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Studies of Oxide Layers Grown at 260˚C on A106 B Carbon Steel in Aqueous Medium with Ethanolamine or Morpholine

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Abstract

The water chemistry of the secondary coolant in the majority of Nuclear Power Plants is controlled by AVT (All Volatile Treatment), wherein volatile amines are used to maintain the alkaline pH required for minimizing the corrosion of structural materials which one of them is Carbon Steel. In this treatment, ammonia, morpholine and ethanolamine are commonly used as conditioning reagents. In this context, experiments were carried out by exposing carbon steel A106 B samples in a simulated secondary coolant in order to study the nature of the oxide films. The tests were performed in a static autoclave at 260˚C using two media: I) hydrazine + morpholine and II) hydrazine + ethanolamine during different exposure periods up to ≈1020 h. The oxide film characterization was mainly studied using Scanning Electron Microscopy and X-ray diffraction. A chemical descaling procedure was used to obtain the material weight loss (W) of samples, the adherent and released oxide. The XRD analyses, for all exposures studied, showed that magnetite was the corrosion product formed in the films grown in both media. The material weight loss, after descaling, could be fitted by a law of the type $W = kt^n$, up to 1020 h of exposure tested, resulting in $n = 0.42$, $k = 6.24$ for films grown in medium I) and $n = 0.39$, $k = 6.08$ for films grown in medium II) respectively (W is in mg/dm^2 and t in h). The higher corrosion product release measured in the medium with morpholine could be important in power plant operation.

Keywords

Morpholine, Ethanolamine, Corrosion, Oxide, Carbon Steel

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1. Introduction

Structural materials of the primary and secondary cooling systems of Water Cooled Nuclear Reactor (WCNR) are exposed to severe high temperature and pressure conditions, so that the materials employed in these plants have to take into account a useful design life of at least 30 years. Nowadays, due to economic reasons, some plants are extending lifetimes by refurbishing and replacement of some components. In WCNR, we must also consider some processes that are not present in fossil plants like water radiolysis, transport of activated corrosion products around the primary heat-transport systems, and so on. The coolant chemistry control is carefully monitored to minimize different corrosion processes *i.e.* flow assisted corrosion, corrosion product transport to steam generators. Oxides deposited on heat exchanger surfaces, for example, will degrade heat transfer if the deposits are thick enough.

The fouling of steam generators (SG) is one of the greatest problems of the secondary cooling system of these plants. The corrosion products, mainly iron oxides, are generated from the carbon steel corrosion which is the main constituent of the pipes, the steam generators shell, tube support plates and some other parts of this circuit as reported by Staehle and Gorman [1]. The transport and deposition of corrosion products can also produce an accumulation of oxides in particular zones of the SG that may induce localized corrosion, so to minimize these risks the secondary coolant chemistry must be optimized.

Secondary circuit of WCNR employs demineralized water to limit the concentration impurities and some chemical conditioning products to achieve an appropriate pH and redox potential to minimize the normal general corrosion produced by the interaction of the materials with the coolant. All volatile treatment (AVT) is now the leading method worldwide for secondary water chemistry. There are two main options of what to add ammonia or an amine (such as morpholine, ethanolamine (ETA)) and nowadays there are made experiences in laboratories also with other amines like dimethylamine (DMA) [2], to be used either in nuclear or and fossil plants. In many countries, alkaline reagents, ammonia, morpholine or ethanolamine are used to fix alkaline pH, which reduces the corrosion of the materials, (Pavagenau *et al*. [3]). Hydrazine is also injected to minimize corrosion by eliminating oxygen in the coolant and maintaining a reducing potential as reported by Delaunay *et al*. [4].

Nowadays, many WCNRs use morpholine as reagent amine in the secondary medium, but other reactors have used morpholine during many years since their start of then they had changed to other amine *i.e.*: ethanolamine. For example, Embalse Nuclear Power Plant (Embalse NPP) is a CANDU 600 nuclear reactor and the secondary circuit of it is built mainly with carbon steel A106 B; for this reason, long-term works have been done in order to know and mitigate several corrosion aspects of this material. Several years ago, Embalse NPP had replaced the use of morpholine by ethanolamine based mainly with calculations, local and international experience carefully investigated, (Radolescu *et al*. [5], Chocrón *et al*. [6]). The few works found in the open literature consisted in studying systematically the oxide films grown on A106 B carbon steel in the presence of morpholine, ethanolamine and also other amines.

