CORROSION OF SPENT NUCLEAR FUEL ALUMINIUM CLADDING IN ORDINARY WATER

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ABSTRACT

Corrosion of aluminium alloy cladding of spent nuclear fuel elements in ordinary water is examined in the spent fuel storage pool of the RA research reactor at the Vinča Institute of Nuclear Sciences, Belgrade, Serbia and Montenegro. Experimental examinations are carried out within framework of the International Atomic Energy Agency (IAEA) Coordinated Research Project (CRP) "Corrosion of Research Reactor Aluminium-Clad Spent Fuel in Water", Phase II. Racks with coupons made of different aluminium alloys were exposed to water influence for period of six months to six years. The project comprises also activities on monitoring of the water chemistry and radioactivity in the storage pool. Visual and microscopic examinations of surfaces of aluminium coupons of the test racks have been done recently and results were presented in this paper confirming strong influence of water quality and exposition time to corrosion process.

1. Introduction

The 6.5 MW heavy water moderated and cooled research reactor RA [1] was bought as a turn-in key project from the ex-USSR in 1956. It started operation in December 1959, with 2% low enriched uranium (LEU) metal fuel elements of the TVR-S shape [2]. The reactor operated with LEU fuel until 1976, when 80% high-enriched uranium (HEU) dioxide TVR-S fuel elements were purchased [3]. Both fuel elements have the same – 'slug' - geometry and similar mass of U-235 nuclide (7.25 – 7.7) g.

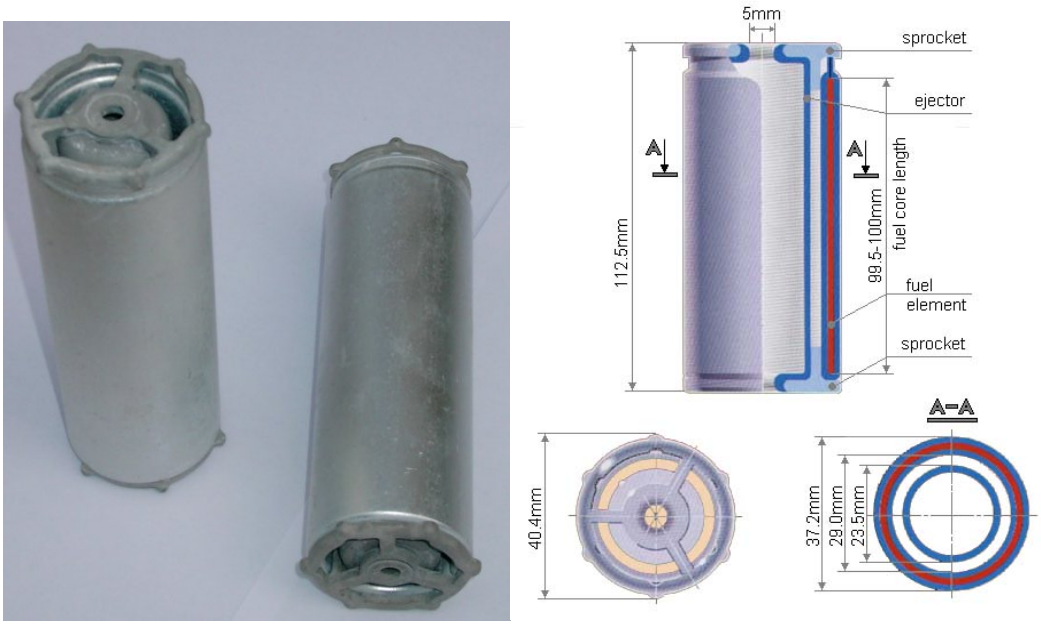

Fig. 1. The TVR-S LEU and HEU fuel elements of the RA reactor [2]

The TVR-S slug is an annular cylinder, with 3.72 cm outer diameter, consisting of a tube with 2 mm thick fuel layer and 1 mm thick inner and outer aluminium cladding. The fuel layer has the total length of 10.0 cm, while the total length of the slug is 11.3 cm. During the RA reactor operation 8030 fuel elements were used. Aluminium, used in the TVR-S fuel elements, is known in Russia as the SAV-1 alloy (0.985 weight fraction is aluminium). Average volume of one TVR-S slug is measured as (60 ± 5) cm^3, while the total area of aluminium in contact to water is estimated at (420 ± 40) cm^2. Average mass of the LEU slug is about 460 g, while average mass of the HEU slug is about 160 g.

