OXIDATION STUDIES OF MTR FUEL PLATES IN REACTOR CONDITIONS

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ABSTRACT

The mechanism of aluminium oxidation has been studied to disclose the behaviour of nuclear fuel plates in MTR reactors. By means of double circuit oxidation loop, aluminium oxides were grown in different conditions and their corresponding thicknesses were measured by Eddy current technique. During different periods of time: 1, 2 and 3 months, aluminium plates were exposed continuously to reactor coolant water. The results were compared with those obtained with plates exposed intermittently to the same length of time to reveal an eventual effect of periodic reactor shutdowns. Aluminium oxide shows a parabolic kinetics growth, while the interruptions seem to flatten the curve for a limited period of time. Although the thickness values reach levels close to the fuel design limits, this does not seem to imply a significant degree of corrosion damage to the plates in the conditions of the experiments. Additionally, following with studies oriented to disclose the oxidation mechanism, experiments were carried out in order to produce exactly the same type of exposure but without heat transfer. This is accomplished using the same heat transfer device but without a temperature gradient across the plate. Previously, tests carried out in autoclaves (similar conditions but different geometry) had produced oxides with an order of magnitude lower thickness.

1. Introduction.

Aluminium alloys are used as fuel cladding material for most of Research Reactors (RR) due to its high thermal conductivity and low neutron absorption. During operation, fuel plate temperature increases with time due to the growth of an aluminium oxide film which acts as a thermal insulator (thermal conductivity of oxide is approximately 74 times lower than that of aluminium [1]). This effect has to be taken into account in the fuel design and in the reactor operation strategy, to avoid fuel damage due to overheating [2].

Argentine RR's use Aluminium Al-6061 as fuel cladding (composition: Al – 0.95 to 1.1 wt.% Mg – 0.55 to 0.65 wt.% Si – 0.15 to 0.45 wt.% Fe – 0.2 to 0.4 wt.% Cu – 0.1 to 0.2 wt.% Cr – 0.1 wt.% Mn – 0.25 wt.% Zn – 0.03 to 0.07 wt.% Ti), several aspects of fuel oxidation are being studied due to increasingly demanding conditions to which they are subjected. This work focuses on the effect of thermal gradient, periodic reactor shutdowns and oxygen mass flow.

In earlier work [2] a strong dependence of oxidation on through plate thermal gradient was reported. This interesting result indicates that the difference observed in in-reactor oxidation with respect to autoclave tests [3] may be due to other cause rather than irradiation effects. However, other interpretations may be considered if the influence of dissolved oxygen is taken into account. Even at the same aluminium temperature, coolant water can hold a higher amount of oxygen in heat transfer conditions than that of autoclave tests, because bulk temperature is lower, giving place to higher oxygen equilibrium content. For this reason, tests are needed to establish the dependence of oxidation on the dissolved oxygen mass flux, which depends on bulk water oxygen content, water temperature and hydraulic conditions. This is important to disclose the origin of oxygen, whether it comes from water decomposition or from the amount dissolved in the water in equilibrium with the atmosphere. Also, it is interesting to compare results obtained in tests designed with the same

experimental concept, to avoid doubts arising from differences such as comparing results with the same coolant speed in flat and curved surfaces as those of rotating samples in autoclaves [2].

In order to predict oxide growth during reactor operation, it is also important to know the effect of reactor shutdowns on aluminium oxidation. During these periods, both thermal and hydraulic conditions change substantially and modifications in oxide growth kinetics may be produced. Aluminium alloy oxide structure is known to present two layers [3], a compact and protective one which grows through a diffusion mechanism and an external crystalline one which is formed after re-precipitation of dissolved material. Coolant convection must strongly influence the formation of this last one, taking away dissolved material before precipitation; so, evaluation of this effect is needed to properly assess in-reactor behaviour.

