CORROSION SURVEILLANCE PROGRAMME OF SPENT MTR-TYPE FUEL ELEMENTS IN WET STORAGE SITES IN ARGENTINA

E. LINARDI, R. HADDAD
Corrosion Department, CNEA-CAC
Av. Gral. Paz 1499, B1650KNA San Martín (Bs. As.) – Argentina

ABSTRACT

Argentine research nuclear reactors employ aluminium-clad fuel elements, which are placed under demineralised water after finishing their in-reactor cycle.

A corrosion surveillance operation is being conducted in different storage sites in Argentina, in order to determine if the storage conditions guarantee the proper maintenance of the spent fuel elements. During the programme, racks with aluminium coupons are immersed in the storage sites, taken out for analysis and replaced after one year, as a means to estimate the fuel elements corrosion behaviour. Water samples are taken periodically for chemical analysis.

This work describes the surveillance operations undertaken since 2011 to the present. It has proved to be an efficient incentive for storage site operators, to sustain good practices in order to insure spent fuel safe maintenance. Also, it has been capable of provide early warning of undesired situations. Additionally, its implementation has permitted to acquire valuable information on aluminium corrosion mechanisms.

1. Introduction:

Argentine research and experimental nuclear reactors employ MTR-type fuel elements. The cladding and structural parts of these fuels are made of AA6061 aluminium alloy, with low enriched uranium as the nuclear fuel. Once in-reactor fuel cycle is completed, the spent fuel elements (SFE) are placed under demineralised water at room temperature in interim storage sites until its final disposition. The Argentine National Atomic Energy Commission (CNEA) owns and operates the research reactors in the country, and is also responsible for the spent fuel management.

As a result of corrosion issues that were observed during the long term storage of the spent fuels in some sites around the world, the IAEA implemented several International Programmes on “Corrosion of Research Reactor Aluminium-Clad Spent Fuel in Water” during the period 1996-2005. Argentina participated in these projects, by carrying out corrosion surveillance programs in storage sites [1-3].

The most important conclusion obtained from these programmes was that water quality is by far the most important factor affecting SFE preservation during long term interim storage in water basins, because it influences all corrosion mechanisms [1,4].

Following the IAEA programme guidelines, it was decided to continue the surveillance operation in storage sites in Argentina. The main objective is to determine if the storage conditions guarantee the proper maintenance of the SFE. This supervision is being carried out in the decaying pools of RA3 and RA6 research reactors and in the FACIRI (Research Reactor Spent Fuel Elements Storage Facility, from its acronym in Spanish). RA1 and RA6 reactor pools are also included in the program, because they are low power reactors in which the fuel elements can stay for long periods of time.

This work describes the surveillance programme undertaken since 2011 to the present in storage sites in Argentina, and includes the description of the corrosion racks and coupon materials, methodology of coupon analysis and water quality analysis procedures.

2. Methodology

The corrosion surveillance programme is carried out by immersion of racks containing coupons of aluminium alloys in the storage sites, as a means to assess the fuel elements corrosion behaviour. These racks remain in the facilities for a period of one year approximately, during which water samples are taken every two months in order to evaluate the water quality. Once the immersion period is finished, the aluminium coupons are withdrawn from the basins and replaced by new ones. The extent of damage in the coupons is analysed in relation with the water quality.
This procedure is an adaptation of the protocol developed by the IAEA for previous surveillance programmes [3].

2.1. Materials and assembly of racks:

Fig. 1 shows the design of the aluminium coupons employed in this work. The coupons are mounted in a stainless steel (SS) rack. The surface treatment of the aluminium coupons consisted of an etching according to the following steps:

- Immersion in NaOH 10% solution at 60 ºC for 1 min
- Rinsing in distilled water at 60-70 ºC
- Immersion in HNO_3 50% solution at 25 ºC
- Rinsing in distilled water at 60-70 ºC
- Rinsing in ethanol and drying in a warm air stream

