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The Effect of Polyacrylic Acid on Iron Oxides Formed on Steam Generator Tubes and on Metallic Copper Present in Pressurized Water Reactors

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Abstract

In order to reduce and prevent fouling of the Steam Generators (SGs) tubes and the blockage of tubes support plates in the secondary circuit, EDF has several approaches. One of them consists in injecting a chemical agent, polyacrylic acid (PAA), to prevent the deposition of corrosion products on the surface of SG tubes and to facilitate their evacuation by the SG blowdown circuit.

First, the dispersing and/or complexing PAA effect on iron oxides, in the secondary circuit physico-chemical conditions ($T = 275\text{ °C}$, $\text{pH}_{25\text{°C}} = 9.2\text{-}9.6$, reducing conditions fixed by H_2) was demonstrated and quantified. For a PAA concentration equal to $500 \times 10^{-3}\text{ g.kg}^{-1}$, the iron content values were about 2500 times higher than the iron solubility limit at the blowdown. Then, the influence of chemical conditioning and pH on the PAA effectiveness was studied. It has been showed that the pH and the conditioning amine nature (amine volatile treatment: ethanolamine, morpholine and/or ammonia) seems to have no significant impact on the PAA effect.

A similar study was performed on the dispersing and/or complexing PAA effect on metallic copper present in several EDF's power plants. The main conclusion is that PAA seems to disperse metallic copper at room temperature but this property disappears at high temperature (275 °C).

Finally, the PAA action mechanism on iron oxide at high temperature is discussed. Complexation seems to be the main interaction mechanism between PAA and iron oxides observed in the studied experimental conditions and materials. The most likely mechanism would seem to be a dissolution of magnetite forming the deposit and then a complexation reaction between PAA and iron(II) ions (reducing conditions). Moreover this complexation would be responsible for the formation of hematite observed on the magnetite powder.

Keywords: corrosion products, polyacrylic acid, dispersant, complexing agent, fouling, clogging, blockage, iron, copper

1. Introduction

In Steam Generators (SGs) of Pressurized Water Reactors (PWRs), corrosion products can deposit on the tube surfaces, especially on the secondary side. Three types of deposits, mainly composed of magnetite have been observed: deposits of metal oxides corresponding to corrosion products on the tube sheet that may form in some cases hard sludge; other deposits observed on the external surface of the tubes leading to fouling and finally when the deposits are located in the quatrefoil-shaped holes in tube support plates leading to clogging (or tube support plate blockage). Fouling and clogging can have thermo-hydraulic impact. It may decrease the heat transfer between the primary and the secondary circuit. Moreover, clogging can have a mechanical impact on the structure. It may lead, over the long term, to SG tubes failures due to excessive vibration fatigue cracking [1].

Since the generalized corrosion and the Flow Accelerated Corrosion (FAC) cannot be completely stopped, one of the approaches of EDF is the use of online dispersant addition that aims in preventing deposition of corrosion products transported in the feedwater on the SG surfaces. By reducing the accumulation and the deposition of the corrosion products, dispersants can facilitate more efficient removal through the SG blowdown. Polyacrylic acid (PAA) injection has been qualified for application during the post-outage long-path recirculation cleanup period [2] and during SG wet layup [3]. Online applications have also recently been performed in France (Golfech 2) and in Belgium (Doel 3).

On the one hand, the PAA dispersing and/or complexing effect on iron oxide (magnetite) was studied in the nominal operating conditions of SGs since it is the main corrosion product in SGs. On the other hand, in several EDF's power plants, metallic copper is present due to the corrosion of brass condensers and may lead, with other impurities, to the hardening of oxides deposited in the SG. Then a comparative study of the PAA action was conducted on metallic copper.

The PAA action mechanism on iron oxide at high temperature and on metallic copper at low temperature is discussed.

The conclusions of these studies led to study a possible impact of pH solution but also of the conditioning of the secondary circuit, in particular the amine volatile treatment, on the PAA effect.

2. Experimental part

2.1. Methodology

First, the dispersing and/or complexing effect of PAA on iron oxide (Fe_3O_4) and on metallic copper (Cu) was studied in the operating conditions of a SG. Four experiments were carried out on magnetite powder. The same experiments were then performed on copper powder:

- one test without PAA in order to determine the quantity of solubilized iron or copper by the aqueous solution containing ammonia (NH_4OH) (Fe-Test 0 and Cu-Test 0);
- two tests with $0.5 \text{ g}\cdot\text{kg}^{-1}$ of PAA to evaluate the quantity of solubilized iron or copper and the reproducibility of the results (Fe-Test 1 and 2 and Cu-Test 1 and 2);
- one test without PAA but with monoethanolamine (MEA) and the major products of thermal degradation of PAA which are acetic and formic acids (Fe-Test 3 and Cu-Test 3).

Moreover, the influence of the chemical conditioning and the pH of the solution on the PAA effectiveness were studied.

