

# STUDY OF THE EFFECT OF PH, SURFACE FINISH AND THERMAL TREATMENT ON THE CORROSION OF ALFENI ALUMINUM ALLOY

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## ABSTRACT

The Jules Horowitz Reactor (JHR) is a research reactor under construction at the CEA Cadarache research center, France. It is scheduled to start operating by 2020. The fuel elements of this reactor core consist of eight concentric rows of cylindrical plates, each row being composed of three thin aluminum coated plates. Cooling water circulates between these plates through very thin gaps smaller than 2 mm. The aluminum alloy used to coat the fuel plates is an alloy called AlFeNi, which contains 1% wt. Fe, 1% wt. Ni and 1% wt. Mg. In the reactor environment, this alloy may undergo corrosion. The oxide layer formed on the AlFeNi alloy is composed of two different types of oxides: an inner oxide layer formed by a diffusion mechanism and an outer oxide layer formed by re-precipitation. As a consequence, formation of an oxide scale on the aluminum coating could reduce the gap between the cladding plates, thus allowing less water to circulate. This could in turn lead to local heating of the fuel cladding. In addition, the metal consumption and the softening of the metal at high temperatures can lead to a decrease of the mechanical strength of the cladding. In order to qualify the fuel elements of the JHR, several specimens of AlFeNi, representative of the future cladding, were corroded at 250°C for different durations (9 to 34 days) in distilled water of different pH: 4.9; 5.2 and 5.6. These pH values have been chosen to simulate the ones currently predicted for the JHR. The effect of surface finish (polished and not polished) and thermal treatment (annealed and not annealed) on the oxide growth rate was also investigated. For long tests over 30 days, the pH 5,6 appears to be more favorable than the pH 5,2 and 4,9 to limit the oxide thickness, but this pH effect is reduced on unpolished samples. In one hand, the effect of surface finish on the corrosion behavior as measured by optical microscopy appears to be strong. On the other hand, the effect of thermal treatment on the corrosion behavior of unpolished AlFeNi samples in the conditions investigated was found to be small.

## 1.Introduction

Aluminum alloys form a passive oxide layer in water. In the operating conditions of a nuclear research reactor, the corrosion rate increases and it is essential to qualify the impacts of different parameters which affect the oxide growth rate. The JHR fuel element described above consist of eight concentric rows of cylindrical plates, each row being composed of three thin aluminum coated plates and between these plates water circulates in a gap smaller than 2 mm. This design imposes limits on the acceptable oxide growth on the AlFeNi fuel cladding in order to assure a sufficient gap for cooling water between fuel plates. Indeed, corrosion phenomena can reduce these gaps and in turn lead to an increase of the temperature of the reactor core. This aluminum alloy was chosen for its high resistance to corrosion at high temperatures (> 200°C). Many factors can increase the solubility of the oxide in water and further decrease its passivating role. Many corrosion studies on aluminum

alloys used in research reactors deal with the effect of pH on the oxide growth rate in dynamic conditions [1-5] and a few studies have been reported on the effect of surface finish and thermal treatment [6, 7]. English and al showed that the as fabricated specimens of X8001 corroded in water at pH 7 and at 260°C during 10 days exhibited slightly higher corrosion rates than the polished ones [7].

The first corrosion tests performed in a water corrosion loop in a dynamic environment at temperature and flow rate respectively from 55 to 106°C and from 10 to 15 m/s, reveals that 6061 and 1100 aluminum alloys showed a lower oxide growth rate at pH 5 than at pH 7 and pH < 4 [4]. The specific pH value was obtained by adding either nitric acid or carbon dioxide. It also seems that 6061 and 1100 aluminum alloys do not undergo severe localized corrosion in a pH range from 4 to 7 [4]. But at pH 7 and at high heat flux when the test conditions are such that the oxide growth rate is very high, oxide spalled from the surface of the specimen [3]. In this paper the corrosion of 6061 and 1100 aluminum alloys were tested in successive intervals of pH (from 5 to 5.3, from 5.3 to 5.6, from 5.6 to 5.9 etc) in a temperature range of 55 to 121°C and a flow rate range of 10 to 15 m/s [3]. It was reported that the oxide growth rate increase with raising pH. These two experiments were carried out in a steel loop during 10 days in order to study the behavior of aluminum alloys under high heat fluxes in support to the conception of the HFIR reactor core.

