Corrosion of Research Reactor Aluminum Clad Spent Fuel in Wet Storage

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Abstract

This paper presents an overview of the activities carried out at IPEN, Brazil in the International Atomic Energy Agency (IAEA) sponsored Coordinated Research Project - CRP 'Corrosion of Research Reactor Aluminum clad Spent Fuel in Water' and in the Latin American Regional Project on 'Management of Spent Research Reactor Fuel'. In both projects aluminum alloy coupons in various configurations were exposed to the spent fuel wet storage basin of the IEA-R1 reactor for various periods and then examined. Pitting was the main form of corrosion and pit distribution on various coupons revealed the marked influence of settled solids. The AA 6061 and AA 1050 alloy coupons withdrawn after two years were stained with a layer of the aluminum oxide 'Bayerite' caused by an increase in the average basin water temperature. This observation, although part of a normal sequence of activities within the project, enabled Reactor Operations to explain the perplexing change in color of most in-reactor aluminum alloy components. This also exemplified the added advantage of conducting a corrosion surveillance program. Analysis of sediments obtained from the basin revealed that the main constituents were oxides of aluminum, iron, silicon and calcium. Coupons of the Russian alloy SZAV, pitted more inside crevices compared to the alloy AA 6061. The former pitted more when coupled with stainless steel. Alloy grain orientation also influenced pitting. Coupons of rolled AA 6061 alloy pitted more than coupons made from extruded AA 6061 alloy. Details about the spent fuel storage facilities in IPEN and the water purification systems of the IEA-R1 research reactor are also presented.

Key words: Corrosion, aluminum alloys, spent fuel cladding, pitting, settled solids, corrosion surveillance.

Introduction

Concerns related to corrosion of aluminum-clad spent research reactor (RR) fuel stored for long periods in light-water filled basins around the world led to the establishment, by the International Atomic Energy Agency (IAEA), of a Coordinated Research Project (CRP) on "Corrosion of Research Reactor Aluminum-Clad Spent Fuel in Water." [1,2] This CRP was conducted in two phases. Brazil was one of fourteen countries that were invited to participate in this CRP. The other participating countries were: Argentina, China, Czech Republic, Hungary, India, Kazakhstan, Pakistan, Poland, Romania, Russia, Serbia and Montenegro, Thailand, and the U.S.A. The IAEA provided a detailed work package and standard corrosion test coupons to each participant. The materials selected for testing were representative of typical aluminum cladding alloys used world wide for research reactor fuel, handling tools, and storage racks. Aluminum alloys AA 5086, AA1100, AA6061, AA6063, and SZAV-1 were used. In addition to the IAEA rack of corrosion coupons, many of the participants immersed site specific alloy coupons in their spent fuel basins.[3]

The participants of the IAEA sponsored Regional Technical Co-operation Project for Latin America (RLA) included Argentina, Brazil, Chile, Mexico and Peru. [4] The objectives of this project were to determine the basic conditions for managing RR spent fuel during operation and interim storage as well as final disposal, and to establish forms of regional co-operation for spent fuel characterization, safety, regulation and public communication. The Energy and Nuclear Research Institute (IPEN) in São Paulo, Brazil took part in both the projects and this paper summarizes the main activities related to this participation.

The IEA-R1 research reactor and the spent fuel storage facilities

IEA-R1 is a pool type, light water moderated, and graphite reflected RR at the "Instituto de Pesquisas Energéticas e Nucleares" IPEN, which is part of the Brazilian Nuclear Energy Commission. Although designed to operate at 5 MW, IEA-R1 has operated at 2 MW during most of its life. It is presently operating at 4 MW in one continuous cycle of 64 hours per week. This reactor is being used to perform research in nuclear and solid state physics, radiochemistry and radiobiology, production of radioisotopes and to provide irradiation services. Since start-up, about 160 fuel assemblies (FAs) have been used and about 20 FAs are expected to be burnt annually.

