purpose of these alloys as cladding materials is to provide the first barrier for product release (fission products and tritium). These alloys protect and prevent corrosion of the core target and fuel materials. The 1100 aluminum alloy is co-extruded with a lithium-aluminum core to form the target material. A special aluminum alloy, 8001, which was developed for high temperature service, is co-extruded with the uranium-aluminum core to form the fuel tubes. The 6063 alloy is used in the Universal Sleeve Housing (USH) which directs the cooling water to the assemblies. Table 1 gives the compositions of the cladding and USH alloys. The microstructure of the aluminum clad tubes is typical of extruded product with an elongated grain structure in the extrusion direction.

The Mark 22 assembly is the current SRS tritium production assembly. A cross section schematic is shown in Figure 1. It is a nested assembly of co-extruded, thin wall clad fuel and target tubes. The Mark 22 assembly is one of several designs for tubular aluminum alloy clad fuel and target elements that have been irradiated at SRS.

REACTOR DISASSEMBLY BASINS

Each of the reactors at Savannah River has a disassembly basin in which irradiated components are cooled, disassembled, and stored after discharge from the reactor. The facility consists of six interconnected concrete basins containing about 3.5 million gallons of light water. The water temperature is maintained below 40°C. Particulate matter is removed by sandfilters. Radioisotopes are removed and the water chemistry is controlled by recirculation of the water through one or two deionizers operating in series. Make-up water is supplied by natural water from the Savannah River. The deionizers have generally not been operated in a continuous manner over the years, but are usually operated immediately after a discharge to the basin and at other intervals as necessary to maintain water chemistry within operational limits. The operating limits for water chemistry control in the basin are shown in Table 2.

ALUMINUM CLAD CORROSION EXPERIENCE

Corrosion performance of fuel and target tubes of assemblies stored in reactor disassemblies basin at SRS has been well documented over the plant lifetime. Tests conducted as early as 1954 on aluminum clad uranium slugs showed the potential for clad-penetrating pitting corrosion caused by a galvanic couple between the aluminum clad and the stainless steel storage containers. During the period of 1974 – 1977, there were four distinct cases of clad-penetrating corrosion in the K-Area disassembly basin. In these cases, tritium and fission product release were detected by analysis of the basin water within one to three months after the assemblies were discharged from the reactor and stored in the basin. Subsequent inspection of the target and fuel tubes revealed extensive corrosion and penetration of the aluminum clad. A committee was formed to determine the cause of accelerated corrosion in the basin. A number of factors were found. Among them were poor cladding material, high concentrations of iron and chloride ions in the water, and a galvanic couple between the aluminum assemblies and the stainless steel hangers. In addition, there were scratches in the oxide layer on the cladding surface which served as initiation sites for the pitting corrosion.

As a result of the findings, the basin water pH was adjusted from 6.5 ± 0.8 to 7.3 ± 0.6 to reduce the pitting and the solubility of heavy metal ions. Chloride concentration was reduced from 25 ppm to about 5 ppm. Tests were conducted which demonstrated that pitting corrosion was reduced using electrically insulated or aluminum hangers. This recommendation was never implemented on a full-scale basis due to the high costs involved. With the changes initiated in 1978, there were no reported specific instances of basin corrosion problems over the next several years.

New evidence of the aggressiveness of the basin water was found in 1989 – 1990.[2] With a suspension of reactor operations, the moderator chemistry in the K-Reactor tank exceeded limits for reactor operations. The pH of the moderator in the reactor tank was lowered from a nominal 4.7 to 3.5 – 4.0. Chloride ion content increased from 30 ppb to 200 ppb and aluminum ion content increased from 100 ppb to 4000 ppb. As a result of these out-of-specification conditions, there was concern over the possible corrosion of the aluminum components stored in the reactor tank moderator. Sleeve housings of 6063 aluminum were selected for analysis and considered representative of aluminum components in the reactor. The sleeve housings were stored in the disassembly basin for 25 – 70 days before a metallurgical examination could take place. Upon examination, sixteen of twenty-four specimens showed evidence of pitting corrosion and seven pits from four different sections had penetrated the 0.050-inch (0.127 cm) wall of the housing.

