

CORROSION OF SPENT ALUMINIUM-CLAD RESEARCH REACTOR FUEL – SYNERGISM IN THE ROLE OF STORAGE BASIN WATER PARAMETERS

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ABSTRACT

Concerns about corrosion of aluminium clad research reactor (RR) fuels in wet storage lead to three IAEA supported projects. The activities within these projects consisted of exposing racks of test coupons of a variety of aluminium alloys in different configurations to spent fuel storage basins in 17 participating countries worldwide. The aluminium alloys were representative of typical RR cladding alloys, handling tools and storage racks. The coupons were evaluated after predetermined exposures times and the storage basin water parameters were monitored periodically during the projects. Pitting was the main form of corrosion and this was influenced by the conductivity and chloride ion content of the water, formation of galvanic couples and settled solid particles. Marked synergism was observed in the influence of these parameters on aluminium alloy coupon corrosion and this paper highlights this phenomenon.

1. Introduction

The International Atomic Energy Agency's (IAEA's) RR spent fuel data base (RRSFDB) shows that there are 62,027 spent fuel assemblies stored in various facilities around the world and another 24,338 assemblies in RR cores. Over 90% of these spent RR fuels are clad with aluminium or aluminium alloys and stored in wet basins. (Table I) The at-reactor storage is often in a different section of the reactor pool or in a separate pool within the reactor building, often referred to as the decay pool. In many countries the fuel has been in storage for periods of up to 50 years in different types of light water pools.

Type of storage	At-reactor	Away-from-reactor
Pool	154	55
Dry well	25	31
Vault	10	12
Other	18	6

Tab I: Spent fuel storage facilities

In the late 1990's, corrosion of aluminum-clad spent nuclear fuel stored in light-water filled basins became a concern and the IAEA implemented the coordinated research project (CRP) on "Corrosion of Research Reactor Aluminum-Clad Spent Fuel in Water.[1] A regional technical co-operation project for Latin America (RLA) titled 'Management of spent research reactor fuel', was also supported by the IAEA and carried out from 2001 to 2005. The CRP and the corrosion activities within the RLA consisted of exposing Al alloy coupons to spent fuel storage basins for predetermined periods followed by their examination. Seventeen countries participated in the two projects and the materials selected for testing were representative of RR cladding alloys handling tools, and storage racks. [1,2] These alloys included mainly, AA 1100, AA 6061 and SZAV-1. In addition to these alloys, many of the participants included site specific alloys in their studies. During the execution stage of the projects, the storage basin water parameters were monitored periodically. The influence of Al alloy composition, galvanic effects (Al alloy/stainless steel), crevices, water parameters, coupon orientation, alloy grain orientation and settled solids on the corrosion of the coupons were evaluated. Complementary laboratory tests were also carried out at some of the participating country's laboratories to determine the effect of specific parameters on the nature, extent and mechanism of Al alloy corrosion.

This paper presents the main observations of these projects with respect to the effect of spent fuel storage basin (SFSB) parameters such as conductivity, aggressive ions, galvanic coupling and settled solids on the corrosion of the coupons and the synergism in the effects of these parameters on Al alloy corrosion.

2. Materials and Methods

Aluminium alloy coupons of AA 1100 (or AA 1050), AA 6061 and SZAV-1 were assembled in stainless steel test racks with alumina separators as shown in figure 1. [1] The separators were used to avoid metallic contact between coupons and between the coupons and the rack. Site specific alloy coupons were also added to the racks. In the participating countries the coupons were exposed to spent fuel basins at two or more sites. The racks also contained Al alloy-Al alloy and Al alloy-stainless steel coupon couples to simulate crevices and bimetallic (galvanic) contacts. At many sites, coupons were exposed both vertically and horizontally to evaluate the effects of settled solids. [3-6] The coupons were exposed to the water in SFSBs for periods of up to 6 years. During this period the water parameters pH, conductivity, chloride content, temperature and other ions that were site specific were monitored periodically. Graphs of variations in the water parameters were plotted to help correlate coupon corrosion with water parameters. After pre-determined periods the racks were withdrawn from the basins and the coupons examined and the extent of corrosion evaluated following standard procedures outlined in CRP Test Protocol. [1]



Fig 1. A typical rack with test coupons.