The wet storage facility**,** located at one end of the IEA-R1 reactor pool contains stainless steel spent fuel storage racks. The racks have been used since 1977. In 2003 the stainless steel racks were lined with an aluminum alloy to minimize bimetallic contact between the fuel cladding and the rack and thus reduce galvanic corrosion of the fuel. Figure 1 illustrates the storage section in the IEA-R1 reactor pool.

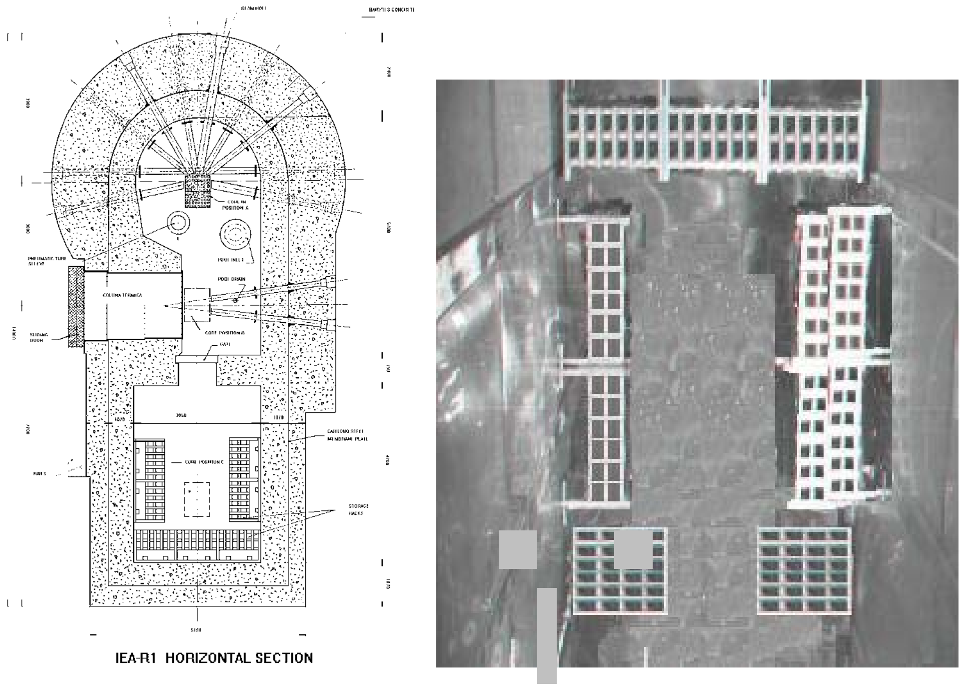


Figure 1. IEA-R1 reactor pool and storage racks

The dry storage facility consists of horizontal silos in a concrete wall. Each silo, made of carbon steel, is 8 inches in diameter and 3.5 m in length. This facility is presently not in use. However it was used for over 40 years to store SFE.

Water purification systems

Table-I presents the typical IEA-R1 reactor basin water parameters. There are two deionization systems to control the water parameters in the reactor basin and in the spent fuel storage section.

<u>Radioactive water deionization system</u>

This system carries out water purification continuously and removes dissolved solids from the primary circuit water. The water is pumped through one of two parallel deionization loops. In both loops a filter is used to remove all the suspended particles. Removal of dissolved impurities is carried out in mixed bed ion exchangers. Softened water from the non-radioactive deionization system is used for regeneration of the ion exchange resins. Conductivity of the water, both entering and leaving the ion exchangers is measured. The system is operated continuously when the reactor is operating.

Non-radioactive water deionization system

This system provides deionized make-up water to the reactor pool, to the horizontal irradiation tubes (beam holes), to the radiochemistry laboratory and for regenerating the ion exchange resins. The system consists of a filter to remove solid particles over 25 microns; a 400L tank of R-H resin to remove mainly the Ca and Mg ions; a coal filter to retain chlorine and organic impurities and a mixed bed ion exchanger, similar to that in the radioactive deionization system. The ion exchangers and filters are connected in parallel, to permit the use of the flow circuit while the resins in the second loop are being regenerated. There are two conductivity indicators in this circuit as well.