2. Experimental set up.

In order to evaluate the oxide growth taking place during burn up, aluminium plates were exposed to water in heat transfer conditions, using a device which simulates a fuel channel during reactor operation. This equipment, called "Oxidation Loop", has been described before [2]. It consists in a double loop; a hot circuit which provides heat to the external side of the channel by means of a thermal fluid and a cold one where reactor grade water takes the energy transferred through the plate thickness, as depicted in **Figure 1**Figure 1.
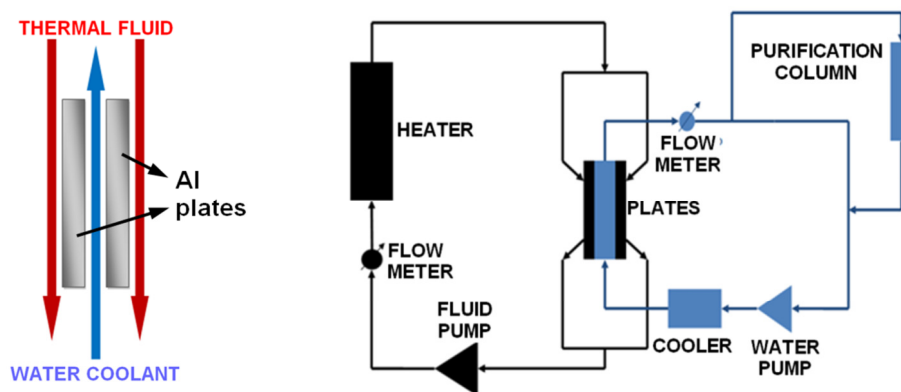

Figure 14: LEFT, simulated fuel channel - RIGHT, simple scheme of double loop.

The plates are manufactured with aluminium alloy 6061 following the same fabrication route that the fuel element plates (without fissile material) bringing the thickness to a final value of 3 mm. They are mounted in such a way that a cooling channel 330 mm height, 40 mm long and 2.5 mm thick is formed, where the heat is transferred only in a central 100 mm height window. The whole system is instrumented to measure and control test parameters such as thermal fluid temperature and flow, coolant water inlet temperature and flow, thermal fluid and coolant water pressure in various points, etc. Aluminium plate temperature is monitored in both plates, at several positions of the transfer window, using 1 mm thick thermocouples inserted into the plate's thickness and 30 mm from the edge of the plate, as shown in **Figure 2**Figure 2. Also, periodic control of the water chemical parameters (conductivity, pH) is performed to maintain the desired quality.

Tests were made simulating the working conditions of the hottest window of one of the hottest fuel plate of RA10 reactor, in order to obtain results corresponding to a demanding condition. Only the coolant speed was set to a lower level than the real case. Selected test parameters were:

Inlet coolant temperature: 50 °C   Coolant speed: 10 m/sec

Initial plate temperature: 100 °C   Water conductivity: ≤ 1 µS/cm

Heat flux density: 4.67 MW/m^2 Initial pH: 7 ± 0.1
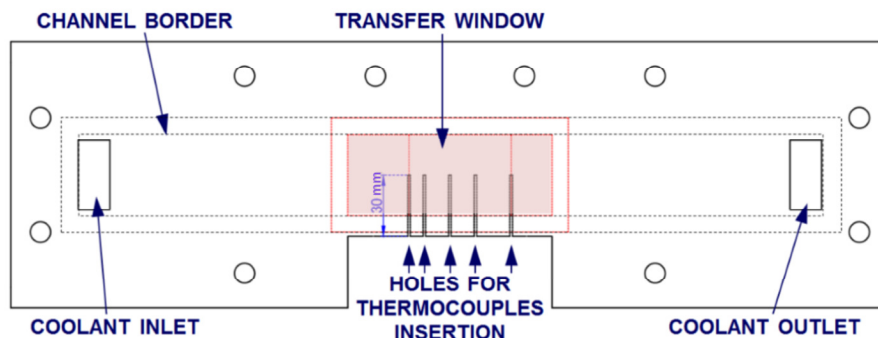
Figure 22: Scheme of test plate, whit five holes to insert thermocouples.

