



EVALUATION OF ALUMINIUM-CLAD SPENT FUEL CORROSION IN ARGENTINE BASINS.

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ABSTRACT

An IAEA sponsored Coordinated Research Program was extended to study corrosion effects in several sites. Racks containing Aluminium samples were placed in different positions of each basin and periodic sampling of all the waters was performed to conduct chemical analysis. Different forms of corrosion have been encountered during the programme. In general, the degree of degradation is inversely proportional to the purity of the water. Maximum pit depths after 2 years of exposure are in the range of 100-200 μm . However, sediments deposited on the coupon surfaces seem to be responsible for the developing of large pits (1-2 mm in diameter). In many cases, what appears to be iron oxide particles were found, originated by the corrosion of carbon steel components present elsewhere in the basin. These results correlate with observations made on the fuel itself, during exhaustive visual inspection.

1. Introduction

Aluminium clad MTR spent fuel is usually stored underwater to shield the gamma emissions. Due to its good corrosion resistance, corrosion problems should not be expected in the few years needed to allow for a fair reduction in the activity levels, provided the water quality is maintained into specifications values for nuclear reactors: conductivity lower than 1-3 $\mu\text{S/cm}$, pH in the range of 5 to 7 and chlorides in the parts per billion range [1]. However, aqueous corrosion starts to be a concern when storage time becomes decades. In relation to this, the International Atomic Energy Agency (IAEA) established an international Program on "Corrosion of Research Reactor Aluminium-Clad Spent Fuel in Water"; as part of it, an extensive spent fuel corrosion monitoring program has been conducted in Argentine research reactors spent fuel storage facilities from years 1996 to 2000. The IAEA sponsored Coordinated Research Program was extended to study corrosion effects in several different sites: the Central Storage Facility and the RA3 reactor Decay Pool, both located at the Ezeiza Atomic Centre, the RA6 Reactor Pool and the RA6 Decay Pool, at the Bariloche Atomic Centre.

2. Experimental Set-up

2.1. SELECTED SITES

MTR-type fuel elements have a residence time of about 2 years in the RA3 reactor; after that, they are moved to a decay pool (RA3 DP), an open stainless steel pool, to cool down enough before they are transferred to another basin, the Central Storage Facility (CSF); although less than a year is supposed to be enough time in the DP, the fuel elements may stay there for periods of up to 10 years. In the CSF the fuel is placed inside buried steel tubes some 3 meters long; lines of 16 of these tubes connected to share the water are arranged to hold several hundreds of fuel elements (two elements can be placed into each tube, one on top of the other). One channel at the extreme of each line is left empty, to be used as a control channel, for water level, etc. Storage in this basin began in the late sixties. The RA6 reactor started to work in 1982; due to its low power some of the fuel elements have not been replaced and have stayed for almost 20 years inside the reactor pool (RA6 RP); some others have been deposited in an adjacent decay pool (RA6 DP).

Due to the different design and conditions of the sites, it was considered of interest to conduct the surveillance program in all these 4 locations, what could provide valuable comparative information.

2.2. RACKS AND COUPONS.

Seven racks, containing some 10 (ten) Aluminium samples each, were placed in different positions of each basin. Isolated coupons, crevice sandwiches and galvanic couples of different Aluminium alloys were included in each rack. In order to study different effects; some of the coupons had been pre-oxidised and some included artificial scratches. The coupons consisted in 100 mm diameter, 3 mm thick discs, mounted on a stainless steel support. The sandwiches-couples were assembled by putting together 2 disks of Aluminium alloys or one of them with a 2 mm thick 304 stainless steel disk of similar shape and diameter. Different Al alloys have been tested: SZ AV-1, 1100, 5086, 6061 and 6063. Provisions were made to avoid contact between the samples, samples and the steel support and samples and parts of the basin, by means of different kinds of separators. Figure 1(a) depict a couple of racks before immersion at channels #46 and #113, two of the control (empty) channels of the CSF; figure 1(b) shows the moment of positioning in the basin; in CSF the racks were immersed up to a distance of 0,20 m of the channel bottom.