Table-I. Typical IEA-R1 reactor basin water parameters

Parameters	Units	Typical Values
pH	-	5.5 to 6.5
Conductivity	μS/cm	< 2.0
Chloride ions	ppm	< 0.02
Iron ions	ppm	< 0.001
Sodium ion	ppm	< 0.4
Temperature	^{o}C	25 to 40
Total solids dissolved	ppm	< 2
^{99}Mo	Bq/L	< 310
^{131}I	Bq/L	< 90
^{133}I	Bq/L	< 430
^{132}Te	Bq/L	< 95
^{239}Np	Bq/L	< 750

Materials and Methods

Coupons of alumnium alloys AA 1100, AA 6061 and SZAV-1 (chemical composition shown in Table II) received from the IAEA, within the context of the two projects were assembled in stainless steel racks with alumina separators. The separators were used to avoid contact between coupons and between the coupons and the rack. A pre-oxidized and scratched coupon of the different alloys was included in the study to simulate the surface of a damaged fuel plate. Site specific alloy AA 6061 coupons were also added to the racks. Surface preparation of the site specific alloy coupons was carried out as per orientations received. The coupons and the racks were photographed and the racks were immersed in the spent fuel storage section (SFSS) of IEA-R1 research reactor.

In the RLA project, six racks were immersed in the SFSB. Three racks were positioned horizontally with its coupons oriented vertically. The other three racks were positioned vertically with its coupons oriented horizontally. One rack from each set was withdrawn after 1, 2 and 3 years of exposure. [5]

Upon withdrawing from the SFSS, the racks were photographed and standard procedures outlined in the CRP 'Test Protocol' were used to handle the rack and coupons.[6] The pH in the crevices of the crevice and bimetallic couples was measured. The coupon surfaces were examined in an optical microscope coupled to an image analysis system.
The pH, conductivity, chloride content and temperature of the water in the reactor pool and the SFSS were monitored periodically. Prior experience had shown that the amount of dissolved impurities in the water was well below detection limits of standard measuring devices and was reflected in the conductivity values. The water in the main pool and the SFSS of the reactor circulates constantly and the conductivity was measured at the inlet to the deionization system.

Table II. Chemical composition of the aluminium alloys.

Alloy	Cu [%]	Mg [%]	Mn [%]	Si [%]	Fe [%]	Ti [%]	Zn [%]	Cr [%]
AA 1100	0.16	<0.1	0.05	0.16	0.48	0.005	0.03	0.005
AA 6061	0.25	0.94	0.12	0.65	0.24	0.04	0.03	0.04
SZAV-1	<0.01	0.53	<0.05	0.71	0.09	<0.005	0.03	<0.005

Results and discussion

Observations made immediately after removal of the racks

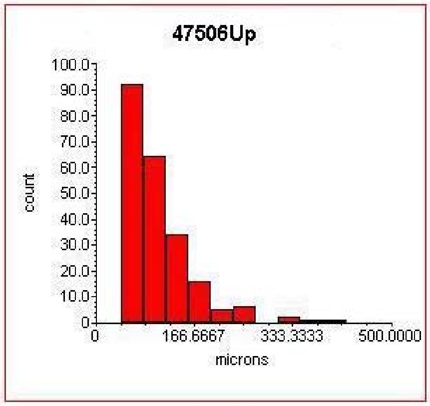
During disassembly of the racks the coupled coupons were difficult to separate due to formation of oxides within the crevice. Also during disassembly of the rack, the pH of the water in the crevice between the various couples was measured. In all cases, independent of coupon orientation, the pH of the water in the crevice was about 5.5, one point below that of the bulk water pH.

Optical microscopic examination of coupon surfaces.

The AA 6061 alloy coupons were almost dark grey where as the pre-oxidized and scratched coupons of this alloy were quite bright and unattacked. The oxide on the coupon surface was removed to enable examination in an optical microscope. The exposed surfaces of the alloys revealed pits, independent of the orientation of the coupon. However, many features were specific to the alloy, the position of the coupon in the rack and the orientation of the coupon. The SZAV alloy coupons pitted where as the AA 6061 coupons did not pit to the same extent. A number of pits were observed on the contact surface of the SZAV alloy compared to that on the AA 6061 alloy coupon, and even more in the SZAV alloy contact surface of the galvanic couple SZAV-stainless steel. The distribution of pits on the coupon surfaces was determined and histograms of the number of pits (counts) as a function of pit diameter were plotted.