Tests were carried out at different times, running 1, 2 and 3 months continuously, in four phases. In some of the tests, plates previously tested were used, in order to accumulate longer exposure times with one or two interruptions in the middle. This way a comparison could be made of the oxide grown during the same period of time in continuous and intermittent tests. The full program is represented in the scheme of **Figure 3**Figure 3. As a result, continuous exposure times of 1, 2 and 3 months were produced; the maximum discontinuous tests accumulated 5 months of working time. Comparison of oxide growth could be made between 2 months of continuous test and the same time in two 1 month periods. Similarly, results from a three months continuous experiment could be contrasted with those obtained with the accumulation of one and two month's tests. After completion of each experiment, oxide thickness was measured using an Eddy Current probe with an accuracy of 1 µm. Oxide profile was surveyed all along the simulated fuel channel, at 1 and 2 cm intervals in the transfer window and outside it, respectively, in three positions along the width of the channel; three measurements were made in each point. A calibration procedure, contrasting Eddy Current determinations with cross section optical and electronic metallography had been carried out previously to validate these results [4].

With the purpose of further studying the influence of thermal gradient on oxidation, experiments were performed in the "Oxidation Loop" using the same test parameters, but keeping the coolant temperature at the same value than that of the thermal fluid. This way, oxide growth with and without heat transfer can be compared. This comparison is more representative than that performed against the rotating autoclave tests [2]. The homogeneous temperature in the tests without heat transfer was set equal to the plate temperature of the test with heat transfer, i.e. 100 °C initially and adjusting it on a weekly basis. Coolant speed in these comparison tests was set to approximately 6 m/sec.

In other series of experiments, all lasting one month, coolant water was set in equilibrium with air or oxygen gas at various pressures, to obtain different degrees of dissolved oxygen in the water. Controlling this variable, together with changes in the coolant speed, permits to establish known values for the oxygen mass flow from the coolant bulk to the metal surface [5]. This way, the influence of dissolved oxygen on oxide growth could be revealed, helping to elucidate the oxidation mechanism. **Table 1**Table 1 contains the information about test conditions. Five situations are compared: three tests without thermal transfer, designated as OMF3, OMF4 and OMF5, one test with thermal transfer (OMF2) and also the situation in this test but outside the transference window (OMF1), which can be assimilated to a test without heat transfer. In OMF1, OMF2 and OMF3 the oxygen concentration was determined by the partial pressure in equilibrium with the atmosphere at the given temperature.

PLATE A1 -3 HOLES

PLATE A1 -3 HOLES   PLATE B1 -3 HOLES   PLATE B1 -3 HOLES   PLATE A1 -3 HOLES   PLATE D1 -3 HOLES   PLATE D1 -3 HOLES

PHASE 1	PHASE 2	PHASE 3	PHASE 4
DURATION: 1 MONTH (600 HOURS)	DURATION: 1 MONTH (600 HOURS)	DURATION: 2 MONTHS (1200 HOURS)	DURATION: 3 MONTHS (1800 HOURS)