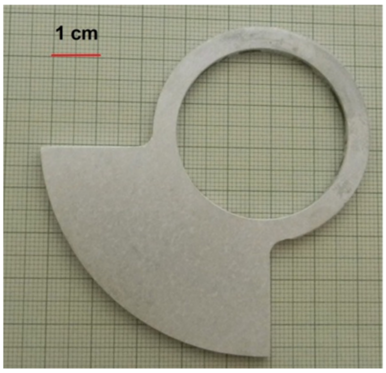

Fig. 1a: coupon AA6061

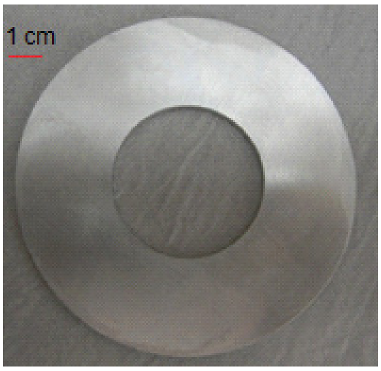

Fig. 1b: coupon AA5083/AA5052

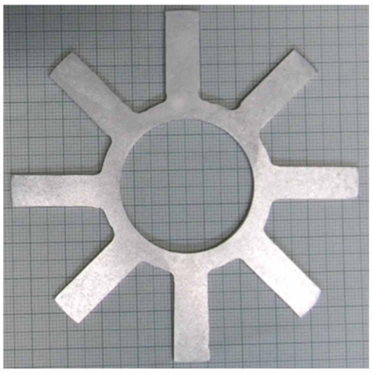

Fig. 1c: coupon AA6061 (MIC)

Fig. 2 presents Optical Microscopy (OM) images of the coupon surface after the surface treatment, before exposure to the water basins. The surface shows small cavities as a consequence of chemical dissolution of the aluminium matrix and some second-phase particles.

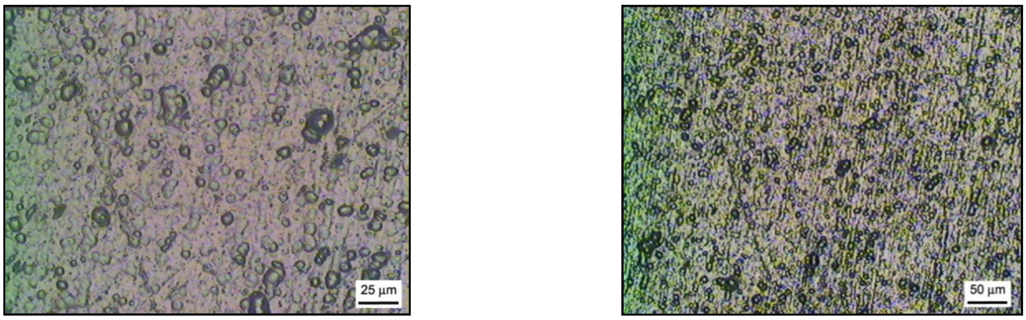

Fig. 2: OM images of the AA6061 after etching treatment.

The assembly details of the racks are shown in Fig. 3. Each rack contained two isolated AA6061 coupons and two pairs AA6061/SS coupons, in order to study the effect of galvanic coupling in the corrosion phenomena. The racks used in FACIRI had one extra AA6061 coupon for Microbiologically Induced Corrosion (MIC) studies and one extra coupon of either AA5083 or AA5052 alloy (both materials are employed in structural parts in the facility). All the coupons are isolated from the stainless steel rack with a ceramic central piece and ceramic rings.

Fig. 3a: Rack

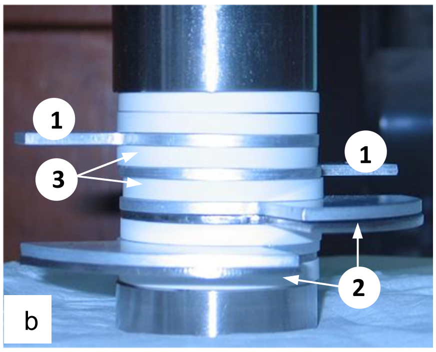

Fig. 3b: detail of racks installed in RA1, RA3 and RA6.