In order to confirm the hypothesis that the pitting occurred in the disassembly basin and not in the moderator, two additional sleeves housing were cut into sections and placed in the disassembly basin. There was no pitting corrosion on sections removed after 14 days, but samples which were removed after 93 days of basin storage showed through-wall pits.[1] Circumstantial evidence from this study and prior evidence led to the conclusion that pitting corrosion did not occur in the moderator, but likely occurred during the 25 to 70 days the sleeve housings were stored in the K-disassembly basin prior to the examination.

Based on these findings that pitting corrosion occurred in the aluminum clad components during disassembly basin storage, a more detailed study was undertaken. An immersion test program was implemented in the reactor disassembly basins in mid–1991.

COMPONENT IMMERSION TESTS

The initial disassembly basin tests were started in the L-Reactor basin. Surveillance corrosion coupons, one-inch wide by two-inches long, of 6063, 1100, and 8001 aluminum alloys were immersed in the basin in May 1991. The first follow-up visual observation was conducted in June 1991 (42 days after the coupons were placed in the basin). The basin water chemistry remained within specifications throughout the exposure period. Visual observations showed formation of white deposits, indicative of corrosion, on the surface of the 8001 aluminum coupons. The coupons were transported from the reactor to SRTC for analysis. Microscopic analysis indicated that the deepest pits formed in the 8001 alloy were on the order of 30 mils (0.076 cm) deep (the thickness of the cladding on the fuel tube). These observations supported the earlier results obtained from field and laboratory tests on the corrosion of aluminum alloys and emphasized the need for further examinations.

In order to better understand the corrosion of aluminum cladding alloys in the disassembly basin environment, components from actual fuel and target tubes were obtained from the SRS Fuel Fabrication Facility. Nine-inch-long cylindrical "tube ends" were cut from the ends of actual extrusions. These ends did not contain uranium or lithium, but consisted of the 8001 and 1100 aluminum alloy cladding with a 5005 and 5052 alloy core, respectively. The components were cleaned using the standard plant caustic cleaning process, but were not given a six minute steam drying treatment normally given the Mark 22 assembly after the hydraulic flow test. The oxide formed in six minutes of steam drying is thin compared to that formed at high temperatures during the irradiation cycle or simple immersion in cold water. As in the actual Mark 22 assembly, the 8001 alloy fuel clad tube was nested inside the slightly larger diameter 1100 alloy clad target. A total of six nested component tube ends were initially placed on 1100 aluminum bar holders and suspended from 3 – 6 feet beneath the surface of the water in the K-disassembly basin.

The first inert components were placed in the basin in December 1991. The basin water chemistry at the time of insertion was generally well within operational limits with pH 7.9 , 5.9 ppm Cl^-, 17.3 ppm $N0_3^-$, 13.7 ppm $S0_4^-$, and 178 µmho/cm conductivity. Removal of the components for evaluation occurred after various exposure periods and was coordinated with the activities of restarting and operating K-Reactor. Additional components were added to the corrosion rack after the removal of earlier specimens. Components added in June 1992 were given an autoclave treatment of four hours at 250°F after the caustic cleaning process to provide additional pre-oxidation protection.

RESULTS

The inert components were removed from the K-Reactor disassembly basin after varying time intervals of basin exposure. As the disassembly basin contains small amounts of tritium and fission products, the samples had to be treated as contaminated for shipment from the reactor area to the Savannah River Technology Center for analysis. Nested components removed from the basin after 75 and 182 days exposure are shown in Figure 2. The random nature of the process is shown by the absence of pitting on the outside of the 182-day-exposure specimen. All other specimens with less exposure showed pitting on the outer surface. Typical pitting corrosion on the inside of 1100 alloy tube is shown in Figure 3. Large pits, typical of those seen on most of the 8001 alloy specimens are shown in Figure 4. These pits were characterized by a large nodule of corrosion product which is shown close-up in Figure 5. Pits on both alloys were generally always filled with corrosion product. Only in the early stages of pitting of the 1100 alloy (45 day exposure) was there an exception to this.