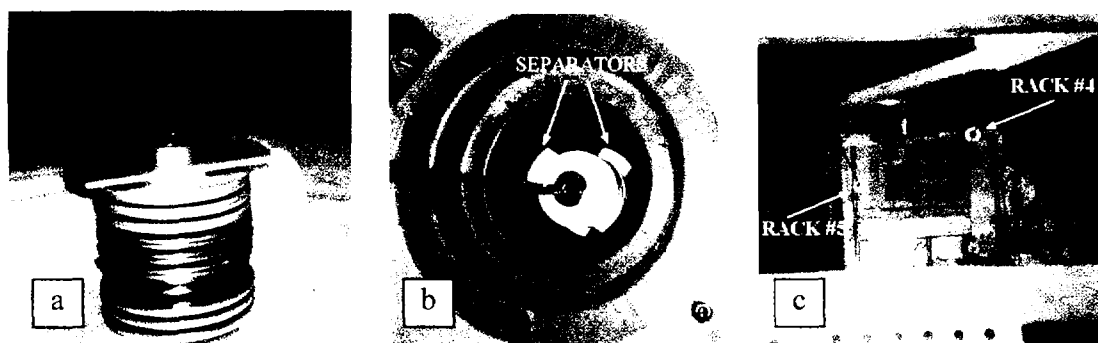


Fig. 1: (a) Racks #2 and #3 before immersion; (b) Rack #3 entering a channel at CSF; (c) Racks in position in RA3 DP.

In figure 1(c), racks #4 and #5 can be seen in place into the RA3 DP, nearby a spent fuel canister. For the location of samples in RA6 DP similar criteria was applied. In the case of the RA6 RP, the racks was hanged at core's height but close to the pool wall.

2.3. MONITORING PROGRAM

During a period of more than 2 years, samples were extracted from the racks at regular intervals in order to look for signs of corrosion. The degree of attack was assessed by visual inspection; upon indication of the development of pitting corrosion, metallography and other analysis were performed to determine number and size of the cavities. Also, periodical chemical analysis of the water in all sites was conducted, to establish pH, conductivity and content of chloride, sulphate, and some other ions. In order to make the material available for laboratory examination, the samples have been decontaminated when needed, washing and rinsing them only with water or alcohol, but no chemical cleaning was conducted, to avoid altering the surfaces.

3. Results

Signs of corrosion have been observed on the Aluminium coupons after exposure in all sites. The intensity of attack depends on site, time, sample location and specific situation of the exposed surface.

3.1. EFFECT OF LOCATION OF EXPOSED SURFACES

A clear distinction can be made on the corrosion appearance of different surfaces, that can be grouped as follow:

- 1) Free surfaces (outer faces of sandwiches or single coupons) and inner surfaces of sandwiches or couples
- 2) Free surfaces facing upwards and downwards
- 3) Free surfaces of samples in upper positions of the racks and those in lower ones.

Figures 2 (a) and (b) show the typical aspect of outer and inner faces of crevice sandwiches or galvanic couples. As it can be seen, the inner surfaces are stained by uneven oxidation, that probably depends on the remaining gap after coupling; depending on site and time, there may be an extended shallow attack with pitting. The outer faces, instead, bear an even oxide and sometimes are pitted. The thickness of all oxides depends mostly on water quality, specially on its conductivity. The amount of pitting strongly depends on which conditions of points (2) and (3) are fulfilled. The fact that surfaces pointing upwards of samples located at the top of the racks are the most pitted suggests that this is related with the sedimentation of particles that may fall on the racks. In fact, brown-reddish deposits have been encountered in some occasions; deep pits associated with these particles became evident after the cleaning-decontamination procedure.

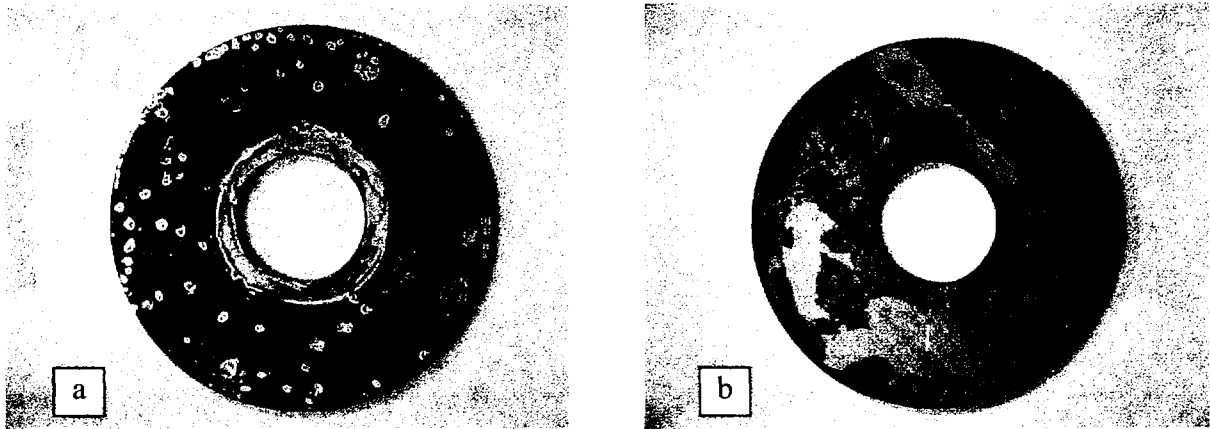


Fig. 2: Aspects of (a) outer surface of a coupon at the top and (b) inner surface of a sandwich.