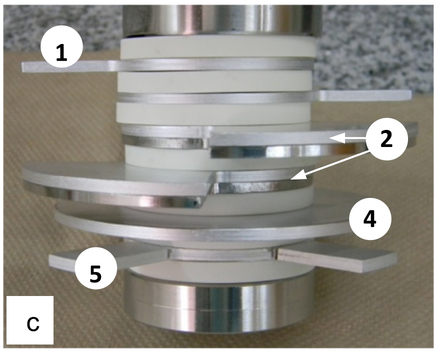

Fig. 3c: detail of rack installed in FACIRI

(1: isolated AA6061; 2: pair AA6061/SS; 3: ceramic rings; 4: AA5083/5052; 5: AA6061 MIC coupon)

2.2. Placement of racks in the storage sites:

The surveillance operation is currently being conducted in the following sites: RA1, RA3, RA6 and FACIRI. In all of these places there are aluminium-clad fuel elements immersed for periods of up to 40 years, either because they are low power reactors or spent fuel basins.

- RA1 reactor pool (RA1 RP): It is a low power (40kW) tank type research reactor; it employs aluminium rod fuel that has stayed in for some 40 years. Its main activities are teaching, training, materials irradiation, BNCT tests and activation analysis.The water is continuously monitored, and the purification is carried out when needed. Due to the little space available near the core, the rack was installed close to the mouth of the reactor, as seen in Fig. 4. The water quality is supposed to be homogeneous in the whole tank, due to circulation.

- RA3 decaying pool (RA3 DP): the only research reactor that currently generates spent fuel is the RA3 reactor (10 MW). Their spent fuel elements are normally maintained in the decaying pool for a limited time before being stored in the FACIRI. Fig. 5 shows the position of the rack installed in the stainless steel decaying pool. The water is stagnant, and the purification is performed when needed.

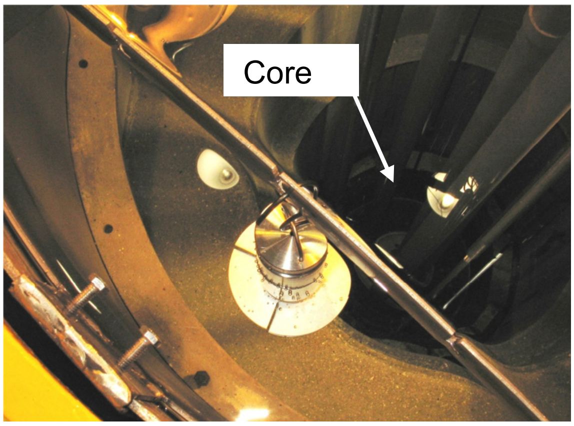

Fig. 4: rack installed in RA1 RP

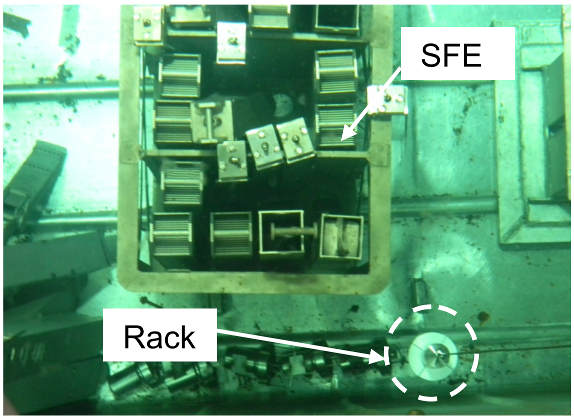

Fig. 5: rack installed in RA3 DP

- RA6 reactor pool (RA6 RP) and decaying pool (RA6 DP): RA6 is a low power (1 MW) reactor employed for teaching, training and research activities. Their SFE are kept in the reactor's decaying pool.Two racks are installed in this facility, one located in the decaying pool (RA6 DP) and one in the reactor pool (RA6 RP) at the level of the core, as shown in Fig. 6 and 7.

