CORROSION OF SPENT RESEARCH REACTOR FUEL: THE ROLE OF SETTLED SOLIDS.

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ABSTRACT

Reactor components or fuels that have remained immersed in a research reactor pool or in a spent fuel storage basin often reveal solids on their surfaces. The sources of these solids are many and include air borne dust, corrosion products and precipitated salts. Results of the IAEA coordinated research project (CRP) "Corrosion of Al-clad Spent Fuel in Water" and the Regional Project for Latin America (RLA) revealed that settled solids contribute to corrosion of Al coupons. Further studies carried out at different sites worldwide to determine the rates of settling of solids, their composition and influence on corrosion of aluminium alloys revealed that the solids consisted mainly of oxides of aluminium, iron, silicon and calcium. Other constituents in the settled solids were site-specific. Short term laboratory tests in which solids with specific composition were positioned on aluminium substrates in relatively pure water revealed their role in initiating pitting and/or crevice type of corrosion.

1. Introduction

Reactor components or fuel assemblies that have remained immersed in a research reactor pool or in a spent fuel storage basin for a reasonable length of time have loose solids on their surfaces. The quantity and nature of these solids vary. These solids settle on all surfaces inside pools or basins. Most of these solids eventually settle at the bottom of the pool or basin and are the main constituent of sludge. The origin or sources of these solids are mainly air borne dust, corrosion products and precipitated salts. Airborne dust in the reactor hall or in the spent fuel basin (SFB) hall settles on reactor pool or SFB surfaces. The dust (fine solid particles) on the pool/basin surface floats until wetted by the water. Surface skimmers in reactor pools remove most of the floating dust. However, depending on properties of the solid, mainly density, it settles at the bottom of the pool or on any surface that it encounters as it descends through the pool or basin water. Solids settle faster in stagnant regions of the pool. Fine solid particles also have a tendency to agglomerate to form larger particles which settle faster. This tendency varies with the composition and density of the particles. The corrosion products on metallic surfaces in contact with flowing water are easily detached and carried in the circulating water, often returning, depending on its size, to the reactor pool or basin. Another source for solids is precipitated solids. Reactor hall operations such as: (a) movement of cranes; (b) opening of doors; (c) immersion of inadequately dusted components in the reactor pool; (d) shifting of immersed components are other sources of settled solids. In away-from-reactor fuel storage facilities the above mentioned scenes plays out to a greater extent.

Experimental work carried out in the IAEA coordinated research project (CRP) "Corrosion of Aluminium-clad spent fuel in water" and the Regional Project for Latin America (RLA) included the exposure of horizontal and vertical coupons of aluminium (Al) alloys to spent fuel basins in many countries. [1] Comparison of the corrosion behaviour of these coupons revealed that horizontal coupons corroded considerably more than vertical coupons. The top surfaces of horizontal coupons corroded more than the bottom surfaces of the same coupon. These observations lent proof to the dominant role of settled solids on the corrosion of Al coupons and by extension on the corrosion of Al-clad spent research reactor fuel. [2] Further studies were undertaken to determine the: (a) amount of settled solids and the rate of settling of these solids at the various sites; (b) composition and/or constituents of the solids; (c) role of specific settled solids on the nature and extent of corrosion of Al alloys. This paper presents details of these studies.

2. Methods and materials

In this study, a stainless steel or aluminium recipient (henceforth referred to as the collector) was used to collect settled solids at 11 different sites where the two IAEA projects were being carried out. This collector was positioned in the vicinity of racks with corrosion test coupons. The collectors remained in the research reactor (RR) or SFB for periods ranging from 4-6 months. After withdrawal of the collector, the water was filtered; the solids collected on a filter paper were dried at 100° C for 24 hours and weighed. The amount of solids and the rates of settling were determined. Representative specimens of the solids were examined in the SEM and/or analysed using one or more of the following techniques: (a) energy dispersive spectroscopy (EDS), (b) x-ray diffraction (XRD), (c) x-ray fluorescence (XRF), (d) mass spectrometry. Fig. 1 shows a collector and settled solids in one of the collectors.

(a)   (b)

Fig. 1. (a) AISI 304 stainless steel collector used at CChen, Chile. (b) Settled solids in a collector

3. Results and discussion

The rates of sedimentation of the solids at different sites and their composition and/or constituents are shown in Table 1. The solids consisted mainly of oxides of aluminium, iron, silicon and calcium. This indicated that the sources of the solids were construction debris, atmospheric dust and corrosion products of aluminium alloy and steel components in the pool or basin. Other constituents in the settled solids were site-specific.