Another study performed during 10 days on the 6061 aluminum alloy with a coolant velocity varying from 9 to 28 m/s in the temperature ranges 95 to 208°C shows that the oxide film growth kinetics is lower at pH between 4.5 and 4.9 than at pH between 5.1 and 6, with a sharp increase at pH 5. This is due to the iron impurities in the loop which precipitate as iron oxides on the hot surface of aluminum samples and thus decreased their corrosion rate [1]

A recent study of AlFeNi corrosion was performed in a static environment [6]. Corrosion results obtained at 250°C during 9 days on annealed and polished samples showed a higher weight gain by surface unit at pH 4.9 than at pH 5.6 [6].

Since pH plays an important role on oxide growth rate at different temperatures either in static or dynamic environments and for around 10 days of corrosion, we decided to study in the present work the effect of pH in static environment for a much longer duration at 250°C. Three pH values were chosen for our studies: 4.9, 5.2 and 5.6 in order to investigate which value would be the most favorable in terms of corrosion for the JHR. The effect of thermal treatment and surface finish on the oxide growth rate on the AlFeNi aluminum alloy was coupled to the effect of pH.

## **2.Experimental procedures**

### **2.1. Sample preparation**

#### **2.1.1. Pre-corroded samples**

Small specimens (10x20 mm) of AlFeNi were machined in rolled AlFeNi plates manufactured by CERCA (Romans, France). One plate was annealed at 425°C and the other was received after cold rolling at a rate of 20%. Some of the annealed specimens were polished with silicon carbide discs down to 10 µm and finally with diamond paste of 3 µm in order to obtain two different surface finishes. Before each experiment, all specimen (polished and unpolished) were cleaned in ethanol and acetone in an ultrasonic bath for at least 5 minutes

and dried in air. Prior to the corrosion experiments, the mass of each sample was measured with a scale up to a precision of  $10^{-2}$  mg.

### 2.1.2. Post corroded samples

After each experiment, samples were cleaned with distilled water and ethanol and dried. The samples were weighted with the same scale in order to obtain the weight gain by surface units during the test. The oxide thickness of each specimen was measured by optical microscopy (Reichert-Jung MeF3). In that purpose, the samples were mounted in a non-conductive resin (araldite resin), polished with silicon carbide discs down to 10  $\mu\text{m}$  and finally with diamond paste of 3  $\mu\text{m}$ . The oxide layer of AlFeNi alloy is composed of two types of oxides: an inner and an outer oxide. Thickness of each separate oxide layer was measured by optical microscopy coupled with ANALYSIS program which can calculate a thickness average.

### 2.2. Corrosion solutions preparation

Three different solutions were prepared from distilled water with nitric acid ( $t = 53,6\%$ ,  $d = 1,33 \text{ Kg/L}$ ) additions, in order to obtain three different pH values: 4.9, 5.2 and 5.6. Chemical composition of these solutions was controlled before and after experiments by ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectrometry)

### 2.3. Autoclaves charging

We performed our tests in three 316L steel autoclaves of 160 mL, embedded in an aluminum block heated by a resistance, thus allowing the three autoclaves to operate at the same temperature. Each autoclave is internally equipped with a Teflon pail allowing tests in an acid environment. Before charging, autoclaves were degreased with ethanol. In each autoclave three different specimens (annealed polished, annealed unpolished, as fabricated unpolished) were immersed in an aqueous solution at a fixed pH. The temperature of corrosion experiments was measured by a thermocouple linked to one autoclave indicating a temperature of  $250^{\circ}\text{C}$ . The temperature of the two others autoclaves was also about  $250^{\circ}\text{C}$

Table 1 presents the test matrix for the corrosion tests presented in this study. In this table the different types of specimens corroded in each of the three autoclaves at pH = 4.9, 5.2 and 5.6 for 9, 12, 19, 25 and 34 days, as well as their surface finish and metallographic state are specified.