After photographing the slightly contaminated specimens, the specimens were decontaminated using a 50% phosphoric acid solution. The solution removed all contaminates and cleaned the corrosion product from the pits. The pits were clearly exposed and photographs of the largest pits were made. Individual pit depths were approximated using the optical microscope to focus on the pit bottoms and the top of the sample. Serial metallography was used to more accurately determine the deepest pit depths.

The maximum pit depth on each alloy tube end as a function of exposure time in the basin is shown in Table 3. As can be seen from Table 3, pits on the 1100 alloy were smaller in diameter, not as deep, and more frequent in number for a given exposure time than on the 8001 alloy. The pit density on the 1100 alloy specimens was greater than 0.125 pit/cm^{-2}. The 8001 alloy pits were generally larger, some up to about 0.25 inches (0.635 cm) in diameter, fewer in number, but greater in depth than the 1100 alloy for the same exposure time. The pit density on the 8001 alloy specimens averaged 0.01 pits/cm^{-2}.

Pit depths in the 8001 alloy exceeded the 30-mil cladding thickness of the fuel tube within the minimum basin exposure period of 45 days. The maximum pit depth on alloy 8001 samples from 45 – 182 days varied from about 27 – 53 mils (0.069 – 0.135 cm) with the deepest found in the 45-day exposure. The pit depths in the 1100 alloy were less than 25 mils (0.06) for exposure times up to 107 days. The deepest pit found on 1100 alloy samples removed from the basin after 182 days exposure was found to be about 58 mils (0.147 cm) or twice the cladding thickness of the target alloy.

A typical cross-section of the deepest pit on the 1100 alloy is shown in Figure 6. This pit was 58 mils (0.147 cm) deep and resulted from a 182-day exposure of the 1100 alloy to the basin environment. A typical pit occurring in the 8001 alloy is shown in Figure 7. The depth of this pit was 36 mils (0.09 cm) and occurred within the 45-day exposure to the basin environment.

The basin water chemistry was monitored throughout the testing period and generally remained within operational limits. The pH of the water exceeded the 7.9 limit to about 8.3 for about 20 days in early 1992, but was brought back under control.

CONCLUSIONS

Component immersion tests conducted in the K-Reactor disassembly basin over the past year have shown that the basin water environment is aggressive to aluminum. Maximum pit depths of the 8001 fuel cladding alloy were found to exceed the 30-mil (0.076 cm) thick clad within 45 days. Pit depths exceeded the 1100 target cladding alloy within 182 days. With the basin storage times of Mark 22 assemblies and other aluminum clad components increasing as processing of fuel is suspended, the implications are significant. Breaching of the aluminum clad can lead to corrosion of the core material and subsequent release of radioactive fission products and tritium to the basin. The basin is monitored constantly for any increase in activity and is currently well within its operational limits. When the limits are approached, the two basin deionizers are operated continuously to insure that limits are not exceeded. Continuous operation of the deionizers requires significant additional effort for regeneration of the mixed-bed resins, especially when large quantities of radioactive fission products and other ions are removed.

The water chemistry of the K-Reactor disassembly basin has generally been kept within operational limits which were established in the early years of plant operations. In comparing the limits of the disassembly basins to other basins around the country and at SRS where aluminum components are stored for long time periods (> 10 years) without corrosion concerns, there are two major differences. At the Receiving Basin For Off-Site Fuels (RBOF) at SRS, the impurities in the water basin such as Cl^-, NO_3^-, and SO_4^- are kept in the parts-per-billion concentration level whereas these same impurity levels are 1000X higher in the parts-per-million level in the disassembly basin. In addition, the disassembly basin conductivity limits are 400 μmho/cm and the measured level during this testing period was in the 170 – 190 μmho/cm range. RBOF as well as fuel storage basins at Brookhaven National Laboratory, Oak Ridge National Laboratory, and Georgia Institute of Technology all maintain basin water conductivity at less than 1 μmho/cm.

The pitting susceptibility of the 8001 fuel clad alloy was shown to be greater than the susceptibility of the 1100 target clad alloy. The 8001 alloy was developed for temperatures above 200°C by additions of Fe and Ni which give the alloy superior corrosion resistance up to 350°C.[3] These elements revise their roles at low temperatures and make the alloy more susceptible to pitting in the basin environment. The elements reverse themselves at low temperature and make the alloy more susceptible to pitting in the basin environment.