2.2. Experimental setup

The experimental device named SOZIE is a one-pass circulation system in which the solution is constantly renewed. This device is designed to work in monophasic flow, from room temperature up to $360 \text{ }^\circ\text{C}$ and from the atmospheric pressure up to 20 MPa. The schematic layout and photograph of the set-up are presented

Figure 1.

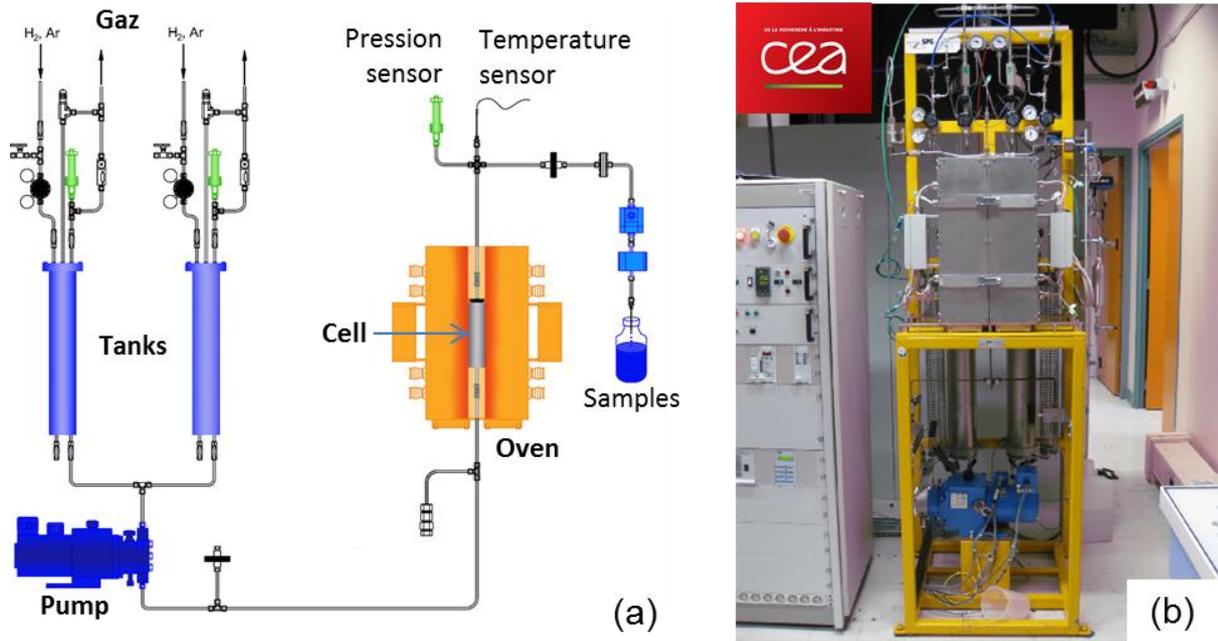


Figure 1 : (a) Schematic layout of the experimental device (SOZIE) for thermodynamic and kinetic measurements in PWR physicochemical conditions; (b) photograph of the device

This device is constructed solely of titanium (tanks, tubes, pump, cell, filters) for the experiments where iron is present. For the experiments on copper, a stainless steel cell is used. The iron oxide powder bed and the metallic copper chips (between 30 and 50 g) are maintained in the reaction cell between two titanium frits. The residence time in the heated section depends on the mass flow rate, which can evolve from 10 to 200 g.h⁻¹. The residence time t_s is given by equation (1) where Q is the mass flow (kg.s⁻¹), V_w the water volume (m³) in the cell and ρ_w the density of water (kg.m⁻³).

$$t_s = \frac{\rho_w V_w}{Q} \quad (1)$$

The iron oxide powder and the metallic copper shavings were analyzed by X-Ray Diffraction before and after test to study the possible evolution of the structure after interaction with PAA.

2.3. Experimental conditions

The residence time is 20 min and the temperature is 275 °C. To stay in monophasic flow, the pressure is maintained constant at 12 MPa, to be above 5.9 MPa, the saturation vapour pressure at 275 °C [4]. The pH of the solution is adjusted with ammonia (NH₄OH, 30 vol%) in order to obtain a pH between 9.1 and 9.6, representative of the

secondary circuit. The solution pH containing the degradation products and the monoethanolamine reaches 10 because of the presence of the amine and the absence of PAA which impose a more basic pH.

For the study on the dispersing and/or complexing effect of PAA on Fe and Cu (8 tests), the PAA is conditioned with monoethanolamine in the OptiSpere PWR6600 (product developed by General Electric). This product contains about 15 wt% PAA of high molecular weight, 7.5 wt% monoethanolamine, 0.02 wt% carboxylic acids (mainly acetic and formic), about 0.01 wt% of metallic iron and water [5].