The temporary spent nuclear fuel storage pool (Figure 2) is designed within the RA reactor building [1]. The pool, 6.5 m deep, consists of four inter-connected basins and an annex to the fourth basin. Each basin has rectangular cross-section with approximate dimension: width 1.60 m and length 3.80 m. The annex is 1.60 m wide and 1.70 m long. Each basin can be separated, i.e., closed (but not hermetically) by a door manufactured from carbon steel. Pool walls and bottom are made from concrete of various thickness (0.60 – 1.3) m and lined by 1 cm thick stainless steel plate. The pool, filled with about 200 m^3 of stagnant, tap water, is connected by special underground water channel to the reactor block that allows transfer of spent nuclear fuel elements to the storage area. Due to water vaporization, tap water is added to the pool once per year.

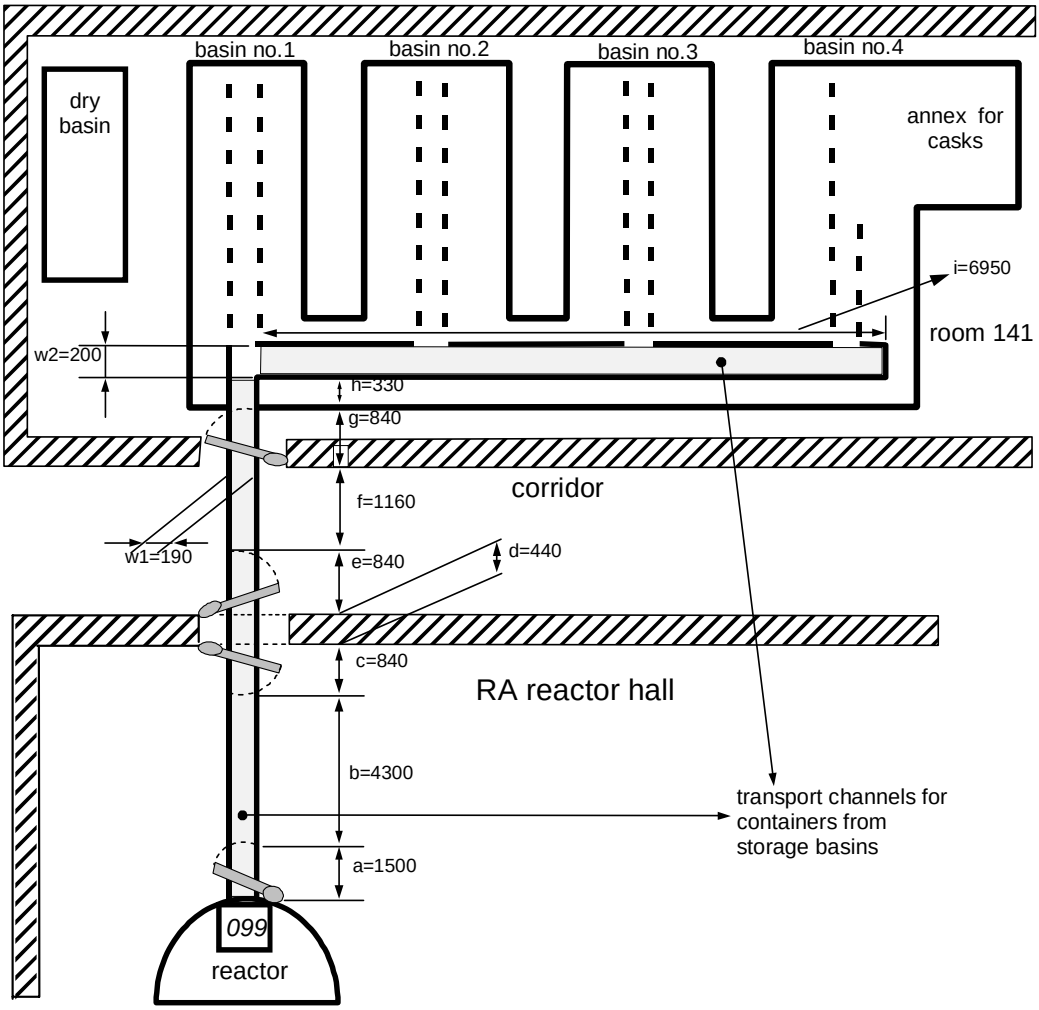

Fig. 2. Spent fuel storage of the RA reactor

2. Chemical and Radioactivity Parameters of Water and Sludge in the Pool

Chemical parameters of the water samples, taken from the basins of the storage pool, were measured few times per year since 1997, and once per month, since 2002. Range and average values of measured chemical parameters in the water samples of the RA spent fuel storage pool in the last two years are shown in Table I [4].

Table I. Ranges and average values of chemical parameters of RA storage pool water measured in 2002 and 2003.

Water parameter	Range in 2002 - 2003	Average ± 1σ
pH factor	7.31 – 8.39	7.53 ± 0.12
El. conductivity (μS/cm)	360 – 570	451.3 ± 27.6
Fe ions (mg/L)	0.07 – 0.21	0.13 ± 0.01
Cu ions (mg/L)	< 0.01	< 0.01
Al ions (mg/L)	< 0.01	< 0.01
Chlorides, Cl (mg/L)	65 – 85	73.0 ± 0.9
Sulphate ions, SO_4 (mg/L)	31 – 70	48.6 ± 1.5
Nitrate ions, NO_3 (mg/L)	< 0.05	< 0.05
Hardness, dH	6.5 – 7.5	6.9 ± 0.1
Temperature (°C)	14.5 – 21.5	18.5 ± 0.5

Water purification system in the RA spent fuel storage pool includes pump (flow rate about 60 L/min) in basin no. 4 with mechanical filter (25 μm) only. The water circulation is performed every day during working hours. After sludge removal in 1996 and day-per-day operation of the purification system, clearness and visibility of the pool water are improved in spite of further accumulation of dust at the water surface.