3.2. EFFECT OF SITE

As expected, the magnitude of corrosion is strongly dependent of the water quality. As Table 1 shows, water chemistry is quite different in each basin. In the reactor pool and all DP's the water is kept at optimum levels, while high conductivity values and some chloride content are measured in the CSF. Consequently, corrosion effects have been evident as early as after a 60 days period immersion (for rack #1 in channel #46 of CSF), whereas no visible signs appeared after 6 months of exposure into the RA3 DP, RA6 DP or the RA6 RP, other than a slight staining of the inner surfaces of sandwiches and couples. Consistently, chemistry excursions verified in these sites during the monitoring period are coincident with the development of corrosion processes.

Table 1: TYPICAL CHEMICAL ANALYSIS CONDUCTED ON WATERS

SITE	CH.#	DATE	Cl ⁻	NO ₂ ⁻	NO ₃ ⁻	SO ₄ ⁼	Cu ⁺⁺	PH ± 0.2	Conduc. µS/cm	Tot. Sol. µg/ml
			µg/ml	µg/ml	µg/ml	µg/ml	µg/ml			
CSF	46	05/28/98	15.6 ± 0.1	ND	ND	4.4 ± 0.1	ND	7.5	79 ± 7	59 ± 1
CSF	113	05/28/98	3.2 ± 0.2	ND	ND	1.4 ± 0.1	ND	8	160 ± 5	106 ± 2
RA6	RP	12/11/98	ND	-----	-----	ND	-----	5.5	-----	22 ± 1
RA6	DP	12/11/98	ND	-----	-----	ND	-----	5.31	-----	27 ± 1
RA3	DP	11/20/98	< 1	-----	ND	ND	-----	-----	-----	-----

ND: NOT DETECTABLE (< 0.5 PPM) ----- NOT MEASURED

As an example, figures 3 (a) and (b) illustrate the variation of chemical parameters with time in channel #46 of CSF and RA6 DP, respectively; the times of sample extraction are indicated.

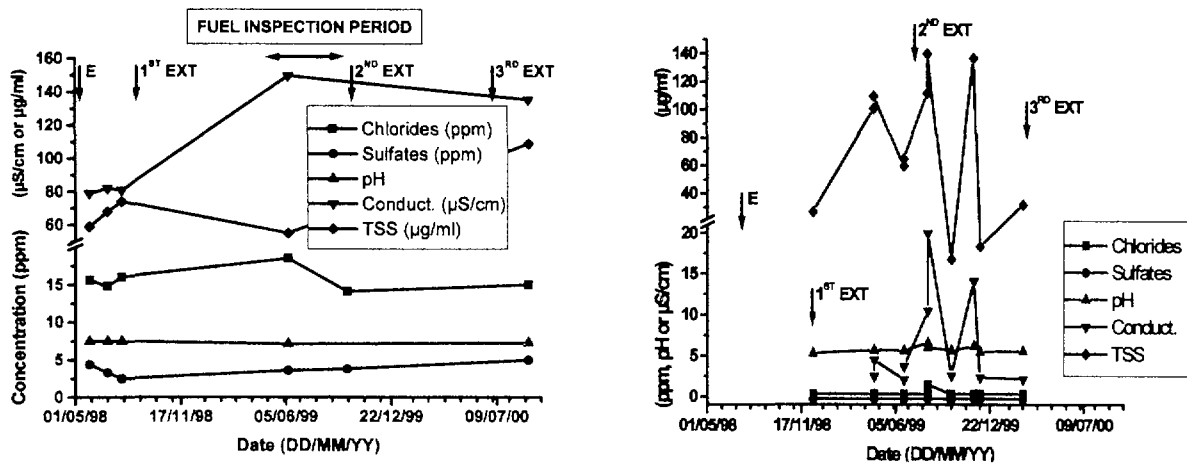


Fig. 3: Evolution of chemical variables in (a-left) channel #46 of CSF and (b-right) RA6 DP. “E” and “EXT” indicate Entry and Extraction time of racks

In CSF, a notable increment in water conductivity, accompanied by alterations in other variables, is verified in coincidence with a period of fuel inspection in which major movements of water were made. Also, in RA6 DP there was a period in which important increases in conductivity and total soluble solids were measured, possible related to some civil work carried out in the vicinity of the pool. As a result, the samples extracted in second term show an increased degree of corrosion. This effect is strong in CSF due to its higher chloride content; in samples extracted from RA6 DP right after the onset of an excursion was noticed, very localised pitting attack was encountered on the upper free surface of the top coupon, as seen in figure 4.