3. Results and discussion

A large amount of data was generated about the corrosion of the aluminum coupons at the different sites. [1,2] Pitting was the main form of corrosion. The number, size and distribution of the pits on the coupons varied from one site to another. This data indicated that the factors that contributed to corrosion of aluminum alloys in the SFSBs were: (a) high water conductivity (100-200 μ S/cm); (b) aggressive ion concentration (Cl^-); (c) galvanic coupling between dissimilar metals (stainless steel/aluminum); (d) settled solids that are cathodic with respect to aluminum. (Fe); (e) sludge (which contains significant amounts of Fe, Cl, and other ions); (f) scratches and imperfections in the surface oxide; (g) poor water circulation. Direct correlations between each of these parameters and pitting corrosion of Al alloy coupons was observed. [1-6] At many test sites, more than one parameter influenced pit formation on the coupons. Comparison of data from the different sites revealed synergism in the effect of these parameters on Al corrosion. That is, the combined effect of two or more of the parameters on Al corrosion was greater than the sum of the effects of individual parameters.

3.1. Synergism in the effects of specific parameters on Al coupon corrosion

Conductivity and chloride ions

Pitting is a localized form of corrosion and occurs on metals that form a layer of surface oxide. Halide ions, and specially chloride ions, are known to cause pitting of Al alloys. [7] Direct correlations between chloride content and extent of pitting has been observed at many sites. [1,2] It is also well known that a few chloride ions are sufficient to initiate and propagate a pit on Al surfaces exposed to neutral pH water. The chloride ions penetrate the surface oxides at imperfections and initiate pits. The growth of pits is an autocatalytic process and the chloride ions are the catalyst. [7] Laboratory data and Al coupon evaluation data have indicated that even though no pits formed in chloride ion free neutral pH waters with conductivity of 10-20 $\mu\text{S cm}^{-1}$ and in distilled water with chloride ions in the ppm range, pitting was observed in waters with even lower conductivity ($\sim 2 \mu\text{S cm}^{-1}$) and with some chloride ions. [5,6] This indicated synergism in the effects of conductivity and chloride ion content on pitting corrosion of Al. Since chloride ions contribute towards the ionic conductivity of aqueous systems, any synergism in the effects of either parameter, conductivity and chloride ions, with that of any other parameter is discussed as a conjoint effect of conductivity and chloride ions.

Galvanic coupling and conductivity/chloride ions

Proof of synergism in the effects of galvanic coupling and conductivity/chloride ions was evident when the contact surfaces of Al alloy coupons in a crevice couple and in a galvanic couple (in the same rack) were compared. The surface of the Al alloy in the crevice couple was stained with Al oxide but had no pits. However, the surface of the same Al alloy in contact with the stainless steel (SS) coupon revealed many pits. (Fig. 2). Further, even though pits were observed on the Al alloy surface a short distance away from the contact region with SS, none were seen on the flip side of the same Al coupon or on the surface of the single coupon of the same alloy in the same rack. (Fig 2) This lent further proof of synergism between the effects of galvanic coupling and conductivity/chloride ions. Since corrosion is an electrochemical process involving anodes, cathodes and an electrolyte, increased pitting of the Al coupon surface in the vicinity of SS is due to the latter functioning as a large area cathode.

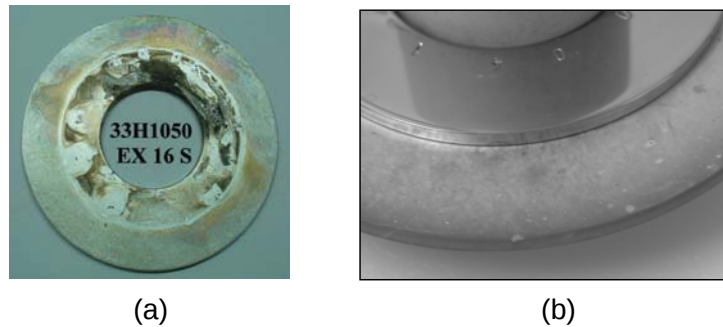


Fig 2. Pits on the Al coupon surface at regions: (a) in contact with the stainless steel coupon and (b) further away from the contact region.