Horizontally oriented coupons (Rack-47) (exposed for one year)

Figures 2a and 2b reveal the histograms of pit count versus pit size on the AA 1050 alloy coupon surface facing upwards and downwards respectively. The surface facing upward revealed a large number of pits, ~90, in the size range 40-50 µm while the surface of the same coupon facing downwards, revealed only 6-8 pits in the same size range. The shape of the pits on this coupon varied from irregular to round. (figure 3).



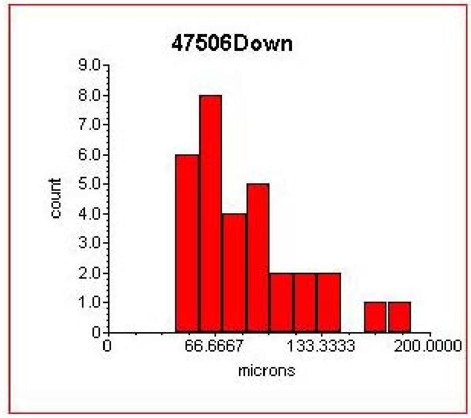


Figure 2. Histograms of pit count versus pit size on the surface facing upwards (47506Up) and the surface facing downwards (47506Down) on a horizontally oriented AA 1050 coupon exposed for one year to the IEA-R1 SFSS.

Most pits revealed a bright region around them, characteristic of a cathode region around a localized anode region. The shape of this region varied from circular to elliptical. (figure 4) On the AA 1050 alloy coupon surface in contact with the AISI 304 stainless steel coupon, larger pits were observed, revealing the deleterious effect of a bimetallic contact. The two surfaces of the pre-oxidized and scratched AA 1050 alloy coupon revealed few small pits and no bright regions around the pits. Also, no pits were observed along the scratch.

Vertically oriented coupons (Rack 44)(One year exposure)

On the surfaces of individual AA 1050 alloy coupons, round and irregularly shaped pits were observed. Many pit clusters were also observed. The bright cathode areas associated with the pits were shaped like a comet with a tail, giving a clear indication of the top and bottom of the vertically oriented coupons. (figure 4)

Almost all the pit features observed on AA 1050 alloy coupon surfaces were observed on the exposed surfaces of AA 6061 alloy coupons. Bright regions or comet tails were not observed around irregular shaped pits indicating that the mechanism associated with the formation of round and irregular shaped pits are different. The contact surfaces of the crevice couple coupons, AA 1050-AA 1050, AA 1050-AA 6061 and AA 6061-AA 6061 couples, were stained and did not reveal any pits. The stains on the surfaces of the two alloys were distinct and characteristic of the alloy. The surfaces of the pre-oxidized and scratched AA 1050 alloy coupon revealed a few small pits and no bright regions around the pits.