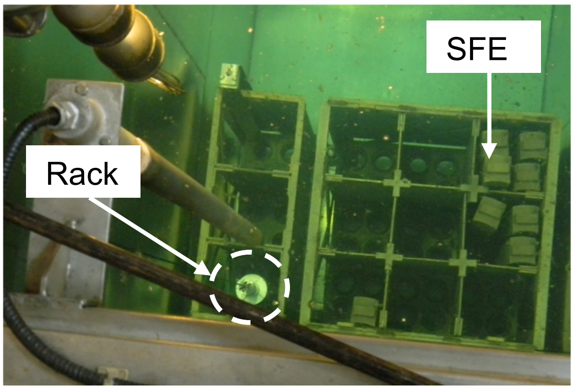

Fig. 6: RA6 decaying pool

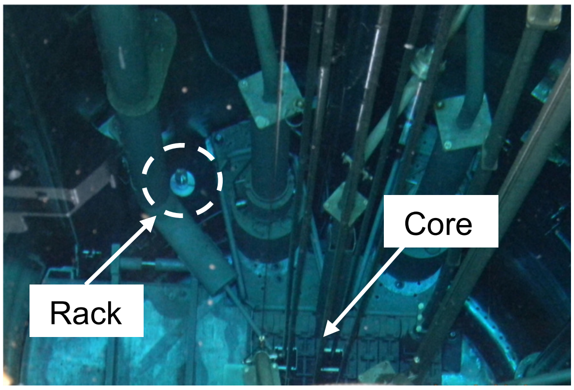

Fig. 7: RA6 rector pool

- FACIRI: it is an away-from-reactor wet interim storage facility built for SFE coming from RA3 reactor. FACIRI is a pool-type storage basin, with a 5 m^2 surface and a depth of 16 m. The storage concept consists of two columns of baskets that hold the SFE, as seen in Fig. 8a. A detailed description of this facility can be found in Ref. 5. The corrosion surveillance in this facility begun one year prior to the start-up, with the placement of one rack at a depth of -8m. When the FACIRI became operational, it was decided to install two racks at two different depths: -8 m and -15 m, and take water samples from three points in the pool: close to surface (-1m), mid depth (-8 m) and bottom of the pool (-15 m). A close view of the rack installed at -8 m depth is shown in Fig. 8b.

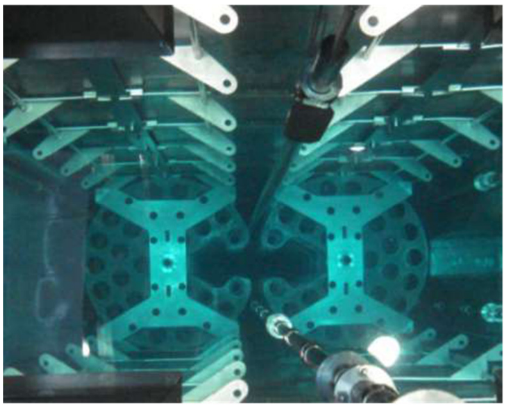

Fig. 8a: top view of the FACIRI pool showing the two columns of gaskets

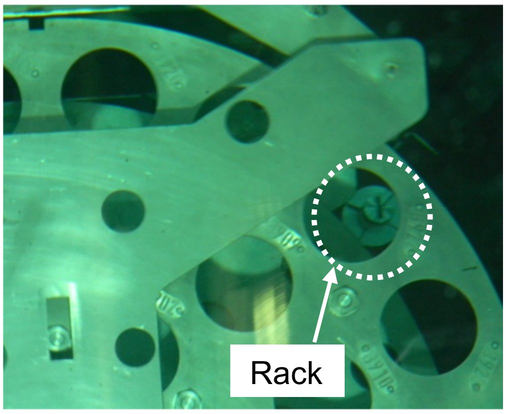

Fig. 8b: view of rack installed at level -8m

2.3. Water sampling:

In all the sites mentioned above, water samples were taken every two months approximately. According to the IAEA guidelines [2], the most important parameters to monitor are the pH and the conductivity (κ). The water conductivity and pH values are measured in-situ at the site, then the samples are submitted to the laboratory for chemical analysis. The water is tested for dissolved metals (aluminium, iron and magnesium) by Inductively Coupled Plasma-Mass Spectrometry technique (ICP-MS) and for different anions which are known to be aggressive for aluminium (chloride, sulphate and nitrate) through Ionic Chromatography (IC).