PLATE A2 -5 HOLES   PLATE A2 -5 HOLES   PLATE C2 -5 HOLES   PLATE C2 -5 HOLES   PLATE A2 -5 HOLES

PLATE A2 -5 HOLES

PHASE 1		
	Nº OF MONTHS	
PLATE	IN	OUT
A1	0	1
A2	0	1

PHASE 2		
	Nº OF MONTHS	
PLATE	IN	OUT
B1	0	1
A2	1	2

PHASE 3		
	Nº OF MONTHS	
PLATE	IN	OUT
A1	1	3
C2	0	2

PHASE 4		
	Nº OF MONTHS	
PLATE	IN	OUT
D1	0	3
A2	2	5
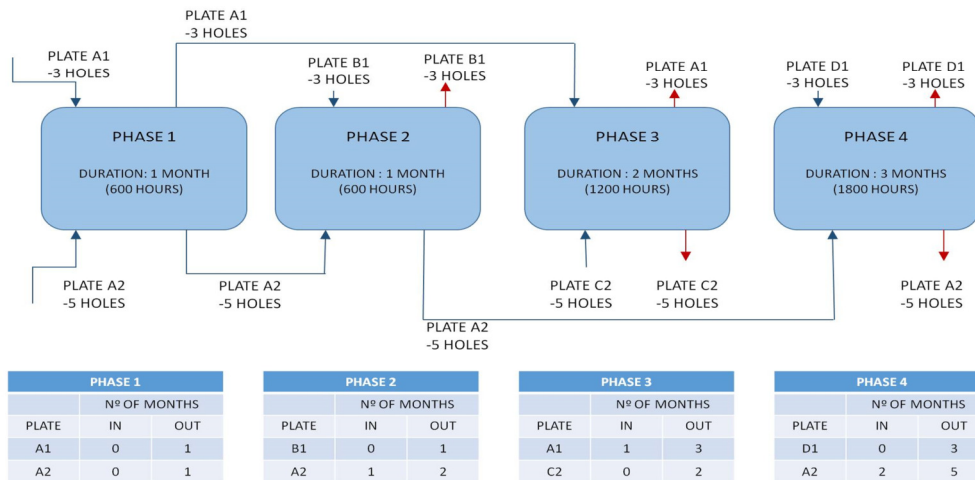
Figure 33: Program to study the effect of reactor shutdowns in oxidation. Number of holes to hold thermocouples in the plate's thickness is indicated.

TEST ID	HEAT FLUX DENSITY (MW/m^2)	PLATE TEMP. RANGE (°C)	BULK WATER TEMP. RANGE (°C)	AVERAGE O$_2$ MASS FRACTION (µg/kg)	COOLANT FLOW (m^3/h)	THROUGH TEST O$_2$ MASS FLOW (µg/m^2.sec)	AVERAGE O$_2$ MASS FLOW idem * 1 E-3
OMF1	0	50	50	6.21 E+3	2,14	4.37 E+3	4.37
OMF2	4.67	100-116	50	6.21 E+3	2,14	9 E+3 to 1.05 E+4	9.71
OMF3	0	100	100	5.25 E+3	2,14	1.28 E+4	12.8
OMF4	0	100-116	100-116	1.9 E+4	5,35	5.77 E+4 to 1.11 E+5	85.8
OMF5	0	100-116	100-116	4.28 E+3	1,07	8.74 E+3 to 1.01 E+4	9.45

Table 14: Tests conditions to study effect of oxygen mass flow.

EXPOSURE STAGES FOR PLATE A2
1ST STAGE (1 MOUNTH)
2ND STAGE (1 MOUNTH)
3RD STAGE (3 MOUNTHS)

1st Stage   2nd Stage   3rd Stage
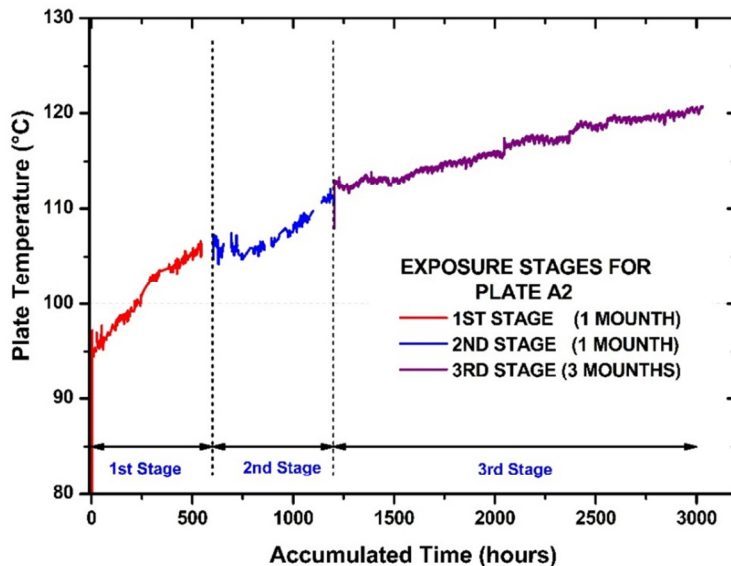
Figure 44: Evolution of plate temperature (channel centre) with time for sample A2 during five months of exposure.