Compared with other reagents used in many plants (*i.e.* ammonia, morpholine), ETA has a higher alkalinity requiring a lower molar concentration, it has also a better thermal stability than morpholine being also more favorable for the environment and has a good compatibility with the use of condensate polishers; consequently it is used in many countries. Also, it is very important to diminish the release products to the medium in the power plants not only for the cleanliness of the system but also to diminish the transport of radioactivity products that are normally incorporated in the oxide films grown on the materials which part of them are after released to the cooling medium and transport them to the different parts of the circuit or components of it.

2. Experimental Procedure

2.1. Material and Autoclaving

Samples of original A106 B provided by the plant, composition in wt%: 0.24 C, 0.09 Cr, 0.47 Mn, 0.22 Ni, 0.15 Si, <0.04 S, <0.001 Cu, <0.001 P, balance Fe, were cut of approximately 33 × 33 × 2.3 mm. The surface samples were mechanically abraded with silicon carbide papers down to 1200 grit. After polishing, all samples were thoroughly cleaned with distilled water, acetone, quickly dried and finally stored in a desiccator with silica gel. Before weighing the samples, vacuum was made in the desiccator and after weighing they remained in it up to their introduction in the autoclave. The oxide layers were grown over 77 h, 560 h and up to 1020 h periods in static stainless steel conditioned autoclaves at 260˚C and 5.1 MPa, simulating AVT conditions ($pH_{25^\circ C} \sim 9.5$) using degassed bidistilled water with: I) hydrazine + ethanolamine and II) hydrazine + morpholine. The morphology of the oxide films were studied by SEM (Scanning Electron Microscopy) and were analyzed by conventional X-ray diffraction with a diffractometer equipped with monochromator and Cu Kα radiation. Two films, grown 560 h in each medium, were analyzed with Raman spectroscopy and a couple of films, grown 1020 h in the media, were studied by XPS (X-ray Photoelectron Spectroscopy).

The specimens were removed at different periods of exposure to measure and calculate: the corrosion of the samples (weight loss), the thickness of the oxide grown and the release product to the coolant system under the controlled chemistry conditions employed. These values were calculated by chemical descaling and gravimetric analysis. The coupons are weighed before and after coolant exposure, after ultrasonic cleaning and after chemical descaling. Coupons, which have not been exposed to coolant, were given the same chemical treatment to provide an estimate of the bare metal attack (blank coupon). The total corrosion of the material (or penetration) is obtained from the difference between the weight of the coupon before exposure and that after descaling, with the correction for the bare metal attack. These three weights allow us to calculate the total metal corrosion; the adherent oxide thickness and the loose oxide and release, considering that ultrasonic cleaning removes only the loose oxide. The coupons were descaled by a standard procedure using Clark solution (5% $SnCl_2$ and 2% Sb_2O_3 in 100 ml concentrated HCl), Singh and Kumar [7]. The solution was used at ambient temperature during around 30 s, depending of the age of the solution and seeing if the oxide is removed. To do this, each sample was held with a zircaloy 4 wire that passed through the hole which is used to hang them in the autoclave for oxidation. During the immersion of each sample in the solution, the sample was stirred thoroughly by hand, using the wire that passed through the hole that has each sample to be hanged in the autoclave for oxidation We learned this experimental procedure when we have regularly taken out the samples from the autoclaves that are located in the primary coolant system (out of pile) of Embalse NPP [8], this methodology was used since 1986. Of course different reagents and procedures were used for the different materials that were inside these autoclaves: carbon steels, stainless steels, Alloy 800 and other materials. Many oxidized samples were taken out from Embalse NPP primary system autoclaves and held to the laboratory; then we have examined them by optical and scanning electron microscopy with and without the oxide.

After the treatment the coupons were washed, rinsed, carefully dried, stored in a vacuum desiccator and around after one hour the samples were weighed. From the weight differences measured, the calculations to obtain oxide thickness, base metal corrosion and the released oxide were made. The iron oxide density, considered as magnetite, was assumed as 5.2 g/cm^3.