The pitting corrosion of the aluminum components in the disassembly basin can be attributed to several factors. The most important factor is the basin water chemistry. The current impurity content at the ppm level is aggressive to the aluminum when combined with the high conductivity of the water. In addition, there is potential for a galvanic couple between the stainless steel storage hangers and the aluminum assemblies. This couple has been shown to promote pitting in previous plant tests.

Recommendations have been made to the Reactor Engineering Department to clean-up the basin chemistry. Studies have shown that multiple deionizers could be brought in to lower the conductivity and the impurity levels. Efforts are currently underway to remove corrosion products on the basin floor and to improve the basin water chemistry. Inserts have been procured to insulate the stainless steel hangers from the aluminum assemblies. These changes should help minimize future corrosion of the aluminum components in storage basins at the SRS.

ACKNOWLEDGEMENTS

The information contained in this paper was developed during the course of work under Contract No. DE-AC09-89SR18035 with the U. S. Department of Energy. The authors would like to thank F. E. Odom, T. H. Murphy, E. E. Kemper, and D. P. Healy for photography, metallography, and laboratory assistance in analyzing the corrosion specimens.

REFERENCES

1. R. S. Ondrejcin and D. E. Rawl, "Corrosion of Aluminum Components in K-Reactor (U)", WSRC-TR-90-291, Savannah River Site, Aiken, SC, 29808, July 13, 1990.

2. G. R. Caskey, "Acceptance Criteria for Aluminum Components in K-Reactor (U)", WSRC-RP-89-1426, Savannah River Site, Aiken SC, 29808, December 20, 1989.

3. J. E. Draley and W. E. Ruther, "Agueons Corrosion of Aluminum, Part 2 – Methods of Protection Above 200°C", Corrosion, Vol. 12 (No. 10), p. 480t, 1956.

TABLE 1
REACTOR ALUMINUM ALLOY COMPONENTS

Alloy	Al	Si	Fe	Ni	Mg
1100 (target)	99.0*	a	a	–	–
8001 (fuel)	b	b	0.6	1.1	–
6063 (flow tube)	98.9	0.4	–	–	0.7

* Minimum
a Si + Fe = 1% Max.
b 1100 Alloy + Fe and Ni

TABLE 2
WATER CHEMISTRY
VERTICAL TUBE STORAGE OPERATING LIMITS

Analysis	Lower	Upper	Units
Alpha	0	10	C/M/ml
Conductivity	0	400	μmho/cm
pH	6.7	7.9	
Tritium	0	0.40	μCi/ml
Cl^-	0	20	ppm
NO_3^-	0	30	ppm
NO_2^-	0	30	ppm
SO_4^-	0	30	ppm
Al	0	0.1	ppm
Fe	0	0.1	ppm
Cu	0	0.1	ppm

TABLE 3
MAXIMUM PIT DEPTH AFTER BASIN STORAGE

Test No.	Basin Exposure (Days)	Maximum Pit Depth (Mils)		Observations
		1100	8001	
1	107	23	39	> 100 small diameter pits on 1100 alloy. Pits on 8001 alloy approx. 0.25-inch diameter, 5 – 6 per sample. Pit density = 0.125 pits/cm^2 for 1100 alloy; 0.01 pits/cm^2 for 8001 alloy.
2	75	13	45	> 100 small diameter pits averaging 3 – 8 mils depth for 1100 alloy. 8001 pits through clad. Pit density = 0.125 pits/cm^2 for 1100 alloy; 0.01 pits/cm^2 for 8001 alloy.
3	182	58	27	1100 alloy pits averaged about 14 mils. 8001 alloy had no pits through clad. Pit density = 0.125 pits/cm^2 for 1100 alloy; 0.01 pits/cm^2 for 8001 alloy.
4	45	2	53	1100 alloy had > 100 small initiation sites per sample. 8001 alloy had 4 – 10 pits per sample. Pit density = 0.125 pits/cm^2 for 1100 alloy; 0.01 pits/cm^2 for 8001 alloy.