Table 1: test matrix for the samples tested in corrosion in water at  $250^{\circ}\text{C}$ .

Corrosion Time \ pH	4,9	5,2	5,6
9 days		Annealed polished Annealed unpolished As fabricated	Annealed polished Annealed unpolished As fabricated
12 days	Annealed polished As fabricated	Annealed polished As fabricated	Annealed polished Annealed unpolished As fabricated
19 days	Annealed polished Annealed unpolished As fabricated	Annealed polished Annealed unpolished As fabricated	Annealed polished Annealed unpolished As fabricated
25 days	Annealed polished Annealed unpolished	Annealed polished Annealed unpolished	Annealed polished Annealed unpolished

	As fabricated	As fabricated	As fabricated
34 days	Annealed polished Annealed unpolished As fabricated	Annealed polished Annealed unpolished As fabricated	Annealed polished Annealed unpolished As fabricated

### 3.Results and discussion

#### 3.1. Effect of pH, surface finish and thermal treatment

##### 3.1.1. Measurement uncertainty and standard deviation

To analyze the curves of oxides thicknesses obtained from the optical microscopy we had to calculate the uncertainty on our measurements. For each sample, about 40 micrographs were taken, and 200 local measurements of the different scales were performed on each image: the mean scale thickness measured value is therefore resulting from around 8000 values. As a consequence, the typical error on the mean oxide thickness measurement is lower than 1 micron. While the precision of the measurements is relatively high, there is some rather large scatter in the oxide scale thickness for different regions. For example, the standard deviation of annealed polished specimens corroded for a long time (25 and 34 days) is high (5 to 6  $\mu\text{m}$ ) because the oxide layer is not homogeneous over the entire surface of the metal, but the measurement uncertainty is approximately  $\sim 0.5\mu\text{m}$ .

##### 3.1.2. Total oxide thickness measurements

Fig. 1 shows the total oxide thickness evolution of different types of specimens corroded in aqueous solutions at three different pH: 4.9, 5.2 and 5.6.