2.2. Analysis of Samples after Autoclave Tests and Discussion

The films grown in both media and in all exposure periods, were very adherent and of dark gray-blackish color. To the naked eye, depending on the incident light, surface brightness was observed due to the final polish finish of the samples.

Previous results, up to 560 h of exposure time, have been reported in an earlier work by Olmedo and coworkers [9]. **Figure 1** shows some of those results.

In the previous work [9], for 77 h and 560 h of testing, the SEM micrographs of the oxide films grown in both media present a similar surface morphology. The crystal sizes have grown between the two exposure periods. In

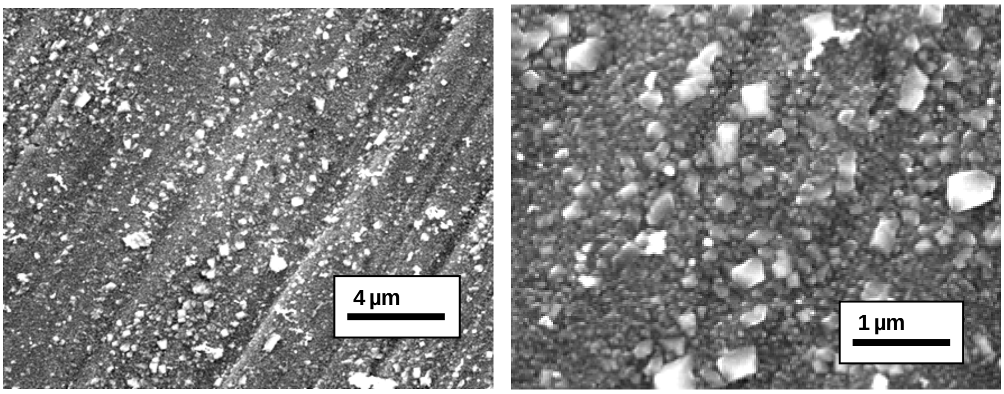

Figure 1. SEM micrographs of the oxide layer grown 560 h in the medium with morpholine.

Figure 1, it can be observed that there are crystals in the range of 0.3 - 0.5 µm over a layer of very small crystallites. The images show particles with different sizes with octahedral habits that resemble magnetite. Similar morphological results were found in the medium with ETA.

Figure 2 and **Figure 3** show the surface morphology of the oxide films grown during 1020 h in both media.

The XRD pattern of the all the films tested in the three periods (77, 560 and 1020 h) studied revealed two crystallographic phases Fe-α, corresponding to the substrate and magnetite (Fe_3O_4) (and/or maghemite: γ-Fe_2O_3). It should be noted that maghemite could not be differentiated from magnetite using conventional XRD analysis since it has the same structure. However, due to the reducing conditions, magnetite is the most probable phase.

Rangarajan *et al*., [10], have observed a similar morphology and crystal size changes with the exposure time in a simulated secondary water chemistry medium, containing ethanolamine + hydrazine ($pH_{25^\circ C} = 9.2$) at 240˚C in tests of 7 and 30 days.

The micrographs of **Figure 2** and **Figure 3** show the surface morphology and some slight differences in the release of their surfaces can be seen; it seems that is higher in the medium with morpholine. This is in accordance with the product corrosion release obtained by chemical descaling.

The corrosion product release, after 1020 h of exposure, was 87.2 mg/dm^2 in the medium with morpholine, while it was 64.6 mg/dm^2 in the medium with ETA. This tendency of a higher release in the medium with morpholine is the same at the shorter exposure times of 560 h. Those releases were 74.9 and 55.7 mg/dm^2 respectively as reported in the previous work [9].

A sample exposed during 1020 h, were also analyzed using Raman spectroscopy with a 780 laser beam. Magnetite was the unique phase found, spectra examples are shown in **Figure 4**. The spectra were taken at different zones of a sample; these are shown with different colors and overlapped he spectra of the different zones in **Figure 4**. This figure shows a very high peak of the Raman shift at 670 cm^{-1}, characteristic of magnetite, in agreement with XRD analysis. Similar spectra was obtained in the medium with morpholine.