3. Results.
3.1. Oxide thickness evolution.

Plate temperature increases with time due to the formation of a growing oxide film which interferes with heat transfer. It normally follows a typical parabolic behaviour, from which a relationship between temperature value and oxide thickness can be derived, that can be used to continuously estimate thickness in real time during the experiment (for the specific test conditions) when properly calibrated. **Figure 4**Figure 4 depicts the case for sample A2, which was tested during 5 months in three stages of 1, 1 and 3 months.

Vertical lines in **Figure 4**Figure 4 correspond to the cooling and heating which takes place between consecutive exposures. As it can be seen, the slope of oxide growth tends to flatten after each interruption, remaining relatively constant for about a week before start growing again. This behaviour has been confirmed in successive tests.

The aspect of the plate at the end of the test is presented in **Figure 5**Figure 5. **Figure 6**Figure 6 shows the measured oxide thickness average profile along the simulated fuel channel; the transfer window position is indicated. Oxide thickness in the transfer window reaches average values of about 43 µm, with peaks reaching up to 50 µm. This value is the maximum commonly admitted in the fuel design; nevertheless, plate temperatures reached a maximum of 118 °C, which is acceptable, and the metal surface has a good appearance, with a smooth and even oxide layer, without signs of localised corrosion.
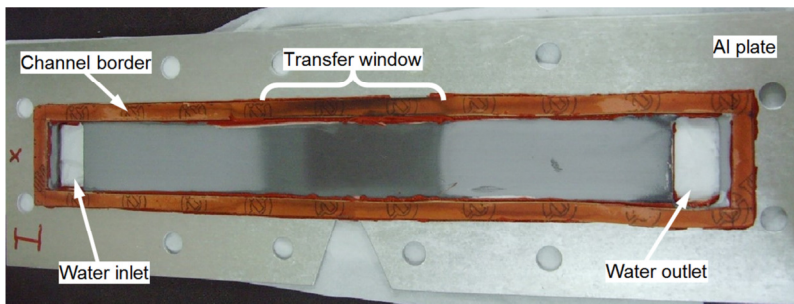
Figure 55: View of the A2 aluminium plate after 5 months of intermittent exposure to reactor grade coolant water under heat transfer conditions.

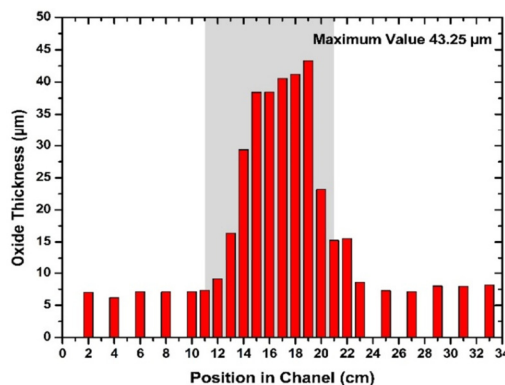**Figure 6**6: Oxide thickness average profile from coolant INLET (0) to OUTLET (32). Shadowed background indicates transfer window position.

Finally, **Figure 7**Figure 7 resumes the data of all tests, to evaluate the oxide thickness variation with time. A slightly parabolic evolution is verified, with reasonable agreement between results of continuous and discontinuous aluminium plate exposure.