Specific (volume) radioactivity in the water of the basins is measured few times per year, since 1996 and once per week, since 2002. Typical measured values in 2002 - 2003 were as following: (90 ± 9) Bq/mL from ^{137}Cs nuclide and < 1 mBq/mL from ^{60}Co nuclide (MDA for the Ge detector) [4]. Relative uncertainties of specific (volume) activities are given for normal distribution of probability and the coverage factor equal to 1.

Few sludge samples, taken out from the pool in 1996, were examined for qualitative composition by using x-ray method in the IAEA Seibersdorf Laboratory in 1997 [5]. It was shown that the main sludge component (about 0.85 weight fraction) is Fe_2O_3, which give red-brown colour to the deposits. Impurities of Pb, Cr, Mn, Ca and Zn are confirmed within few percents, while traces of Cu and Ni were found too. According to the CRP-II recommendation, sediments in the pool were collected for seven months by using special designed pot. The sediments were weighted as the total sludge mass of (5.038 ± 0.005) g. The sedimentation rate was determined as (11.3 ± 0.5) mg/cm^2 per month [4]. The sludge from the pot is examined also at the calibrated Ge spectrometer and radioactivity originated from ^{137}Cs and ^{60}Co nuclide was measured only. Specific (mass) activity has been estimated as (12.70 ± 0.35) kBq/g attributed to ^{137}Cs nuclide and as (960 ± 20) Bq/g attributed to ^{60}Co [4]. Sludge average density of (0.84 ± 0.05) g/cm^3 is used.

3. Test Racks Description

Various (test) racks with coupons of different aluminium alloys and stainless steel were prepared and distributed to participants within phase I (CRP-I: 1996 – 2001) and phase II (CRP-II, 2002 – 2005) of the IAEA CRP on "Corrosion of Research Reactor Aluminium-Clad Spent Fuel in Water". Five racks were received and immersed in the RA reactor spent fuel storage pool (Table II) near containers with spent fuel elements, in the 'vertical position', i.e., the rack axis was vertical and the coupons surfaces were horizontal.