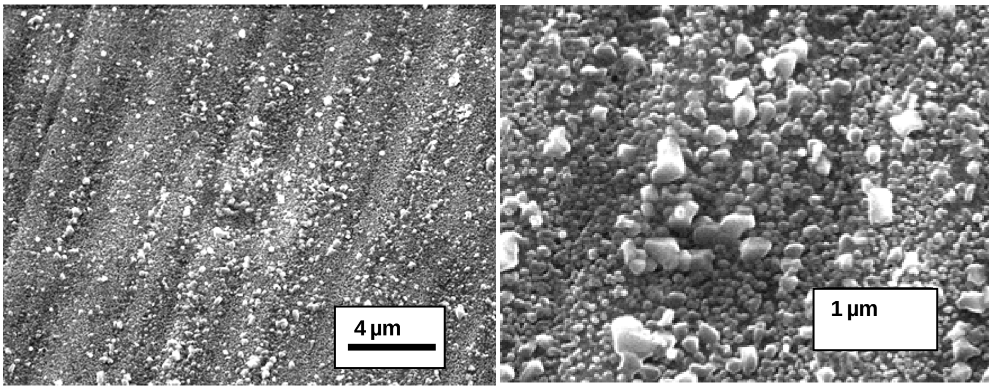

Figure 2. SEM micrographs of the oxide layer grown 1020 h in the medium with ETA.

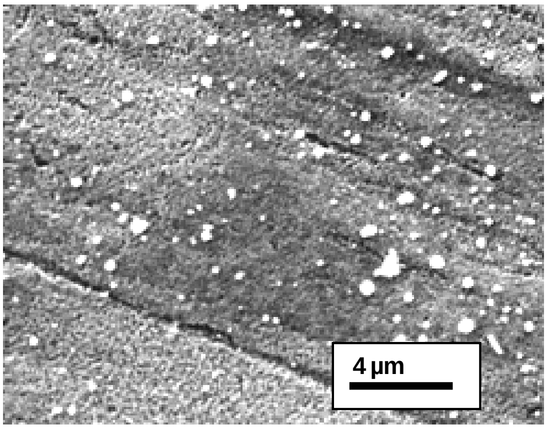

Figure 3. SEM micrograph of the oxide layer grown 1020 h in the medium with morpholine.

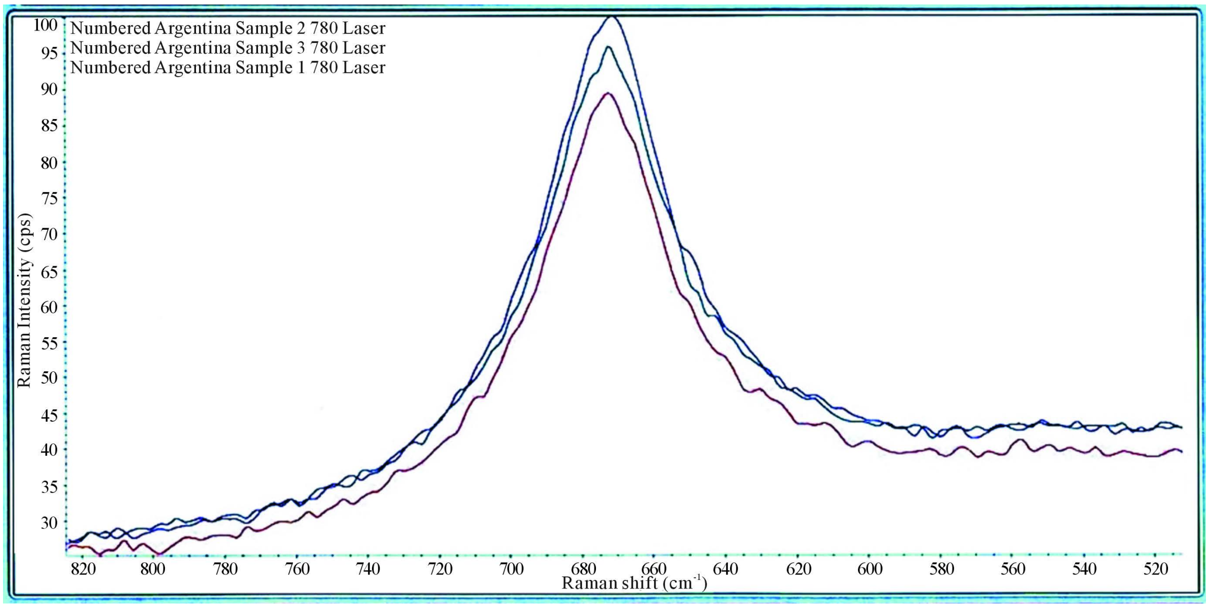

Figure 4. Raman shift at 670 cm^{-1} corresponding to the oxide grown 1020 h in the medium with ETA.