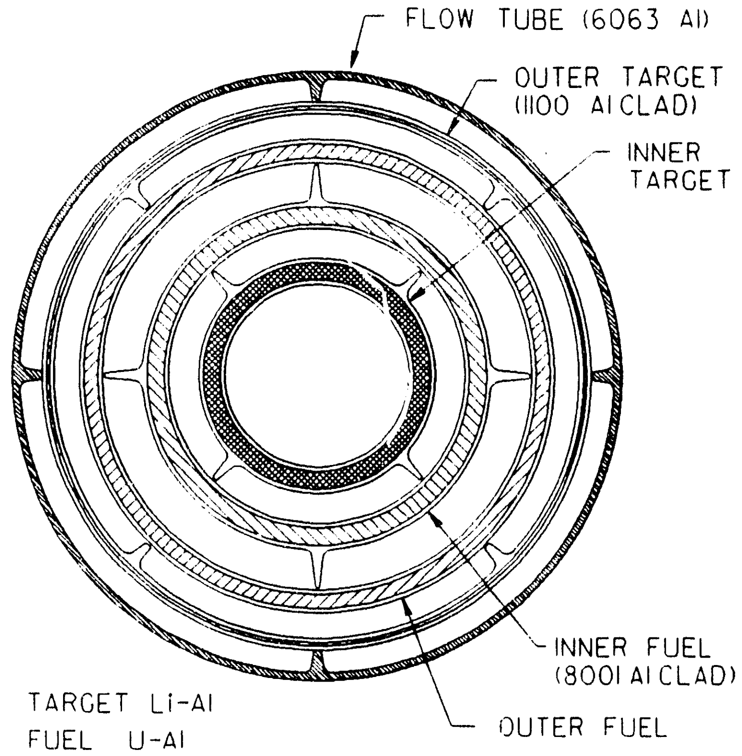

FIGURE 1 - Mark 22 assembly cross-section.

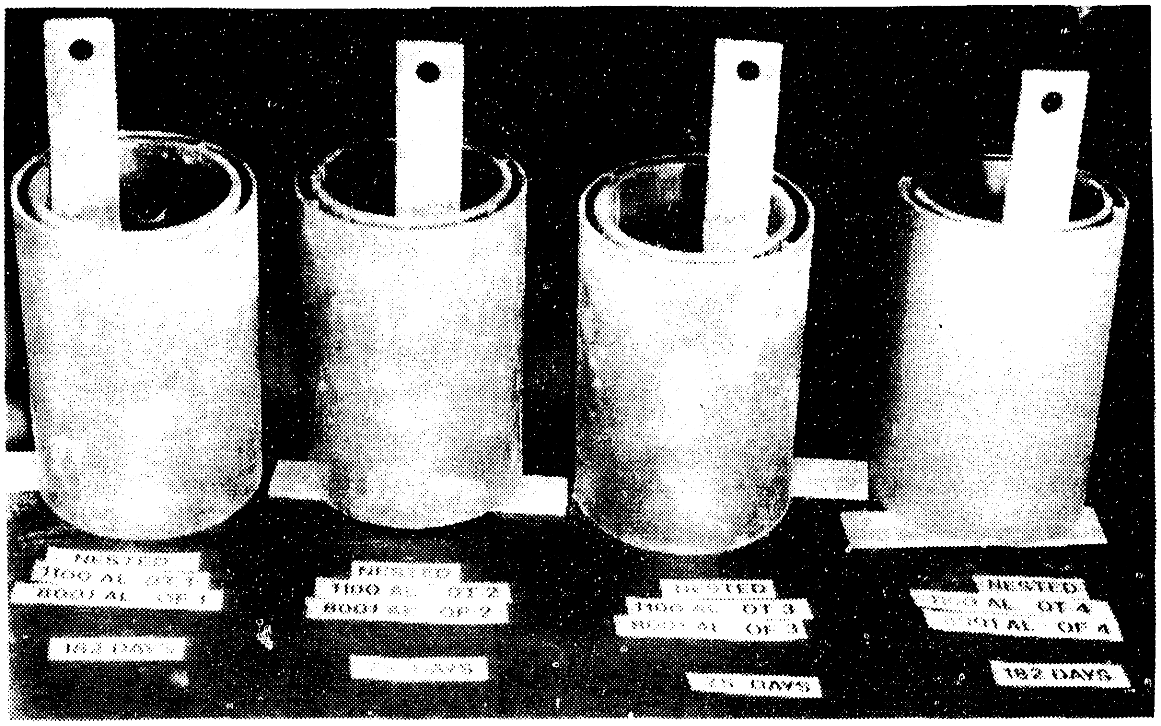

FIGURE 2 - Aluminum components after removal from basin.