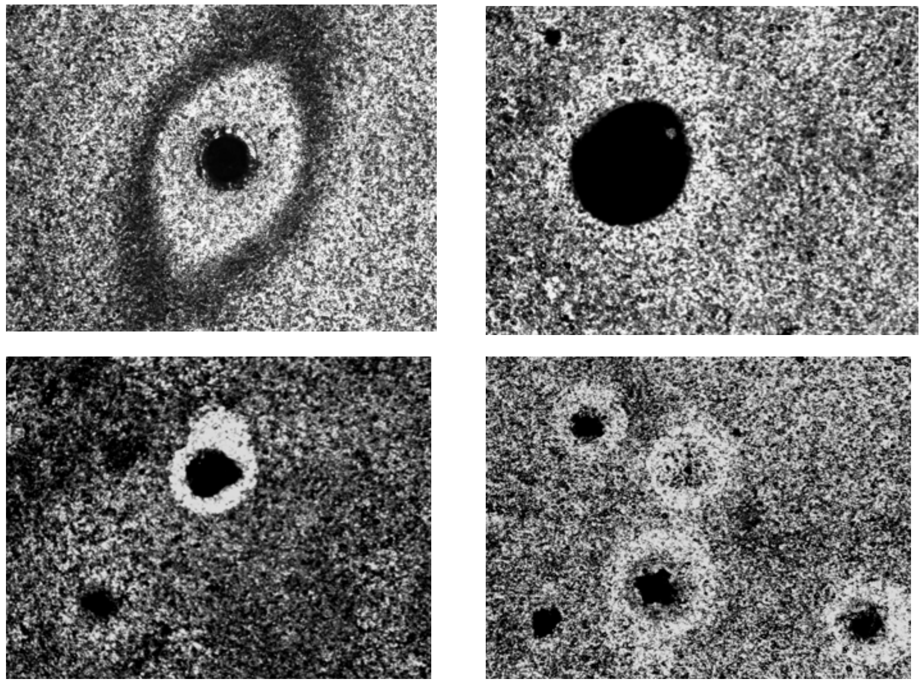


Figure 3. Micrographs revealing pits and bright regions on horizontal AA 1050 alloy coupon surfaces.

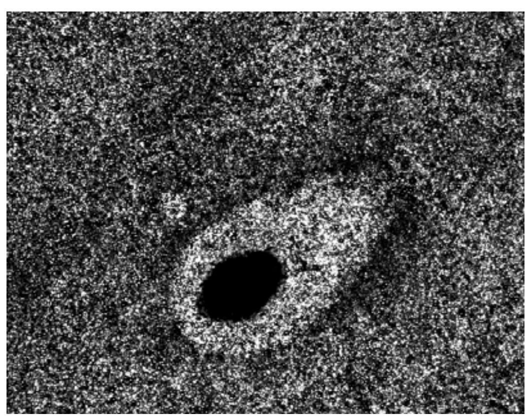
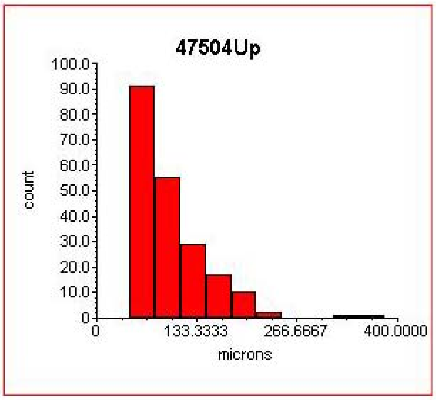


Figure 4. Optical micrograph of vertically oriented AA 1050 alloy coupon surface revealing the comet shaped bright region around a pit.

Histograms of number of pits versus pit sizes on the surfaces of coupons exposed both horizontally and vertically for two and three years were also obtained. Observations similar to those made from the histograms of coupons exposed for one year were made.

Effect of coupon orientation on pitting corrosion

Comparison of pit histograms of the horizontally oriented surface of AA 1050 coupon facing upwards exposed for one year, with that of the surface of the same alloy oriented vertically (Figure 5) revealed that twice as many pits (size range 40-50 µm) form on the horizontal coupon as compared to that on the vertical coupon.



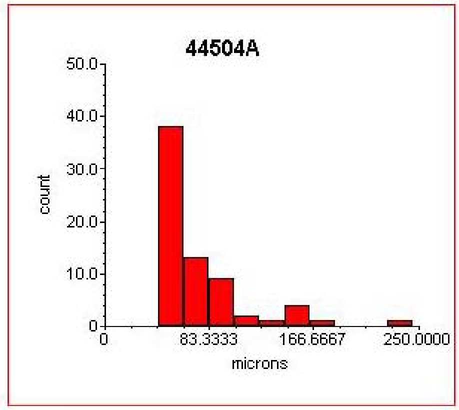


Figure 5. Histograms of pit count versus pit size on the AA 1050 alloy coupon surface facing upwards (47504Up) and a vertically oriented surface of the same alloy (44504A)

Comparison of pit histograms of vertically and horizontally oriented AA 6061 alloy as well on coupons of both alloys exposed for 2 and 3 years also revealed similar behavior. This indicated that among the many parameters that control pit formation, such as alloy composition, metallurgical state and water parameters, settled solids contribute to pit initiation and formation.