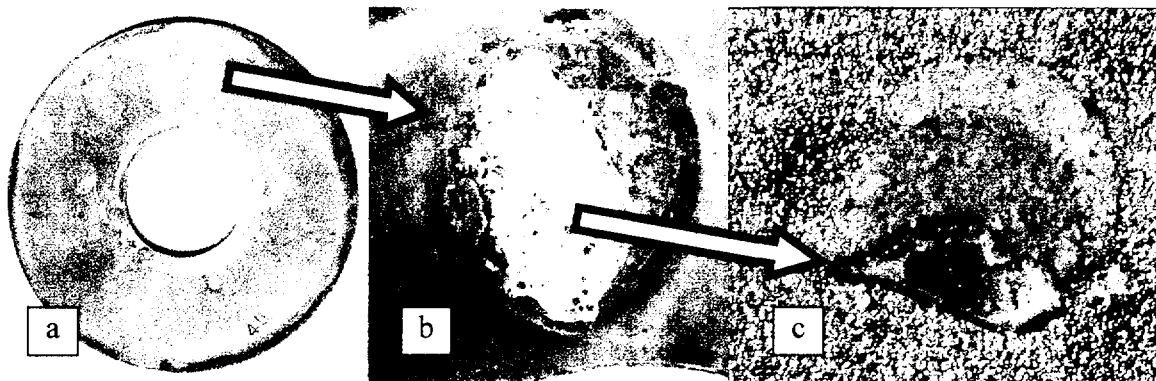


Fig. 4: Localised pitting attack on an otherwise intact sample: (a) general view of the 10 cm diameter coupon; (b) magnification of the pitted zone; (c) detail of one of the pits.

3.3. DEPTH OF ATTACK

When possible, metallographic examination was performed on pitted coupons, to establish the depth of the penetration. Fig. 5 (a) and (b) illustrates two typical cases; the first corresponds to corrosion of the inner surface of a crevice sandwich in an aggressive environment; the second, is a cross section of a pit produced under a deposited particle, that are some 10 times deeper.

4. Discussion

As expected, the degree of corrosion attack observed is strongly dependent on the purity of the water of the basins where they are immersed. For higher conductivity values, thicker oxides are formed and the crevice and galvanic corrosion are more extended. As for the depth of the attack, it has been found that the effect of particles deposited on Aluminium surfaces overrides the influence of other variables. The size of cavities produced this way may be in the range of millimetres for the mouth and about 1

mm for the penetration; pitting produced inside crevices or galvanic couples, instead, do not seem to penetrate more than about 100 μm .

Although no chemical analysis has been performed of the sediments found, their appearance and colour in several cases suggest there may be iron oxide in their composition. This compound may come from steel components present around the storage sites, from sludge removed from the bottom of the pools during large manoeuvres with fuel, from civil work conducted near the places, etc.



Fig. 5: Cross sections of pits produced: (a) inside of crevice; (b) under deposited particle. (100 X)

These findings explain the extensive corrosion encountered on the fuel stored in the CSF [2]: through-clad pits, nodules in scratches and crevices, galvanic corrosion produced by contact of Aluminium with stainless steel, etc., all these phenomena have been reproduced by the monitoring program. As a counterpart, in the DP's and in the RA6 RP there is no visible damage on the fuel. This is consistent with the measured differences in water quality. However, it is probable that the most damaging factor has been the possibility of having particle pitting produced by iron oxide accumulated on Aluminium surfaces. For example, in the CSF, some the positions are closed at the top by means of carbon steel caps filled with lead. In the humid environment of the channel they may have undergone corrosion, with production of iron oxide that may have fallen on the racks. Something similar have happened in the RA6 DP, that is also covered with a painted carbon steel plate. In both places particle pitting was found, although water chemistry is very different.

The fuel stored at CSF was considered suitable for transport and storage at the SRS [2] and has already been shipped to this final destination. The experience obtained with this program will help in the development of a new mixed facility in which the fuel will be kept in wet storage for a limited time before going into a Long Interim Dry Storage.

5. Conclusions

- 1) All forms of corrosion of Aluminium alloys in spent fuel storage sites increases as the purity of the water decreases.
- 2) Pitting produced inside crevices or galvanic couples may have grown less than 100 μm in more than 2 years, in the worst conditions.
- 3) Penetration of pitting induced by deposits may be up to 10 times higher, regardless of water quality.
- 4) The state of fuel elements stored in the different basins is consistent with the state of the coupons immersed in each place.
- 5) The monitoring program was able to detect the effect of excursions in water chemistry produced. Hence, it is recommended to establish it as a routine for every basin.

6. References

- [1] J. P. Howell, Corrosion 97, paper 107, 1997, p. 107/1.
- [2] Savannah River Technology Center Report, WSRC-TR-2000-00152, July 2000.