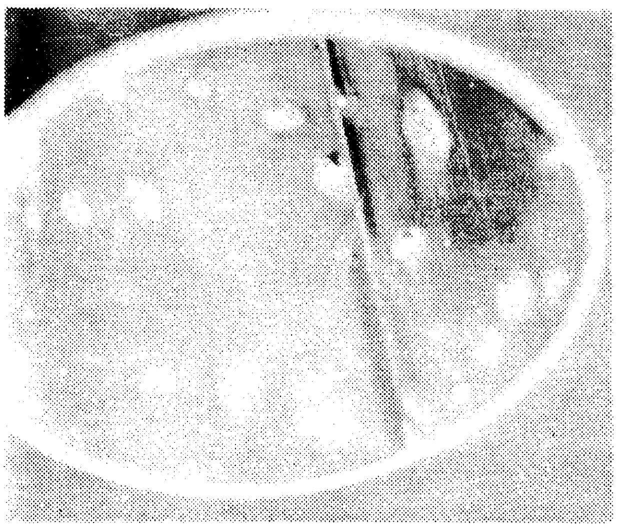

FIGURE 3 - Pitting corrosion inside 1100 aluminum tube.

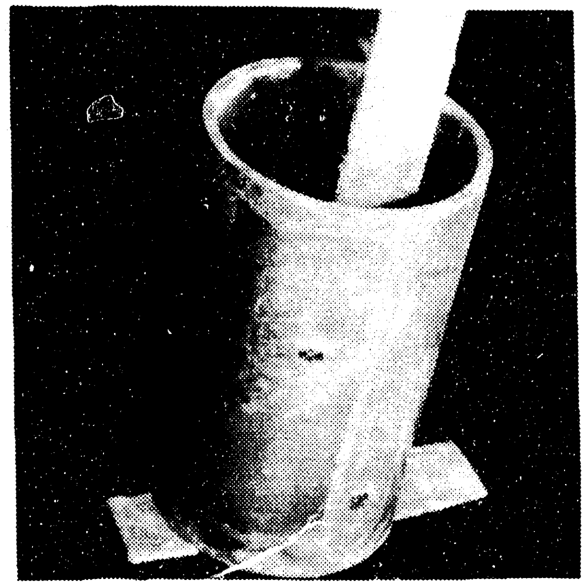

FIGURE 4 - Typical pitting corrosion on 8001 aluminum tube.

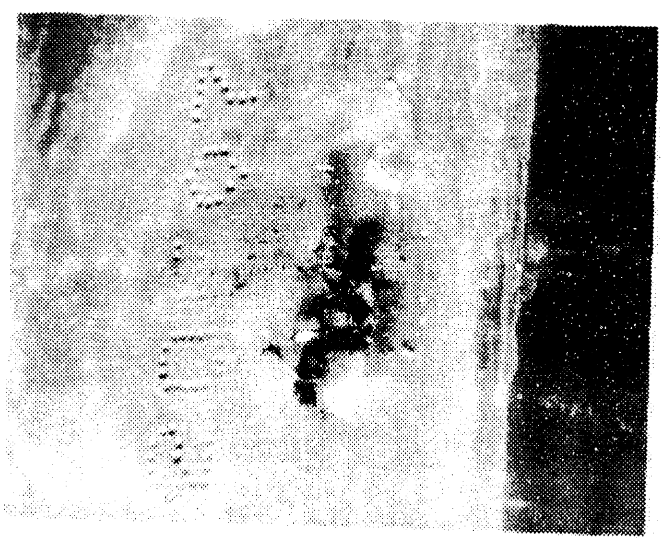

FIGURE 5 - Corrosion nodule on 8001 aluminum tube.

FIGURE 6 - Cross-section of 1100 aluminum pit (58 mils).

FIGURE 7 - Cross-section of 8001 aluminum pit
(36 mils)

END

DATE
FILMED
2/17/93