Table II. Immersion data and exposition time of the racks

Rack Name /CRP-phase	Immersion date /Basin no (B-#)	Removal Date	Exposition Time (months)	Status as of May 1st, 2004
Rack#1 /CRP-I	July 1996 /B-4	30 July 2002	72	examined
Rack#2.1 /CRP-I	26 February 2002 /B-1	25 July 2003	16	examined
Rack#2.2 /CRP-I	26 February 2002 /B-1	2 March 2004	24	examined
Rack#1 /CRP-II	26 March 2003 /B-3	26 September 2003	6	examined
Rack#2 /CRP-II	26 March 2003 /B-2	6 April 2004	12	under examination

Aluminium and stainless steel coupons are manufactured [6] in form of disks (3 mm thick) with ID/OD = 30/70 mm or ID/OD = 30/100 mm. Chemical composition of aluminium alloys used for the test coupons of the racks, produced entirely in the AEKI FRL [7], is shown in Table III. Percent weight fractions are given for main impurities, while the Al contents are calculated is such a way that the total sum of all components is equal to 100 %. Numbers equal the given limits are used for impurities which fractions are given by limit values, e.g., values given as <0.1 or >0.2 are used in the calculations as 0.1 and 0.2, respectively.

Table III. Chemical composition of aluminium alloys

Alloy type	Al [%]	Cu [%]	Mg [%]	Mn [%]	Si [%]	Fe [%]	Ti [%]	Zn [%]	Cr [%]	Br [%]
1100	99.100	0.16	<0.1	0.05	0.16	0.48	0.005	0.03	0.005	
5086	99.561	>0.2	4.1	0.43	0.19	0.33	0.04	0.045	0.10	0.004
6061	97.690	0.25	0.94	0.12	0.65	0.24	0.04	0.03	0.04	
6063	98.325	0.16	0.73	<0.05	0.37	0.24	0.04	0.03	0.055	
SAV-1	98.570	<0.01	0.53	<0.05	0.71	0.09	<0.005	0.03	<0.005	

Positions of coupons made of aluminium alloys (AA or SAV-1) and stainless steel (SS) within the racks (from top to bottom) are given in Table IV. Spacers between coupons are manufactured as ceramic rings (7 mm thick, ID/OD = 28/58 mm) made of alumina (Al_2O_3). Supporting elements of the racks assembly were manufactured from X8CrNiTi 1810 stainless steel (mainly) and from 99.9 % pure aluminium (DIN 1712). Total height of the racks is about 150 mm. Site-specific coupons were not prepared in the Vinča Institute due to lack of appropriate aluminium material and technology.

Table IV. Composition of the racks (positions of coupons from top to bottom)

Rack Name /CRP-Phase				
Rack#1/CRP-I (Batch-I)	Rack#2.1/CRP-I (Batch-II)	Rack#2.2/CRP-I (Batch-II)	Rack#1/CRP-II (Batch-I)	Rack#2/CRP-II (Batch-I)
Ceramic ring	Ceramic ring	Ceramic ring	Ceramic ring	Ceramic ring
SAV-1/04	SS 316/133	SS 316/114	SS 304/330	SS 304/332
SAV-1/60	AA 6063/145	AA 6063/135	AA 6061/302	AA 6061/305
Ceramic ring	Ceramic ring	Ceramic ring	Ceramic ring	Ceramic ring
SS 316/02	SS 316/121	SS 316/115	AA 6063/249	AA 6063/208
AA 6063/68	AA 6061/123	AA 6061/142	AA 6063/228	AA 6063/244
Ceramic ring	Ceramic ring	Ceramic ring	Ceramic ring	Ceramic ring
SS 316/01	AA 6063/159	AA 6063/150	AA 6063/204	AA 6063/221
AA 6063/59	AA 6063/196	AA 6063/198	Ceramic ring	Ceramic ring
Ceramic ring	Ceramic ring	Ceramic ring	AA 6061/312	SS 304/360
AA 6063/05	AA 6061/217	AA 6061/212	Ceramic ring	SAV-1/366
AA 6061/60	AA 6063/227	AA 6063/200	SS 304/350	Ceramic ring
Ceramic ring	Ceramic ring	Ceramic ring	SAV-1/377	AA 6061/321
AA 6063/04	AA 1100/229	AA 1100/240	Ceramic ring	Ceramic ring
AA 6061/56	AA 1100/236	AA 1100/214	SAV-1/358	SAV-1/376
Ceramic ring	Ceramic ring	Ceramic ring	SAV-1/346	SAV-1/353
AA 6061/18			Ceramic ring	Ceramic ring
AA 1100/56			SAV-1/335	SAV-1/317
Ceramic ring			Ceramic ring	Ceramic ring
AA 6061/07			SAV-1/312	SAV-1/329
AA 1100/53			Ceramic ring	Ceramic ring
Ceramic ring				