Influence of average basin water temperature on coupon corrosion.

This part of the study was initiated when IEA-R1 reactor operations reported greying of all Al surfaces inside the reactor pool. Consequently some racks were withdrawn after 22 months of exposure instead of the planned 24 months.The surfaces of coupons exposed for 22 months (nominal 2 years) were darker and stained compared to those exposed for 12 months. These stains obscured the pits from being observed in an optical microscope. The stained regions were analyzed by SEM and XRD and found to be the aluminium oxide Bayerite, as shown in the micrographs in figures 6 and 7. This oxide forms at temperatures below 70º C. The pool water temperature was reported to be 10º C higher than normal during a six month period. The rack with coupons exposed for 12 months were withdrawn prior to the increase in reactor water temperature. This six months period also coincided with reactor operation at 5MW. The increase in pool water temperature was attributed to insufficient cooling capacity of the heat exchanger. The reactor power has subsequently been reduced to 4MW awaiting installation of a new heat exchanger. This exemplifies the added advantage of conducting a corrosion surveillance program.

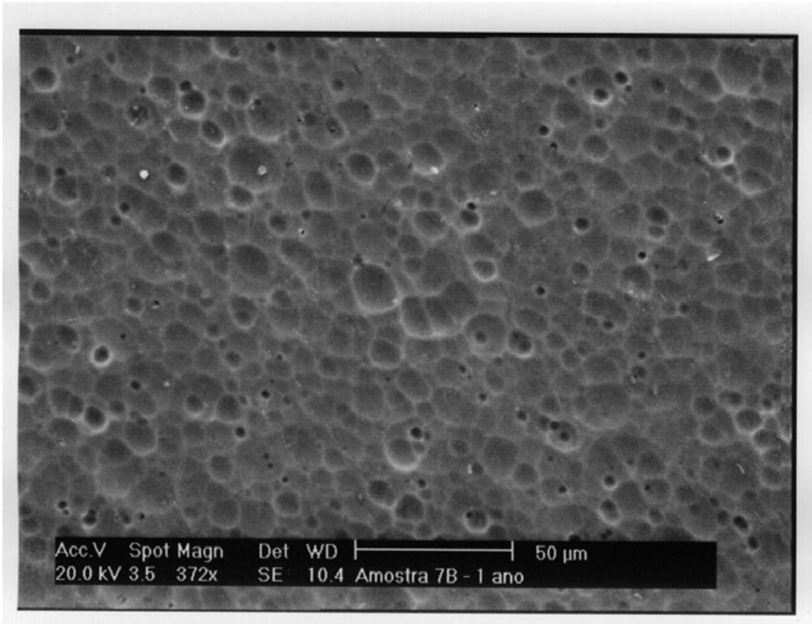


Figure 6. Scanning electron micrograph of AA 1050 alloy coupon surface exposed for 12 months in the IEA-R1 SFSS.

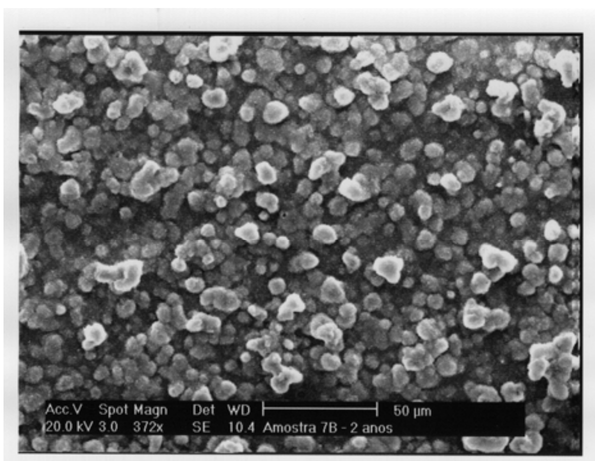


Figure 7. Scanning electron micrograph of AA 1050 alloy coupon surface exposed for 22 months in the IEA-R1 SFSS.