3.2. Effect of test interruptions.

The effect of test interruptions can be seen in Figure 7. 2 and 3 months tests performed in one and two stages are compared. After the interruption, the oxide growth -as monitored through the plate temperature- shows a delay in its evolution; this is in both cases of the order of one week. Then, it recovers the original pace, growing at the same rate that the one corresponding to the continuous test. Correspondingly, final oxide thicknesses are slightly lower in experiments with interruptions. **Figure 9**Figure 9 and **10** (a) and (b) show the measured values for two and three month's tests, with continuous and discontinuous exposure, respectively.
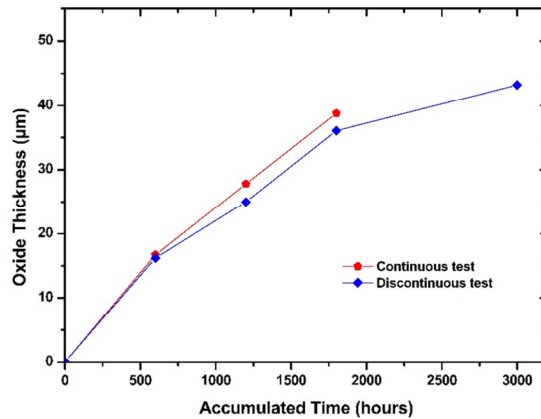
Figure 77: Oxide thickness evolution with time.

(a)   (b)
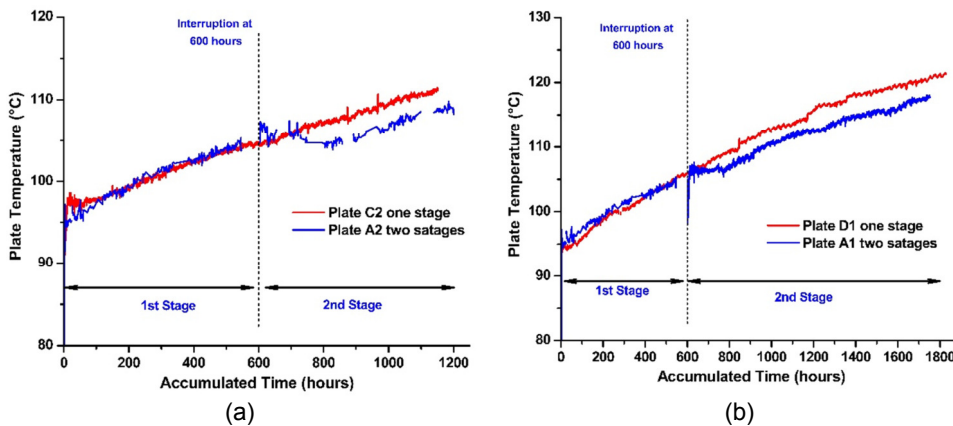
Figure 88: Effect of tests interruption in (a) two months and (b) three months test.