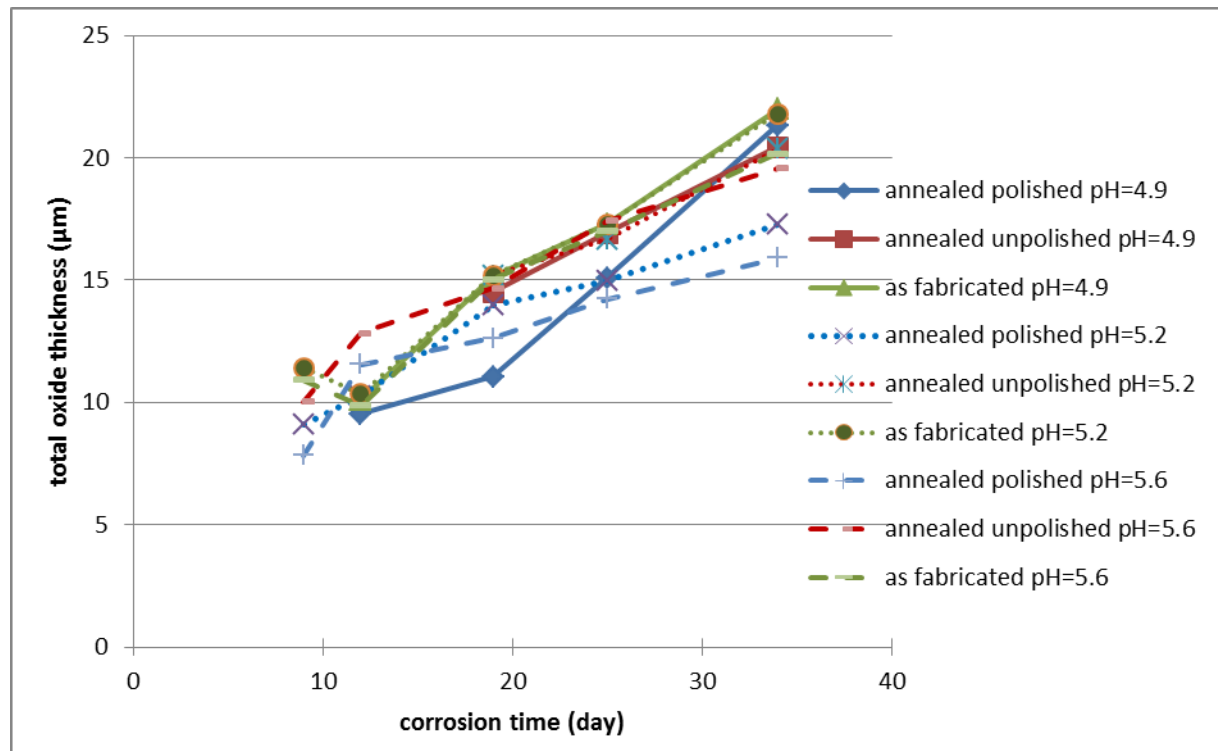


Figure 1: Evolution of total oxide thickness of annealed unpolished, annealed polished and as fabricated AIFeNi specimens corroded in a three different pH: 4.9, 5.2 and 5.6.

It can be seen that the thermal treatment (annealed in red lines or as fabricated in green lines, both unpolished) does not have a significant effect on the evolution of total oxide thickness. Indeed, the largest measured difference of oxide thickness formed on the surface of two specimens which were corroded in the same conditions but have two different thermal treatments is 2  $\mu\text{m}$ .

The effect of surface finish (annealed unpolished in red lines, annealed polished in blue lines) is more important, a difference of more than 5  $\mu\text{m}$  can be observed. Polished specimens have a total oxide thickness lower than unpolished specimens, but they are very sensitive to pH variations. Indeed at pH 4.9 we can observe a drastic acceleration of the oxide growth rate on the polished specimens especially after 19 days of corrosion. Whereas, on the unpolished specimens the impact of the pH on the total oxide thickness is hardly measurable for times up to 35 days.

However on the as fabricated samples, a weak acceleration of the oxidation rate is observed between 25 and 34 days of corrosion at pH 4.9 and 5.2: after 34 days oxide thickness differences do not exceed 2  $\mu\text{m}$  in the pH range 4.9 to 5.6.

### 3.1.3. Inner and outer oxide measurements

Total, inner and outer oxide thicknesses were measured by optical microscopy and the results are presented in Fig. 2, 3 and 4 respectively for annealed polished, as fabricated and annealed unpolished specimens.