3. Results:

Figs. 9 to 12 present the water pH and conductivity (κ) values obtained in all the sites described in section 2.2, since the beginning of this programme up to 2016. The recommended range for pH (4.5 – 8) and the limit value for κ (1 μS/cm) are included in the plots as reference. The roman numerals in the upper part of the plots indicate each monitoring term corresponding to one rack.

The pH values recorded in all the sites were within the expected range, with the only exception of two points in the RA6 RP at the starting of the programme. From the analysis of the k values in the RA1, it can be seen that at the beginning they were higher than the limit, reaching ~7 μS/cm, and then begun to decrease to values between 1–2 μS/cm. The water in RA3 DP showed k values also in the range 1–2 μS/cm. For the RA6 facility, it can be seen that the conductivity in the decaying pool was always higher than in the reactor pool. This might be related to some lack of control in the decaying pool, unlike the water quality control performed in the reactor pool. It is again observed that the k values are higher at the beginning of the monitoring.

In the case of the FACIRI, high water k values were recorded at the beginning, which were attributed to the different operations carried out before the facility start-up. From Period II on, the water quality was improved, showing lower k values, around 1–2 μS/cm. Another characteristic that can be observed from the plot (Fig. 12) is the little variation in the k and pH values among the three levels, except for a period beginning in December 2015. A rise in the k values occurred in these period, mostly at the levels -8 m and -15 m. As discussed with the facility operators, this rise was coincident with the entry of new spent fuel elements. After that, the k values in the three levels went back to ~1 μS/cm. The homogeneity in the k values is an indication of the good performance of the water purification and recirculation systems of the facility.

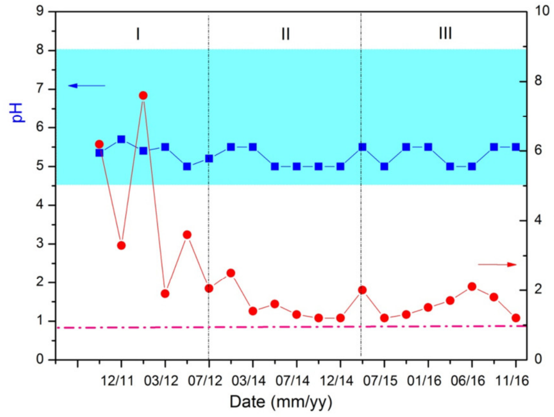

Fig. 9. RA1 reactor pool

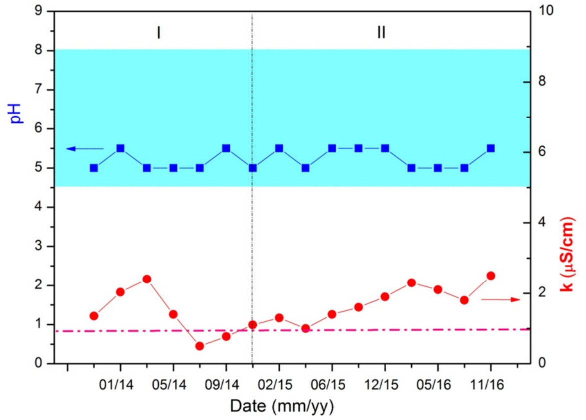

Fig. 10. RA3 decaying pool

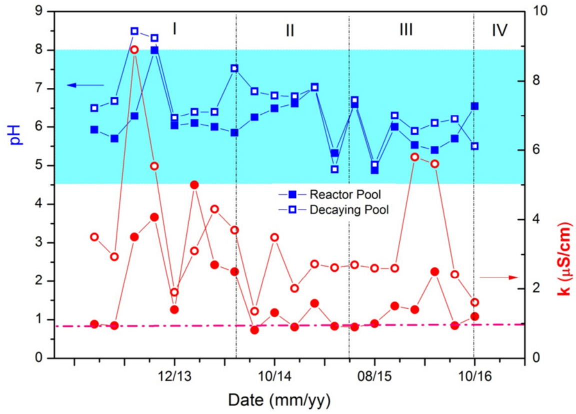

Fig. 11. RA6 reactor pool and decaying pool.