3.3. Effect of thermal gradient and oxygen mass flux.

Exposure of aluminium plates to hot water (around 100 ºC) without heat transfer gave place to oxide layers having the same thickness all along the simulated fuel channel, as seen in **Figure 11**Figure 11. The initial test temperature was 100 ºC (both for thermal fluid, plates and coolant water) and it was increased every week to match the growing plate temperature values measured during the test with thermal transfer using the same hydraulic conditions. The measured oxide thickness profile is depicted in **Figure 12**Figure 12.
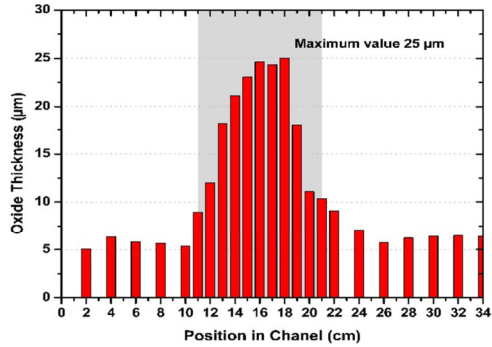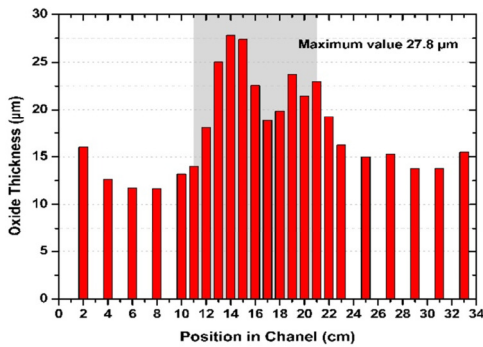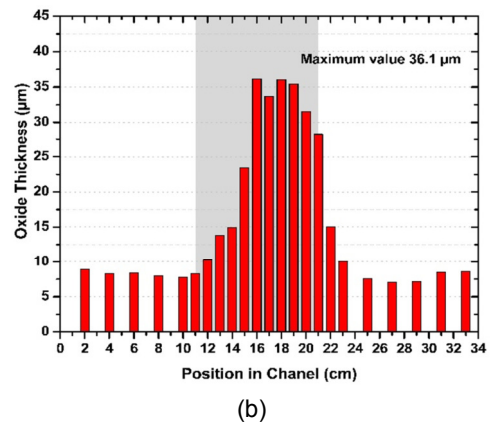
Figure 99: Comparison of oxide thickness profile produced in two months tests from coolant INLET (0) to OUTLET (32). (a) Continuous exposure and (b) Discontinuous exposure.

As there is no heat transfer through the central window, oxide thickness is the same all along the simulated fuel channel. The average value of 12.7 µm is roughly one half of the one obtained in tests with heat transfer, keeping the same plate temperature but with the bulk water at 50 ºC to 54 ºC from inlet to outlet [2].
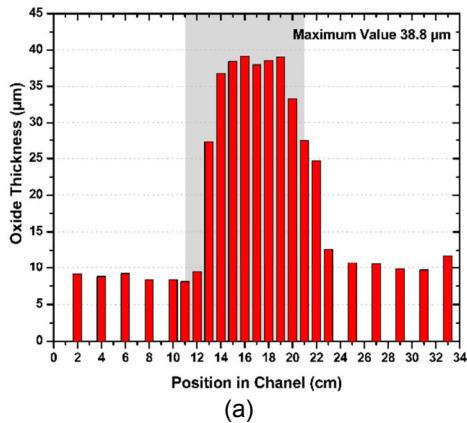

Figure 10: Comparison of oxide thickness profile produced in three months tests from coolant INLET (0) to OUTLET (32). (a) Continuous exposure and (b) Discontinuous exposure.
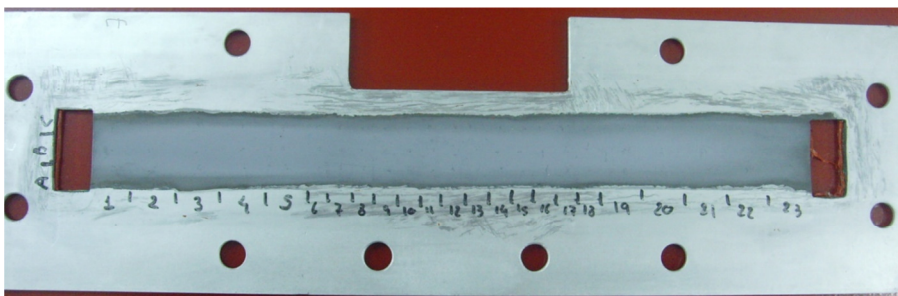

Figure 1144: Aspect of a plate tested in water at 100 ºC, without thermal gradient.
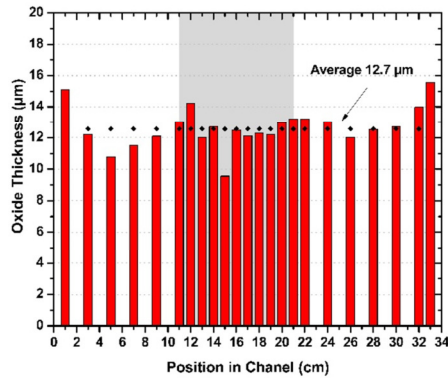
Figure 12: Oxide thickness profile produced in a one month test at 100 ºC without heat transfer.