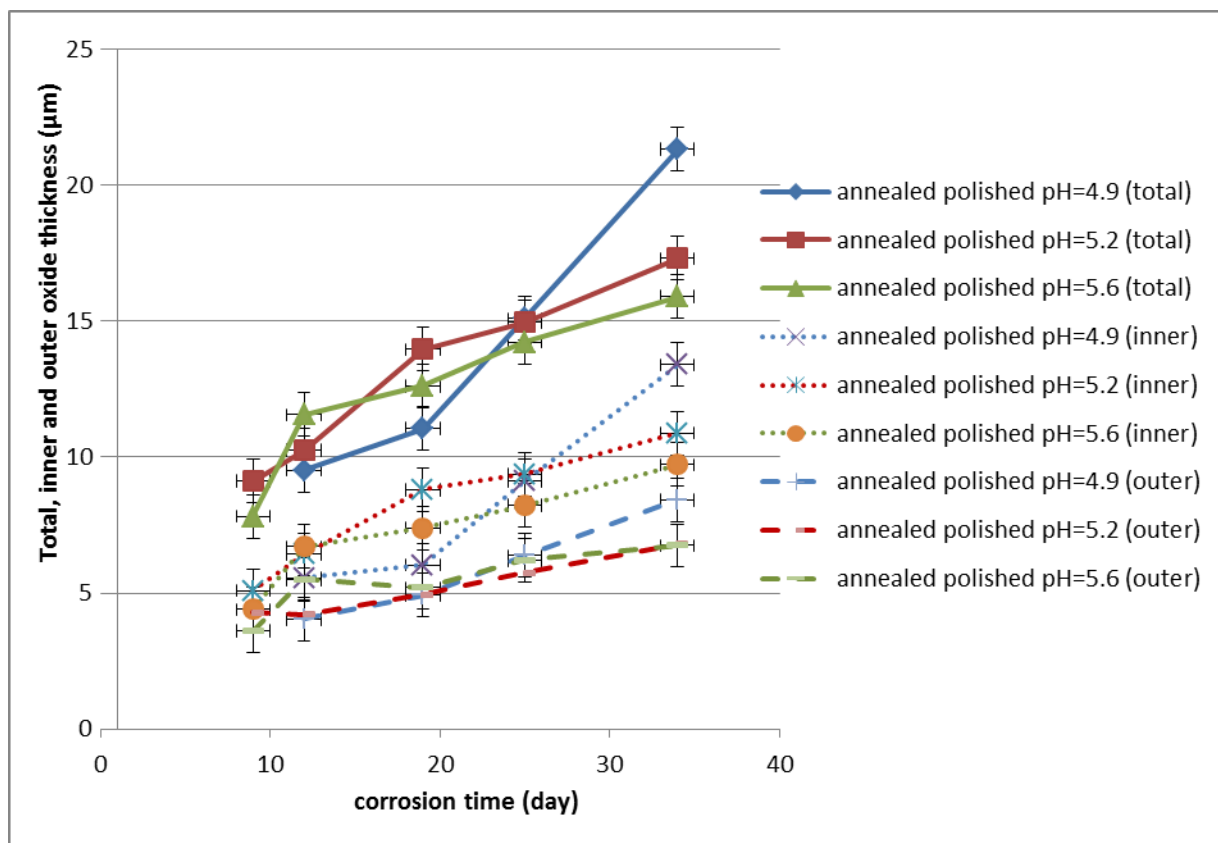


Figure 2: Evolution of total, inner and outer oxide thickness of annealed polished specimens which were corroded at pH 4.9, 5.2 and 5.6 from 9 to 34 days.