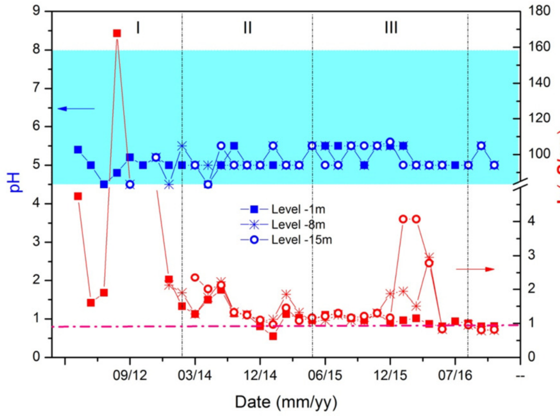

Fig. 12. FACIRI

According to the operators of the different sites, eventual increases in the k value have always been related to environmental factors, such as civil constructions in the surroundings of the basins, settlement of solid particles coming from debris, peeled paints, rust, etc.

The detailed results of the water chemical analysis for the different aggressive anions (chloride, sulphates and nitrates) and the dissolved metals are not included in this report. Nevertheless, it is worth to mention that in all the sites included in this programme the aggressive anions concentration was below 1 ppm (1 mg/l).

The observation of a high conductivity at the beginning of the programme in all sites, with the exception of the RA3 DP, and then a decrease in this parameter, is an indication that the operators become aware of the importance of the water control as the programme progresses. This points out the importance of implementing a continuous surveillance programme in any facility where aluminium-clad spent fuel elements are present.

After each period of immersion, the coupons were withdrawn from the sites, and they were visually inspected. In order to analyse the different corrosion phenomena found in the coupons, they were classified into four general categories: oxide-covered surface (homogeneous), oxide-covered surface (not homogeneous), corrosion under settled solid particles, and stained regions around settled particles. Table I summarizes the corrosion phenomena identified in the coupons in each site throughout the development of the programme.

	RA1 RP	RA3 DP	RA6		FACIRI	
			RP	DP	Level -8 m	Level -15 m
Oxide-covered surface (homogeneous)	■	■	■	■	■	■
Oxide-covered surface (not homogeneous)						■
Settled particles	■	■	■	■	■	■
Stained regions around particles				■		

Table I. Corrosion phenomena identified in the coupons.

In the following section some examples of the coupons withdrawn from different sites are presented (all images correspond to the upward-facing side of the coupon). Fig. 13a presents one coupon that stayed 1 year in RA6 RP. A dark grey oxide is covering the whole surface of the coupon. A similar behaviour can be seen in Figs. 13b and 13c. This oxide growth is consistent with the water chemistry, the temperature and the fluid dynamics regime in the basins. This is generalized corrosion, and is not supposed to be a concern in spent fuel storage basins [4]. Some other coupons showed oxide in the surface but only in certain regions (Fig. 13d). As this kind of behaviour was observed only in the coupons installed in the FACIRI at the bottom of the pool (level -15 m), it was ascribed to the unique characteristics of the basin at that position.

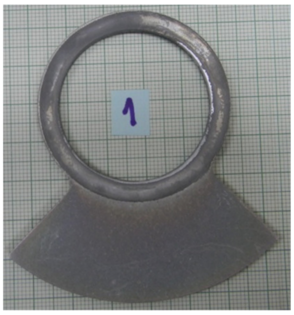

Fig.13a. Coupon after Period II at RA6 RP.

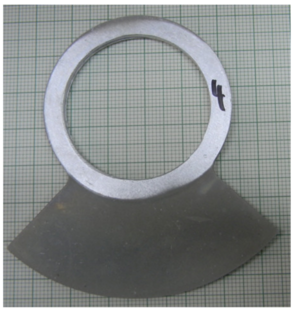

Fig.13b. Coupon after Period II at RA3 DP.