Settled solids and conductivity/ chloride ions

Evidence of the effect of settled solids on corrosion of Al coupons and synergism in the effects of settled solids and conductivity/chloride ions were observed at various sites among the participants of the three projects. Two examples highlight the synergistic effects of settled solids and conductivity/chloride ions. (1) Civil construction in the vicinity of the RA6 reactor in Argentina lead to increase in airborne dust and consequent increase in dissolved solids and conductivity of the reactor and decay pools as shown in Fig 3. The construction also lead to an increase in the amount of settled solids on the Al coupons. The Al coupons withdrawn and examined in early 2000 revealed pits in apparently very good quality water. The pits were observed on the top surface only, and more pits were observed on coupons higher up in the rack. Parts of the same coupon without any settled solid (bottom surfaces) did not reveal any pits even though the coupon was exposed to identical conductivity oscillations. (2) In laboratory tests, an Al surface with hematite particles was exposed for 20 days to a solution with 40 ppm of NaCl. This surface did not reveal pits but some stains. However, a similar surface coupled to stainless steel and exposed to the same solution revealed pits after only 7 days.

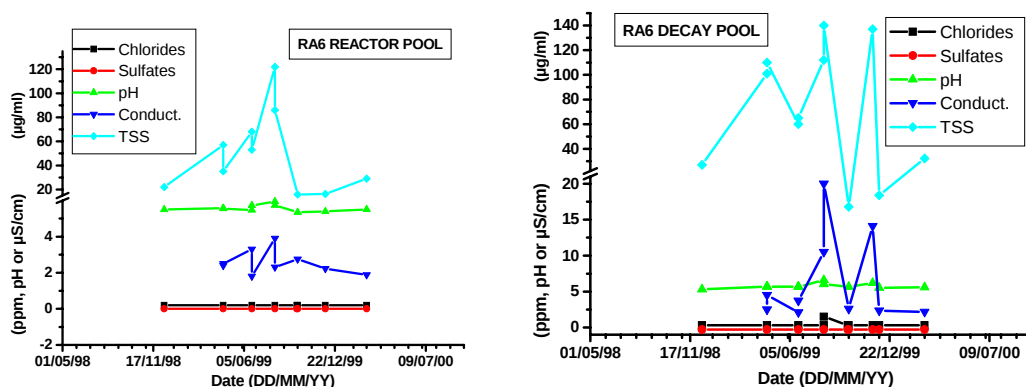


Fig 3. Variation of water parameters in the RA6 reactor pool (left) and decay pool.

Settled solid particle-induced corrosion of aluminium could be due to one or more of several reasons: (a) the nature of the solid and consequently the nature of products that could leach out; (b) formation of crevices under the solid and thereby crevice corrosion in the presence of aggressive ions; (c) the solids if conducting, could become the cathode and the cathodic reaction could cause a localized increase in pH and metal dissolution.

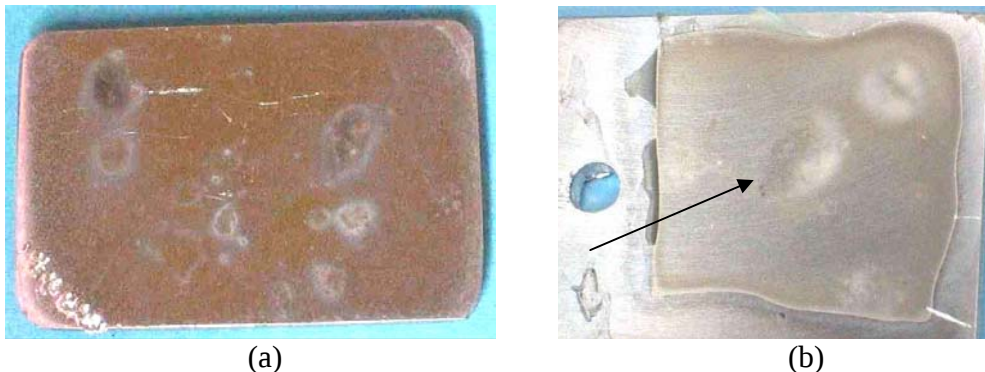


Fig 4. Al alloy surfaces with hematite particles that were exposed to water with 40 ppm NaCl: (a) for 20 days – reveal stains but no pits; (b) for 7 days, but connected to SS – arrow reveals pits.

4. Concluding remarks

In spent fuel storage basins the four main parameters that lead to corrosion of the aluminium cladding of RR fuel are conductivity of the water, dissolved aggressive ions, galvanic coupling and settled solids. Separately these parameters do not cause significant pitting damage of the Al cladding. However, when two or more of these parameters are present or operate conjointly, there is synergism and the extent of corrosion of the Al cladding is much more than the sum of the effects of these parameters operating separately on corrosion.

5. References

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