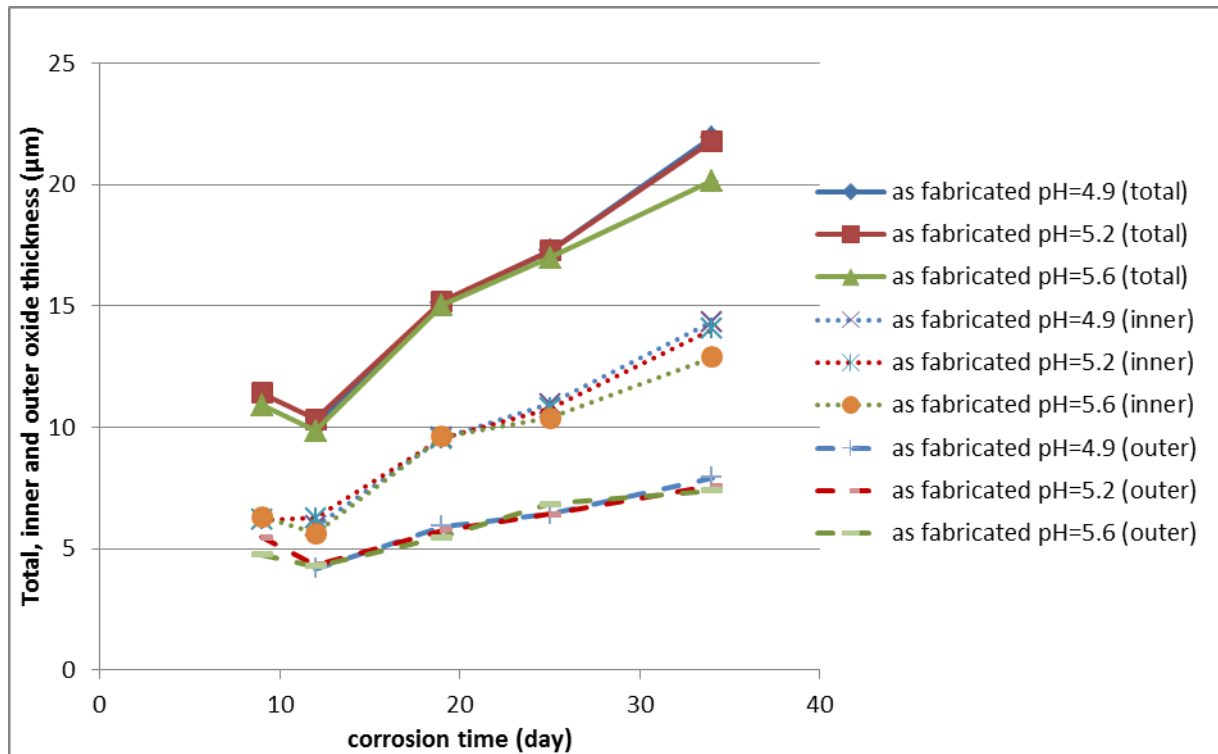


Figure 3: Evolution of total, inner and outer oxide thickness of as fabricated specimens which were corroded at pH 4.9, 5.2 and 5.6 from 9 to 34 days.

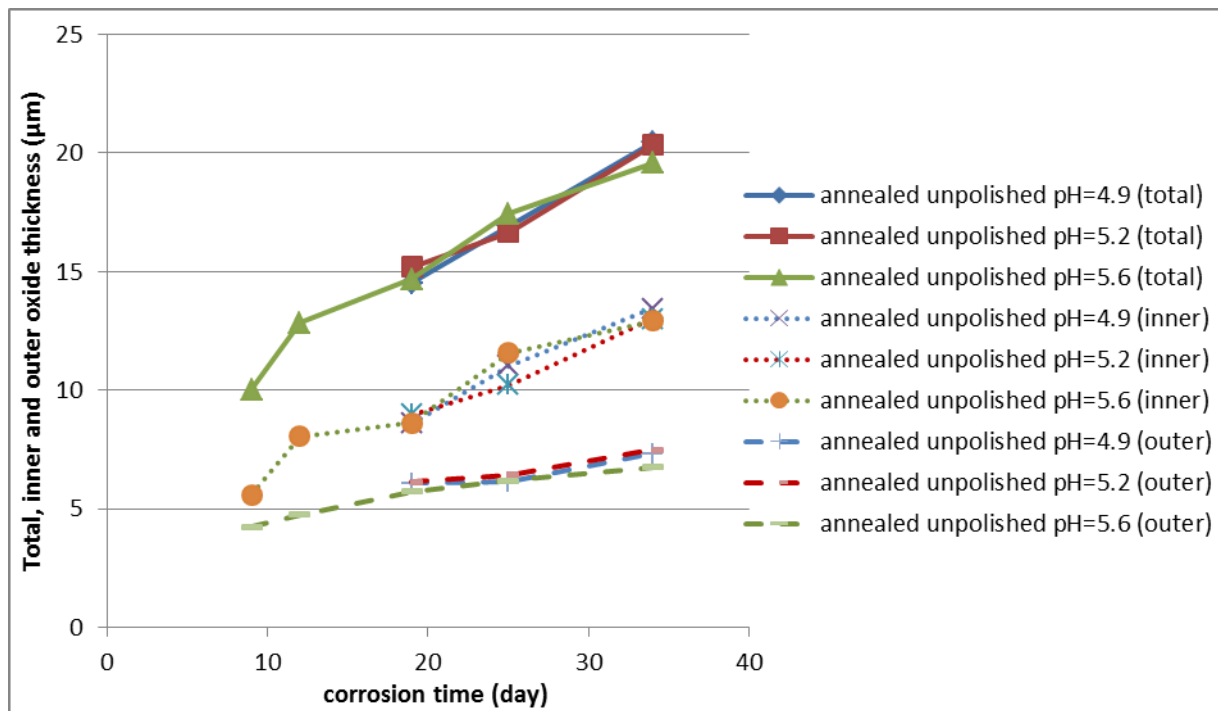


Figure 4: Evolution of total, inner and outer oxide thickness of annealed unpolished specimens which were corroded at pH 4.9, 5.2 and 5.6 from 9 to 34 days.

Figure 2, 3 and 4 show that the total and inner oxide thicknesses have similar growth rate. The slopes of curves which represent total and inner oxide thicknesses of specimens with different surface finishes and thermal treatments are very close and it is obviously seen on as fabricated specimens.