Fig.13c. Coupon after Period II at FACIRI (level -15m).

Fig.13d. Coupon after Period III at FACIRI (level -15m).

Another phenomenon frequently found in the coupons is the settlement of solid particles. In some cases, they are visible to the naked eye, such as the detail shown in Fig. 14. According to the test protocol for coupon analysis [3], the region with the particle is observed through OM, the surface is cleaned and observed again. Figs. 14b and 14c show the OM image of the particle "A" in Fig. 14 before and after the cleaning procedure. It is observed that the settlement of particles did not cause a severe damage in the material, just a shallow attack.

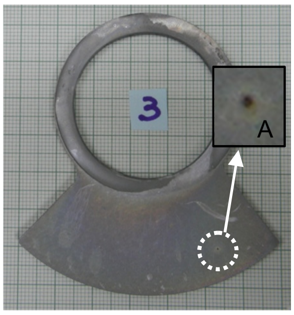

Fig.14a: Coupon after Period III at RA6 RP.

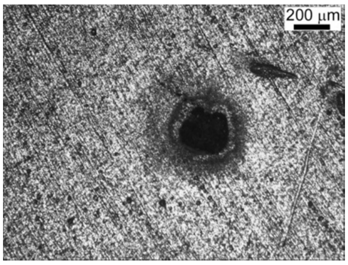

Fig. 14b: OM image of detail “A”

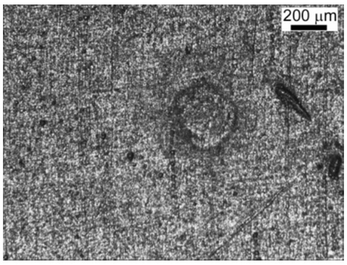

Fig. 14c: OM image “A” after cleaning

In other coupons analysed, the surface was covered with oxide and some settled particles surrounded by a stained region that seemed to propagate in radial direction around the particle, as shown in Figs. 15a and 15b. This was only found in the coupons exposed to the water in the RA6 DP during Period III. After cleaning the zone with the particles, it was found that the corrosion attack was more severe than in the prior example (Fig. 14). The images in Figs.15c and 15d obtained by SEM (Scanning Electron Microscopy) clearly show that this kind of corrosion has produced dissolution of the metal matrix. Moreover, the morphology of this attack is similar to the pitting corrosion caused in aluminium in the presence of chloride ions [6].

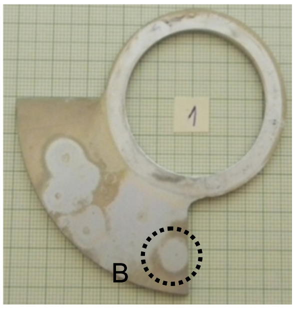

Fig. 15a: Coupon after Period III at RA6 DP.

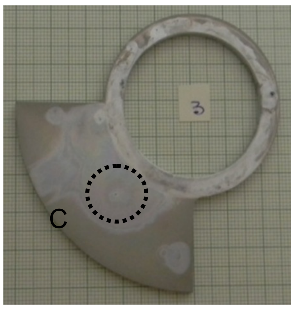

Fig. 15b: Coupon after Period III at RA6 DP

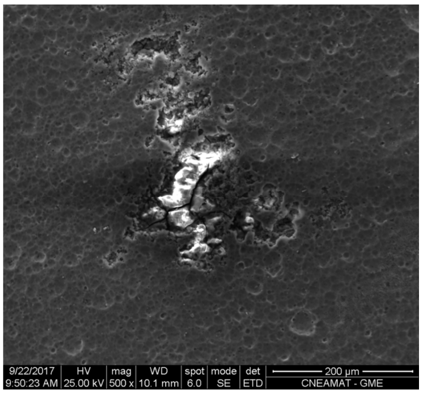

Fig. 15c: SEM image of detail “B” after cleaning.