Test site	Rate of sedimentation ($\mu g/cm^2$/month)	Composition or constituent of settled solid
RECH-1, Chile.	58.6	Al; SiO_2 (quartz);SiO_2 (cristobalite) $(Ca,Na)(Si,Al)_4O_8$ (anortite)
RECH-2, Chile.	1.5	SiO_2 (quartz)
CDTN, Brazil.	18.1	Amorphous $CaCO_3$ (calcite); Fe_3O_4 (magnetite), SiO_2 (quartz); $CaMg(CO_3)_2$ (dolomite)α-$Al_2O_3.3H_2O$ (gibbsite), Fe_2O_3 (hematite) $Mg_3Si_4O_{10}.(OH)_2$ (talc)
ININ, México.	17.666	Iron oxides (hematite, magnetite), aluminosilicates, sodium and calcium carbonates
România.		Fe, Zn and Cd
SF pool, Thailand.	195	Fe, Al, SiO_2, Cu, Ba; Light particles of plant tissue, bio-mass floating in water with some fine dust.
Reactor pool, Thailand.	141	Fine light brown dust. Main component is iron.
Cooling pool, Kazakhstan.	36.000	Deionizing column resin
Water storage, Kazakhstan.	12.000	Deionizing column resin
RA3 Decay Pool, Argentina	19.5	Silicon oxide and combined oxides of Si, Al and Fe
IPEN, Brazil.	178.2	56.79 Al_2O_3, 21.04 SiO_2, !4.93 Fe_2O_3, 2.35 CaO, 1.6 Cr_2O_3, 0.76 TiO_2, 0.6 NiO (wt%)

Tab. 1. Rates of sedimentation of solids and their composition or constituents.

3.1. Effect of settled solids on corrosion of aluminium alloys

Aluminium and its alloys normally corrode in aqueous solutions with low or high pH. Pitting is the main form of corrosion and aluminium alloys are prone to pitting corrosion in solutions with not only chloride ions but also other anions like sulphates and nitrates. Aluminium alloys do not generally pit in environments totally free of aggressive ions. Nevertheless, Al alloys have been observed to pit in very low conductivity water in the presence of solids on the surface. This solid particle-induced corrosion of aluminium could be due to one or more of several reasons: 1) The alkaline nature of the solid or leaching of alkaline products from the solid; 2) Formation of crevices under the solid and consequent crevice corrosion in the presence of aggressive ions; 3) The solids if conducting, become the cathode for the cathodic reaction, result in localized pH increase and consequent metal dissolution.

Reason (1) is considered to be operative if the solid is a concrete particle. Fig 2a reveals the surface of an AA 6061 alloy with a concrete particle and exposed for 40 days to nuclear grade demineralised water. [3] Aluminium alloys are also susceptible to crevice corrosion, which occurs in the presence of aggressive ions. [4] In pure water, this form of corrosion sometimes occurs in the presence of aggressive ions originating from the sediment itself. Figs 2b and 2c show corrosion of AA 6061 alloy with hematite and magnetite particles on the surface. These figures reveal that the crevice corrosion mechanism could be operating at the microscopic level. The alloy surface around the hematite particle is corroded, where as the surface around the magnetite particle is unaffected. [5]
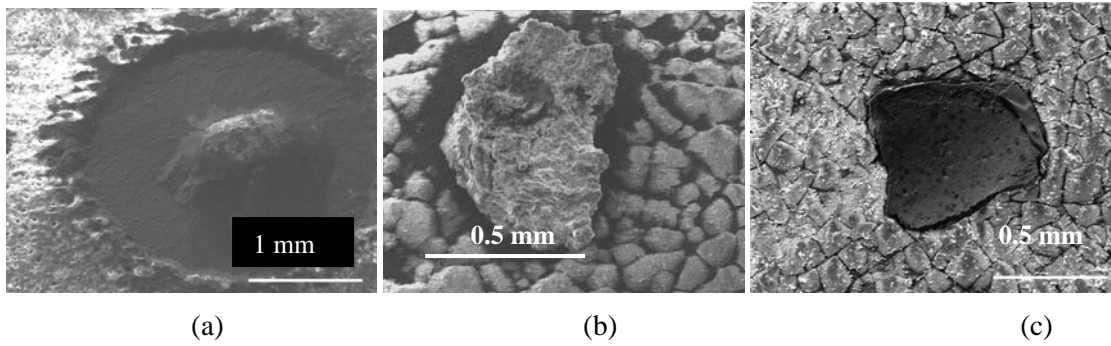
Fig. 2: Corrosion of AA 6061 alloy exposed for 40 days to nuclear grade demineralised water: (a) with a concrete particle; (b) with a hematite particle; (c) with a magnetite particle.
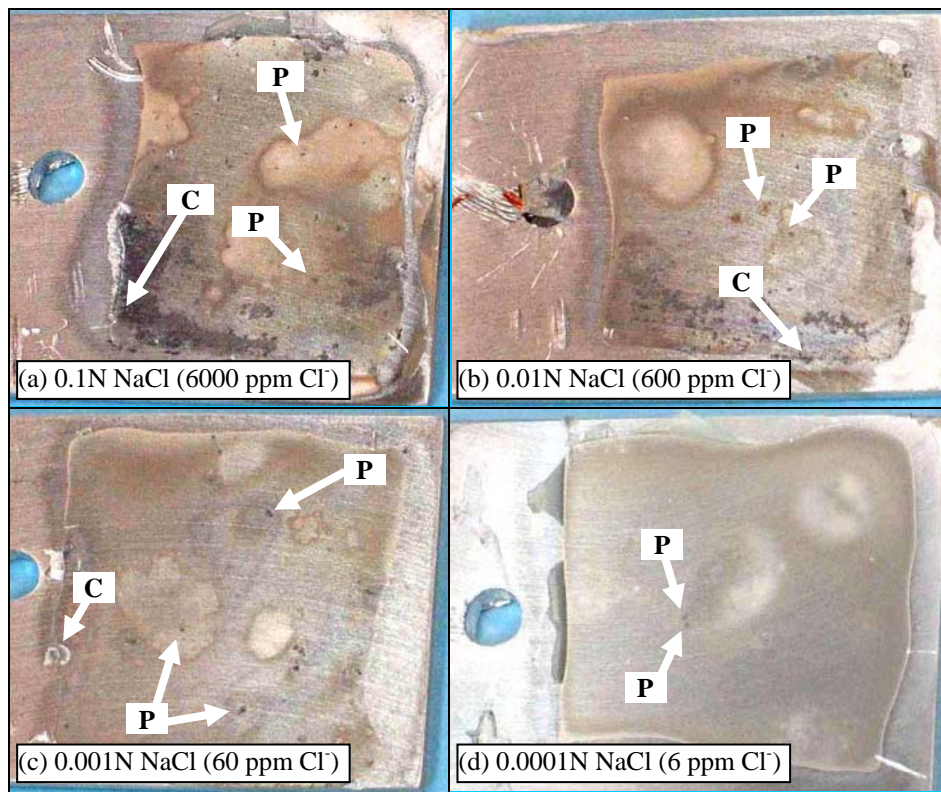