Fig.2 shows that pH has a strong influence on the oxides thicknesses of annealed polished specimens. At pH 4.9, the oxide growth rate is low for short durations of corrosion (9 and 12 days) but faster from 19 days and beyond. This growth kinetics curves is of the type exponential. Whereas at pH 5.2 and 5.6 the growth kinetics curves is of the type parabolic: at short times of corrosion it is fast and then become slower from 19 days of corrosion. Thus pH 5.6 is favorable to limit the oxide layer thickness for long corrosion times. Moreover, these results show that short corrosion tests of annealed polished specimens (<20 days) lead to contrary conclusions since the pH 4.9 appears to be the most favorable at short times.

The effect of pH is less pronounced on as fabricated specimens. Up to 25 days, oxide thickness measured at pH 4.9 and 5.6 is the same regardless of the time of corrosion. However, the influence of pH can only be observed after 34 days of corrosion where total and inner oxide growth rates tend to increase at pH 4.9 and 5.2. Nevertheless, this variation should be verified by corrosion tests at longer durations (beyond 34 days).

Finally, the effect of pH, observed in Figure 4, on the oxide growth rate of annealed unpolished specimens is negligible. But it should be also interesting to verify the thickness evolution of this type of specimens at longer times of corrosion in order to see if the effect of pH is less important at short corrosion times because of effects such as surface finish and thermal treatment which could be predominant at shorter times

So in conclusion, it can be seen that the value of pH 5.6 and 5.2 are more favorable than pH 4.9. And probably for a long corrosion time, the pH 5.6 is even more favorable than pH 5.2.

#### **4.Conclusion**

Based on the results presented in this study, the effect of surface finish is more pronounced than that of thermal treatment on the oxide growth rate of AlFeNi. Moreover, for a long time of corrosion, between 25 and 34 days, pH 5.6 is more favorable than pH 4.9 and 5.2 for the annealed polished specimens. This point is to be confirmed for the annealed unpolished and as fabricated specimens for a time of corrosion beyond 34 days. It should be noted that for a short corrosion time of annealed polished specimens, pH 4.9 is more favorable than 5.2 and 5.6. Indeed, in our static test conditions, the effect of pH on the oxide thickness inverts around 25 days of corrosion.

#### **5.References**

1. S.J. Pawel, D.K. Felde, and R.E. Pawel, *Influence of coolant pH on corrosion of 6061 aluminum under reactor heat transfer conditions*, ORNL/TM-13083, October 1995.
2. J.C. Griess, H.C. Savage, T.H. Mauney, and J.L. English, *Effect of heat flux on the aluminum by water. Part I: Experimental equipment and preliminary test results*, ORNL-2959, 13 May 1960.
3. J.C. Griess, H.C. Savage, J.G. Rainwater, T.H. Mauney, and J.L. English, *Effect of heat flux on the corrosion of aluminum by water. Part III: Final report on tests relative to the High Flux Isotope Reactor'*, ORNL-3230, 20 December 1961.
4. J.C. Griess, H.C. Savage, T.H. Mauney, J.L. English, and J.G. Rainwater, *Effect of heat flux on the corrosion of aluminum by water. Part II: Influence of water*

*temperature, velocity, and pH on corrosion product formation.*, ORNL-3056, 27 February 1961.

5. J.C. Griess, H.C. Savage, and J.L. English, *Effect of heat flux on the corrosion of aluminum by water. Part IV: tests relative to the advanced test reactor and correlation with previous results*, ORNL-3541, 1964.
6. M. Wintergerst, *Etude des mécanismes et des cinétiques de corrosion aqueuse de l'alliage d'aluminium AlFeNi utilisé comme gainage du combustible nucléaire de réacteurs expérimentaux*, 2006, Université Paris XI, U.F.R. Scientifique d'Orsay.
7. J.L. English, L. Rice, and J.C. Griess, *The corrosion of aluminum alloys in high velocity water at 170 to 290°C*, ORNL-3063, UC-25-Metals, Ceramics and Materials TID-4500 (16th ed.).