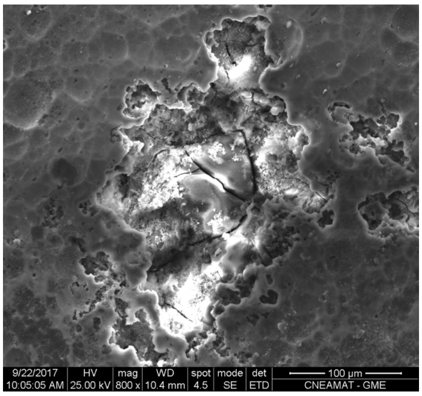

Fig. 15d: SEM image of detail “C” after cleaning.

The type of corrosion described above is termed as under-deposit corrosion. It occurs by the settlement of solid particles (rust, cement, sand, etc.) and the extent of the attack depends both on the type of particle and on the conductivity of the aqueous environment [7].

Coupon in Fig. 14 was exposed to RA6 RP water and coupon in Fig. 15 was immersed in RA6 DP in Period III. The main difference between the RP and DP water during that term was the conductivity value. Fig. 11 shows a higher k value in the decaying pool than in the reactor. This is likely to be the reason why the damage in DP coupon was more severe than in RP coupon. Even though there were settled particles in both coupons, the under-deposit corrosion mechanism was enhanced by a high conductivity. This fact shows a clear example of the effect that a slight rise in the conductivity water can cause in an aluminium plate.

No significant differences were found in the coupons that were isolated or coupled with stainless steel. Regarding the AA5083 and AA5052 coupons used in the FACIRI racks, they only showed generalised corrosion. Their behaviour was not significantly different from the AA6061 alloy, so it was decided to continue the programme using only AA6061 coupons. The MIC studies conducted in the FACIRI are discussed elsewhere [8].

4. Conclusions:

From the analysis of the coupons in correlation with the water quality, it was verified the association of a poor water quality with corrosion phenomena. Even though there are a number of factors affecting the aluminium behaviour in water, the most important parameter to control is the water conductivity. This work proved once again that the maintenance of the water quality is of major importance to assure the integrity of the MTR fuel elements stored for long periods of time.

Aside from the valuable data obtained about aluminium corrosion mechanisms in high purity water, this programme has proven to be an efficient incentive for reactors and basins operators, to sustain good practices in order to assure SFE safe maintenance. Also, it has been capable of provide early warning of undesired situations.

On the other hand, the acquired experience will be useful to contribute to the design and operation of storage facilities in the future, taking into account the current construction of a new research reactor in Argentina.

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References:

1. Corrosion of Research Reactor Aluminium Clad Spent Fuel in Water, IAEA TECDOC 1637, Vienna, 2009.
2. Good Practices for Water Quality Management in Research Reactors and Spent Fuel Storage Facilities, IAEA Technical Report NP-T-5.2, Vienna, 2011.
3. Corrosion of Research Reactor Aluminium Clad Spent Fuel in Water, Technical Report Series No. 418, IAEA, Vienna, 2003.
4. Howell, J. P, Criteria for corrosion protection of aluminium-clad spent nuclear fuel in interim wet storage, CORROSION, NACE 2000.
5. O. Novara, O. Beuter, M. Ratner and M. Flores, Use of a deep and narrow pool to store spent fuel, Proceedings of RRFM 2017, Netherlands, 2017.
6. J. R. Galvele, G. S. Duffo, Degradación de materiales, Jorge Baudino Ed., Buenos Aires 2006, p. 172.
7. S. Rodriguez, L. Lanzani, A. Quiroga, R. Haddad and E. Silva, Study of the effect of sedimented particles on the corrosion behaviour of aluminium clad spent fuel during storage in water, in Research reactor utilization, safety, decommissioning, fuel and waste management. Proceedings of an international conference, Santiago, Chile, 2003.
8. E. Linardi, M. Flores, M. Ratner, O. Oppezzo and A. Forte Giacobone, Tracking microbiologically induced corrosion in a spent fuel elements storage pool, Poster RRFM, 2018.