The results of the experiments performed with a controlled amount of dissolved oxygen in water are exposed in **Table 2**Table 2 and **Figure 13**Figure 13.

TEST ID	AVERAGE O_2 MASS FLOW ($\mu g/m^2.sec$) *10 E-3	OXIDE THICKNESS (μm)
OMF1	4.37	5,83
OMF2	9.71	24,1
OMF3	12.8	12,7
OMF4	85.8	24,29
OMF5	9.45	5,88

Table 2: Measured oxide film thickness as a function of O_2 mass flow.

A strong influence of dissolved oxygen in oxide growth is verified; however, it seems that there is a film formed (6 to 7 µm in one month of exposure) even when the values tend to zero. The result for the test with heat transfer falls completely outside the curve obtained for isothermal tests. This value is comparable with that corresponding to the highest oxygen content and oxygen mass flow.
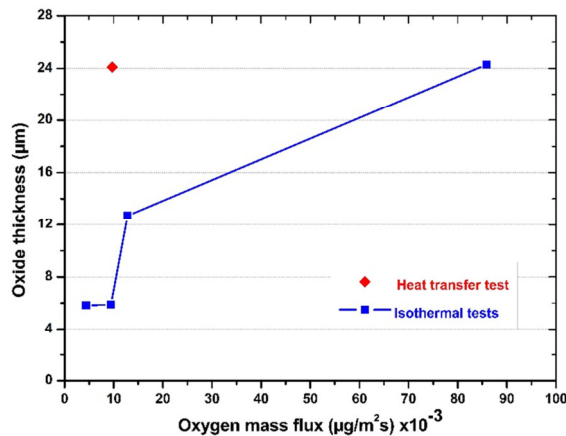

Figure 13: Oxide thickness as a function of oxygen mass flow.

4. Discussion and conclusions.

4.1. Oxide thickness evolution.

In the simulated reactor conditions of the experiments carried out, exposure of aluminium plates to water produces an oxide film which grows with a parabolic kinetics, what is consistent with a diffusion controlled mechanism. After 5 months of test, both oxide thicknesses and plate temperature reached values (50 µm and 118 °C respectively) near the limit of the fuel design for RA10 reactor; nevertheless, the films are smooth and even, bearing no signs of localised corrosion.

4.2. Effect of test interruptions.

Oxide growth does not resume immediately upon restarting plate exposure. There seems to be an incubation period lasting for several days before the conditions are fulfilled for the process to be reinitiated. If oxidation proceeds by diffusion of reacting species through the oxide film, this time may be needed for this concentration profile to be formed again. This would be the limiting step, rather than the reconstruction of the waterside profile, which would take place immediately after restarting the tests.

As a result, oxide thickness produced during a given amount of time is lower if the exposure takes place in several stages than if it is done in only one run. Even a continuous exposure of 3 months has given a thicker film than the one obtained in 5 months accumulated in 3 periods.

4.3. Effect of thermal gradient and oxygen mass flux.

There seems to be an enormous influence of cross plate temperature gradient on aluminium oxidation. Oxide thickness in heat transfer conditions are of an order of magnitude higher than in isothermal tests at the same plate temperature and oxygen mass flow. As both the oxygenation and thermo-hydraulic conditions of the tests have been controlled through air/oxygen pressure, coolant speed and water temperature, this fact indicates an influence of the thermal gradient on the solid state oxide formation mechanism, probably in the diffusion of reacting species through the oxide film.

Oxidation is enhanced by a higher availability of oxygen; however, it looks like a minimum thickness might be obtained even when oxygen mass flow tends to zero. This may be related with the possibility of obtaining oxygen out of water decomposition at the metal surface.

6. References.

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