Evaluation of settled particles on coupon surfaces

A sediment collector was installed in the SFSS close to the corrosion test racks for a period of four months.

Table III. Quantitative x-ray fluorescence spectroscopic analysis of sediments from the dust collector

Oxide	Percent
Al_2O_3	56.785
SiO_2	21.042
Fe_2O_3	14.93
CaO	2.352
Cr_2O_3	1.594
TiO_2	0.757
NiO	0.580
K_2O	0.563
P_2O_5	0.432
PbO	0.336
MnO	0.186
ZnO	0.136
ZrO_2	0.102
Ag_2O	0.102
CuO	0.063
MoO_3	0.041

After this period the collector was removed, the water and settled solids retained in it were stirred, filtered and the sediments collected on a filter paper. Subsequently the sediments were dried in an oven at 100º C for 24 hours, weighed, mixed and representative specimens examined in the SEM and analysed by x-ray fluorescence spectroscopy. Table III shows the quantitative analysis of the sediments. It consisted primarily of oxides of Al, Si, Fe and Ca. The rate of sedimentation during the four month period was found to be 0.17823 mg/cm^2/month.

General discussions

Comparison of pit histograms of horizontally oriented top surfaces of AA 1050 alloy coupons with that of vertically oriented surfaces of the same alloy for one, two or three years revealed that twice as many pits (size range 40-50 µm) form on the former as compared to that on the vertically oriented coupon. Comparison of pit histograms of vertically and horizontally oriented AA 6061 alloy coupon surfaces also revealed a similar behavior. This indicated that among the many parameters that control pit formation, such as alloy composition, metallurgical state and water parameters, settled solids contribute to pit initiation and formation. Microscopic examination of the crevice surface of the SZAV-SZAV crevice couple revealed a number of small pits besides the aluminum oxide. The contact surface of the SZAV coupon with stainless steel in the galvanic couple revealed many more pits compared to the contact surface with the same alloy. The contact surface of AA 6061, either in contact with AA 6061 or stainless steel, on the other hand did not reveal a similar distribution of pits. No pits were observed on the pre-oxidized AA 1050 and AA 6061 surfaces. No pits were observed along the scratch on the pre-oxidized and scratched coupons. The facing surfaces of the crevice couple coupons, AA 1050-AA 1050, AA 1050-AA 6061 and AA 6061-AA 6061 were stained and did not reveal any pits. The stains on the surfaces of the two alloys were distinct and characteristic of the alloy.

Conclusions

1. Pitting was the main form of corrosion of aluminum alloy coupon surfaces exposed to the spent fuel storage section of the IAE-R1 reactor.
2. The top surfaces of horizontally oriented coupons pitted more than the surfaces facing downwards. The extent of pitting on the top surface of horizontal coupons decreased with the position of the coupon from top to bottom in the rack.
3. The two sides of vertically oriented coupons of both alloys pitted to the same extent.
4. The extent of pitting of vertically oriented coupons was considerably less than that of the horizontally oriented coupons. This indicated that pit formation is influenced by, among other factors, settled solid particles on the coupon surface.
5. The horizontally and vertically oriented pre-oxidized coupon surfaces pitted to a lesser extent than the corresponding un-oxidized alloy coupon surfaces.
6. Coupon orientation had no noticeable effect on crevice or galvanic corrosion.
7. The contact surface of SZAV coupons, from a crevice or a galvanic couple, revealed a number of small pits. The surface in contact with stainless steel revealed more pits.
8. Rolled AA 6061 coupons pitted more than extruded AA 6061 coupons.
9. The surfaces of coupons exposed to water at 45º C were stained with a layer of the Bayerite.
10. The main constituents of the SFSS sediments were oxides of aluminum, iron, silicon and calcium.
11. Overall, coupon orientation has a marked effect on the corrosion behavior of aluminum alloy coupons.

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