The oxide films grown in both media were very uniform in all samples. The data obtained have shown a very consistent interaction demonstrating a uniform coating up to the time studied.

SEM micrographs taken from a cross section of the films of both samples showed an adherent thin layer at the metal/oxide interface (see **Figure 5**). This feature is a characteristic of a duplex film that grows in this and other materials at high temperature and pressure as reported by Olmedo *et al*. [9], Tapping *et al*. [11] and Alvarez *et al*. [12].

SEM micrographs have shown that the oxide films present a similar surface morphology in both media, but the crystal sizes grow with the exposure time [9]. In **Figure 1**, there is a lot of crystals in the range of 0.3 - 0.5 µm over a layer of very small crystallites. The SEM images show particles with different sizes with octahedral habits that resemble magnetite. A similar morphology was observed in the medium with morpholine.

Figure 2 shows an example of the surface morphology for the oxide film grown 1020 h in the medium with ETA. The morphology for the film grown in the medium with morpholine is shown in **Figure 3**. In this last figure, it seems that a greater quantity of the external layer crystallites has gone to the coolant as compared with the SEM micrographs obtained with ETA. This was also measured by the calculations of the release products to the medium. After 1020 h of exposure, the corrosion product release was 87.2 mg/dm^2 in the morpholine medium, while it was 64.6 mg/dm^2 in the medium with ETA. The tendency of a higher release with morpholine is the same at the shorter exposure times. Previous results have shown that the release was 74.9 and 55.7 mg/dm^2 for the tests at 560 h in the medium with morpholine and ETA respectively, Olmedo *et al*. [9].

The XRD pattern of the all the films analyzed at all periods of exposure revealed two crystallographic phases Fe-α, corresponding to the substrate and magnetite (Fe_3O_4) and/or maghemite (γ-Fe_2O_3). It should be noted that maghemite couldn't be differentiated from XRD analysis since it has the same structure. However, due to the reducing conditions, magnetite is the most probable phase. Rangarajan *et al*. [10], have observed the same morphology and crystal size changes with the exposure time in a simulated secondary water chemistry medium, containing also ethanolamine + hydrazine ($pH_{25^\circ C} = 9.2$) at 240˚C.

Figure 6 and **Figure 7** plot the XPS spectra Fe 2p and O 1s for oxide films grown during 1020 h in both media, obtained at the surface and after 5 minutes of sputtering. It is seen that the spectra are nearly the same for both media.

The Fe 2p spectra of the surface correspond to iron oxohydroxides or hydroxides and also a contribution of magnetite can be inferred. The O1s spectra show clearly, at least, two components. The component with the minor binding energy of O1s (~530 - 530.1 eV) corresponds to O^{2-} from the oxide (metal-O-metal bond, OM oxygen) and the other component ~532.5 eV is attributed to water physically adsorbed.

The Fe 2 $p_{3/2}$ centroid, after 5 minutes of sputtering, is displaced to lower binding energy and its position is

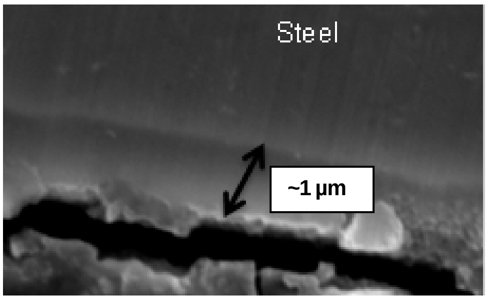

Figure 5. Cross section of a sample oxidized during 1020 h in the medium with morpholine. It shows the adherence of the film in the interface metal/oxide.