4. Visual examination

All test racks are treated and examined according to the IAEA established Test protocol [6]. After the rack withdrawn, it was noted that red-brown sediments have covered top - front side surfaces of all coupons. There was not notice of sediments at bottom (exposed to water, too) sides of the coupons. The racks were disassembled and the coupons were cleaned from deposits and decontaminated using 5 % solution of phosphoric acid and demineralised water. The pH factors were determined using pH paper at outer and inner surfaces of the coupon couples and compared to the pH factor of the pool bulk water. It was very hard to separate some of the coupled coupons and in few cases a tool has to be applied. Pitting, as a main localized form of corrosion of aluminium in water, has been seen at surfaces of all coupons, except of the pre-oxidized ones. Spots of different shades of grey colour and black colour (assumed to be aluminium-oxide) were observed at coupon's surfaces too. Results of all examinations of the coupon's surfaces were recorded in the CRP Progress report [4]. In this paper, the results related to the influence of the rack exposition time to the water at the corrosion effects of aluminium alloys are presented. Photographs of the racks, immediately after withdrawn from the pool water are shown in Figure 3.

(a) (b) (c) (d) (e)

Fig. 3. Racks after exposition time of: 6 (a), 12 (b), 16 (c), 24 (d) and 72 months (e)

Evidences of colour dislocation and strains were found out at surfaces of aluminium coupons. Spots of different shades of grey and black colour were observed at coupons. Crevice corrosion was found at coupled sides of coupons, while pit of various size and shape covered both sides of aluminium coupons. Intensive corrosion processes at aluminium surfaces under ceramic rings and galvanic corrosion effects at aluminium coupons coupled sides to stainless steel coupons were noted. Uneven oxidation with pits of different shape and size are found.

Fig. 4. Galvanic and crevice corrosion at Al coupons after exposition time of 6 months

Fig. 5. Crevice corrosion at SAV-1 couple after 12 months of exposition time

Fig. 6. Crevice corrosion at coupled side of 6061 coupon and dull side of front 1100 coupon after 24 months of exposition time

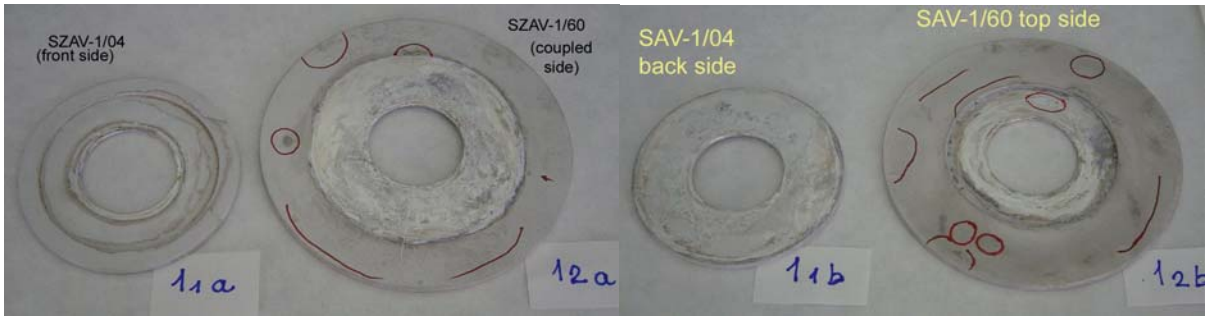

Fig. 7. SAV-1 crevice couple after 72 months of exposition time

5. Examination under microscope

Examinations of aluminium coupons from the racks are carried out under a microscope with magnification (M) x10 and x20, with the aim to study pits and other effects of corrosion process. Pits of irregular shape and various depths are found, but no corrosion pits were observed under scratched line made at pre-oxidized coupons.