Fig. 3: Appearance of AA 6061 sample surfaces with hematite sediments after 7 days of exposure to NaCl solutions of different concentrations. Pitting is indicated with 'P' and crevice corrosion with a 'C'. The stains produced by the sediments are still visible.

The sediment induced pitting produced in the laboratory resembles, to some extent, observations made on Al surfaces exposed to SFB waters. However the pits were not as deep as those observed on certain spent fuels stored for extended periods. To evaluate the short term influence of sediments on the corrosion of Al, immersion tests were carried out in waters similar to that in SFBs. In these tests, particles of hematite, magnetite and glass were deposited on aluminium surfaces exposed to sodium chloride solutions of various concentrations.

3.2. Effect of short term exposure of deposited solid particles on Al alloy corrosion

The Al surface with hematite particles that was exposed for 60 days to a solution with 40 ppm of chlorides did not reveal pits but some stains. However, a similar surface coupled to stainless steel revealed pits after only 7 days. The results also indicated the marked effect of chloride ion concentration as shown in Fig 3. In waters with high chloride ion concentrations, both pitting and crevice corrosion was observed. Pits formed both under the deposits and on the free surface. In the solution with 0.001N NaCl, very few pits formed at regions away from sediments. In 0.0001N NaCl all the pits were under the particles. The Al surface with magnetite particles and exposed for 7 days to 0.001N NaCl (60 ppm chloride) revealed pits only around particles that had transformed from magnetite to hematite. Glass pieces were used to simulate inert particles. The Al surface with glass pieces was exposed for 7 days to 0.001N NaCl and it revealed pits that could be observed through the glass.

4. General discussion

Although these tests were of short duration, the results demonstrate that spent fuel elements that are stored for extended periods can undergo these forms of environment assisted degradation. It is quite probable that corrosion occurs in what is considered to be innocuous environments and sediments could trigger the onset of pitting. The results also demonstrate the deleterious synergistic effect of galvanic contacts and sediments. These conditions facilitate the onset of corrosion processes, which in more dilute environments are prone to occur beneath the deposits. Similar conditions are encountered in some spent fuel storage sites in which fuel bundles are positioned inside steel structures and without proper electrical isolation.

5. Recommendations

The composition of the settled solids at a specific site helps indicate the possible source. Knowing the source, steps can be taken to reduce or eliminate it. The actions are usually site-specific. However, some general recommendations can be made to reduce or eliminate airborne dust from settling on RR pool or SFB water surface. These include:

1. Increase in efficiency and/or frequency of water circulation through a filter.
2. Use of a skimmer and filter system.
3. Increase in water flow in the vicinity of stored spent fuel.
4. Use of stainless steel doors or lids for away-from-reactor storage basins.
5. Use of adequate corrosion protection schemes, if plain carbon steel doors or lids are used.
6. Installation of double doors, in case of a dusty atmosphere just outside a SFB.
7. Vacuuming of all surfaces in reactor hall and inside the pool, in the case of in-reactor basins.
8. Improved air circulation and pumping of filtered air into the reactor hall.
9. Reduction in water turbulence in the SFB.

6. References

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