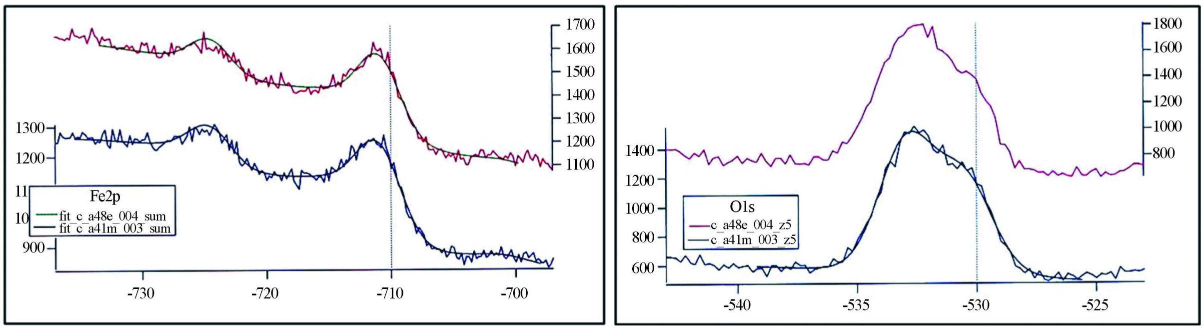

Figure 6. XPS Fe 2p and O1s spectra obtained at the surface for the films grown 1020 h. The red spectra correspond to the film grown in the medium with ETA.

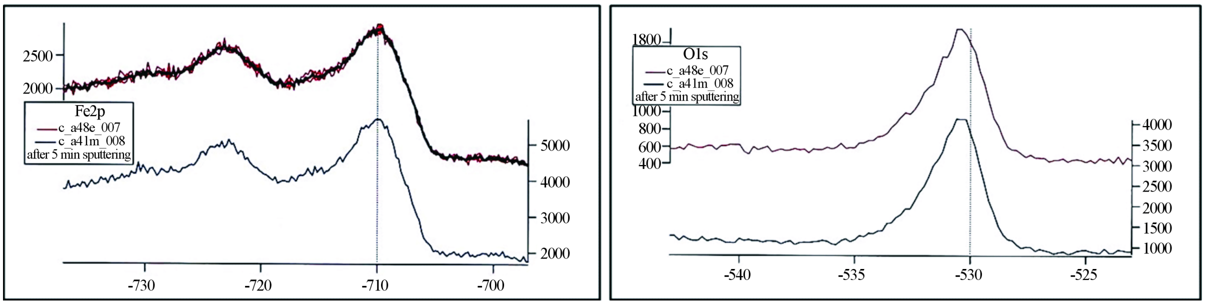

Figure 7. XPS Fe 2p and O 1s spectra obtained for the films grown 1020 h after 5 minutes of sputtering. The red spectra correspond to the film grown in the medium with ETA.

related to magnetite. The sputtering eliminates, at least partially, the hydrated oxides or oxohydroxides as it is also shown in the O 1s spectra.

Deconvolution of O1s peak using three components, made with similar oxides grown at high temperatures and pressure simulating a primary medium, gave also a component around 1 - 1.4 eV greater than that corresponding to O^{2-} from the oxide and is attributed to the oxygen in OH bond (OH oxygen), which value is the same for different oxohydroxides and hydroxides of Fe, Cr, Ni, Mo and so on. This feature is well documented in several works *i.e.* Asami *et al*. [13], Mc Intyre *et al*. [14]-[16], Mathieu *et al*. [17], Olmedo [18].

The peaks in **Figure 6** and **Figure 7** have been identified by comparison with previously published XPS studies on bulk iron. The binding energies of Fe 2p and O 1s peaks as well as the broadness of the latter one, suggested the presence of hydrated oxides or oxohydroxides, in the outermost part of the film. The Fe $2p_{3/2}$ peak observed at the outermost layer at a binding energy of ~711.0 eV is due to Fe^{3+} oxide. Slight sputtering shifts the peak centroid to lower energy indicating that some Fe^{2+} is probably due to a partial elimination of the hydrated layer by sputtering. The crystals scattered over the surface that were detected by SEM are presumably Fe_3O_4 and the contribution of the inner layer explain the presence of Fe^{2+} as indicated by XPS. A binding energy of around

710.4 eV has also been reported for different spinels like magnetite. In this kind of oxide films, it is very difficult to distinguish between α-Fe_2O_3, γ-Fe_2O_3 (or their hydrates) and Fe_3O_4 on the basis only of XPS analysis since their binding energies are nearly identical for standard bulk samples [11] [17] [18]. Deconvolution of the Fe $2p_{3/2}$ peak in two components corresponding to Fe^{2+} and Fe^{2+} cannot resolved quantitatively, as has been done in other cases by many workers [11] [17] [18]. This would require thinner and more homogenous passive layers.