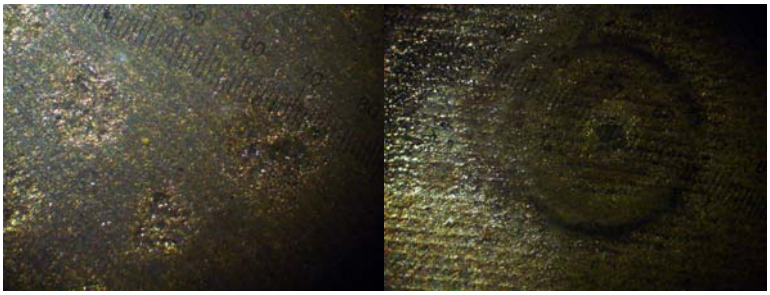

Fig. 8. Deep pits at top surface of SAV-1 coupon and circular pits at 6061 coupon after 6 months of exposition time (Mx10)

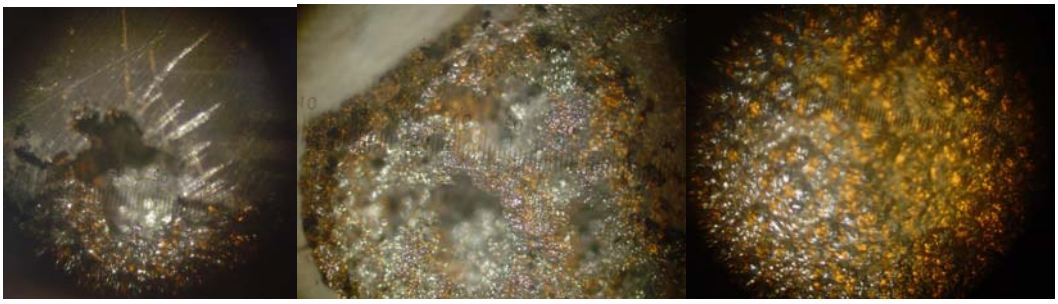

Fig. 9. Deep pits at both surfaces of 6063 coupon after 16 months of exposition time (Mx10)

Fig. 10. Deep pits at both surfaces of 6063 coupon after 24 months of exposition time (Mx10)

Fig. 11. Deep irregular shape pits at surfaces of 6063 and 6061 coupons and a pit covered by a white blister at SAV-1 coupon, after 72 months of exposition time (Mx10)

Conclusion

The Vinča Institute of Nuclear Sciences, Belgrade, Serbia and Montenegro, participates in the IAEA CRP on "Corrosion of Research Reactor Aluminium-Clad Spent Fuel in Water – Phase II". Information related to study of water and sludge characteristic in the RA reactor spent nuclear fuel storage pool and corrosion process at test racks with coupons made of various aluminium alloys are given in this paper. The racks with coupons were exposed to the pool water influence for period of 6 months to 6 years. Effects of corrosion process are noted at all coupons and studied visually and under a microscope. It is believed that the final results of the Vinča's studies, carried out at the extreme bad tap-water conditions, will improve the management and storage practices and procedures at research reactor interim spent fuel wet storage facilities through better understanding of the localized corrosion of aluminium cladding and the ranges of water chemistry parameters that provide resistance to corrosion.

Acknowledgement

This work was supported by the Ministry of Science and Environmental Protection of the Republic of Serbia through the Project no. FI-1958 "Transport of Particles in Fission and Fusion Systems" and by the IAEA Coordinated Research Project no. 11968 "Corrosion of Research Reactor Aluminium-Clad Spent Fuel in Water", Phase II." Authors of the paper are grateful to Mr. Lalgudi Ramanathan from the IPEN, Brazil for the help offered in conducting experiments and understanding and interpretation the corrosion effects created at the aluminium coupons.

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