After 40 minutes of sputtering, the O 1s corresponds only to the oxygen of the oxide, and the peak maximum of Fe $2p_{3/2}$ is well located at 710.0 eV indicating only the presence of magnetite availing the results of XRD. There is always uncertainty in attempting to identify species present in oxide films of iron by using only a single technique. However, through complementary techniques, our findings suggest the formation of hydrates iron oxides or oxohydroxides in the outermost part of the film and the formation of a spinel type oxide as found by XRD and Raman. The formation of hydrated oxides in the outermost part of films that were grown in high temperature aqueous media is commonly found in these conditions [11] [17] [18].

In the previous work [9], for the oxidation of the samples up to 560 h, it was shown that the thickness of the adherent oxide film and the release of oxidation products to the medium were slightly higher in the medium with morpholine. Up to 1020 h of oxidation time, the tendency is similar. For the last oxidation period (average of 3 or 4 samples for each medium) the adherent oxide film was 1.13 µm and the release of corrosion products was 87.3 mg/dm^2 for the samples exposed in the medium with morpholine, but in the medium with ethanolamine these values were slightly lower: 1.04 µm and 64.6 mg/dm^2 respectively, although they are of the same magnitude order.

Figure 8 shows the weight loss: W (after the descaling the samples) vs. oxidation time The material weight loss (W) could be fitted by a law of the type $W = kt^n$, up to 1020 h of exposure, resulting in $n = 0.42$, $k = 6.24$ for films grown in medium with morpholine and $n = 0.39$, $k = 6.08$ for films grown in medium with ETA; where W is in mg/dm^2 and t in h.

This last figure shows that the metal loss, which is related with the oxide thickness grown on the metal and the corrosion product release to the medium, is higher in the medium with morpholine and this tendency continues with increasing the exposure time. This means, that it could be important in a plant circuit, since the exposure time is much longer. The slope of the plot is also slightly higher in the medium with morpholine.

3. Conclusions

The morphology found at different oxidation periods in both media exhibits a typical duplex structure reported previously by carbon steels in high temperature aqueous medium. The composition of them also coincides with those reported in literature in similar media and temperature.

The existence of hydrated or oxohydroxides in the outermost part of the oxides layer grown in both media was detected by XPS. The formation of spinel oxide of magnetite is suggested by in-depth sputtering of the film and is also availed by XRD and Raman spectroscopy.

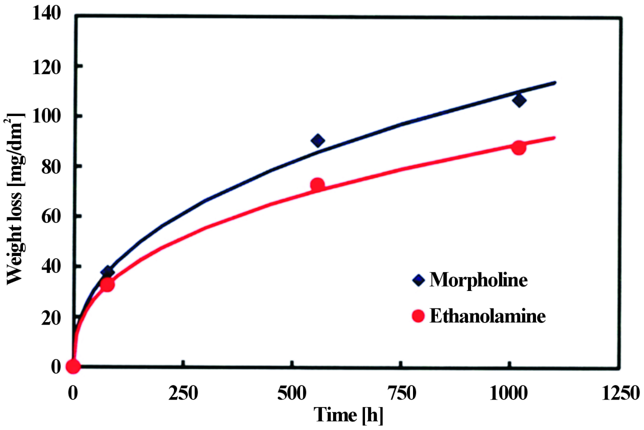

Figure 8. Weight loss, after descaling the samples vs. the oxidation time in autoclave.

The release of corrosion products and the oxide thickness were higher in the medium with morpholine than in that with ethanolamine, although of the same order of magnitude. However this tendency increases in the medium with morpholine. This increase could be important in a plant circuit that operates for much longer periods of time compared to those tested in this work.

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The oxidation autoclave testing and analysis of the films were already finished at around the end of 2012.

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