To study the chemical conditioning and pH influence, PAA is conditioned with morpholine. Thus, the OptiSpere PWR6610 (also developed by General Electric) was used.

The chosen PAA concentration for the different tests is 500 mg.kg^{-1} . This concentration would correspond to the one in the steam generator. Since PAA is a non-volatile compound, its concentration in the steam generator is one hundred times its concentration in the feed water. Moreover, Lamouroux et al. [5] show that 50 % of PAA are degraded after 20 min of residence time at $275 \text{ }^\circ\text{C}$. As a consequence, $500 \times 10^{-3} \text{ g.kg}^{-1}$ PAA content in the steam generator would correspond to $10 \times 10^{-3} \text{ g.kg}^{-1}$ in the final feed water.

All the solutions are degassed under primary vacuum. After loading into the device tanks, the solutions are put under pressure (0.2 MPa) of a mixture argon (95 vol%) and dihydrogen (5 vol%) in order to obtain a reducing environment.

Three parameters were followed during the tests: pH, cationic conductivity and iron or copper concentration. Input and output measures were carried out, which corresponds to the initial time and after 20 min of residence time respectively.

The presence of metallic cations has been determined by atomic absorption spectroscopy. Samples were collected for analysis, after filtration into a $0.45 \times 10^{-6} \text{ m}$ particle filter, in flasks containing a drop of nitric acid in order to avoid precipitation of iron and copper when exposed to air and/or absorption on the walls. With this technique, the quantification limit for iron and copper is $0.54 \times 10^{-6} \text{ g.kg}^{-1}$ and $0.28 \times 10^{-6} \text{ g.kg}^{-1}$ respectively. It has to be noted that the sampling technique with solution cooling and acidification do not permit to distinguish soluble and insoluble iron. Besides, $0.45 \times 10^{-6} \text{ m}$ particle filters are put in the device flow line.

3. Results and discussion

3.1. Evolution of iron oxide and metallic copper structure after interaction with PAA

First, the copper shavings were analysed by X-ray diffraction (XRD) before (Figure 2 (a)) and after interaction with PAA (Figure 2 (b)). The comparison of the XRD pattern performed on the copper shavings used in this study with the ones of metallic copper Cu and oxide copper Cu₂O given by the JCPDS database (see) shows that the shavings are made of metallic copper but also that their interaction with PAA, in alkaline solution at 275 °C with a 20 min residence time, did not change their phase.

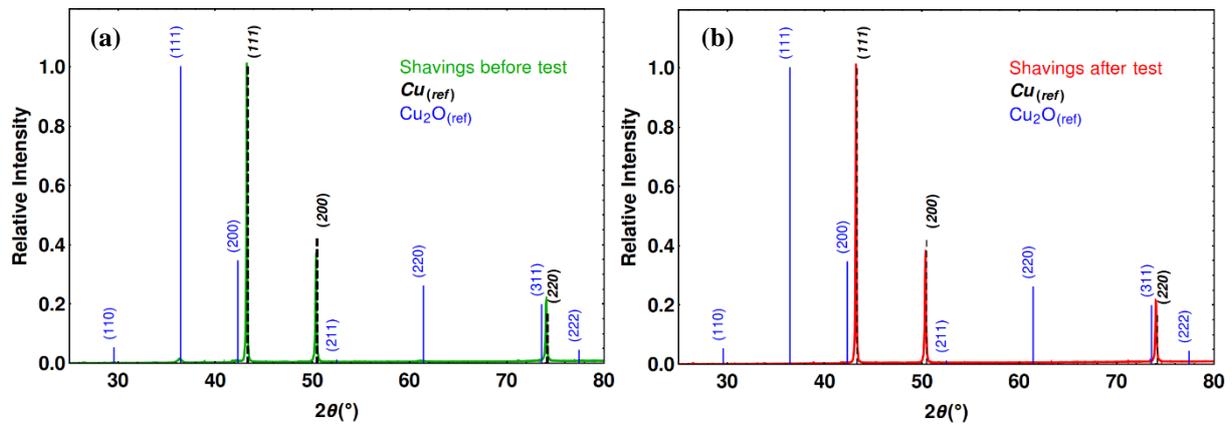


Figure 2 : (a) X-ray diffraction pattern of copper shavings before interaction with PAA, JCPDS data for metallic copper (Cu_(ref)) and for copper oxide (Cu₂O_(ref)) (b) X-ray diffraction pattern of copper shavings after interaction with PAA at 275 °C with a 20 min residence time

Secondly, the evolution of the iron oxide powder phase is studied. The tested powder was analysed by X-ray diffraction (XRD) before interaction with PAA (Figure 3 (a)). The XRD patterns showed only the presence of magnetite. The same powder was analysed after interaction with PAA at 275 °C with a 20 min residence time (Figure 3 (b)). Magnetite is still present but several peak patterns of hematite clearly appeared, the most intense peak is the (104).

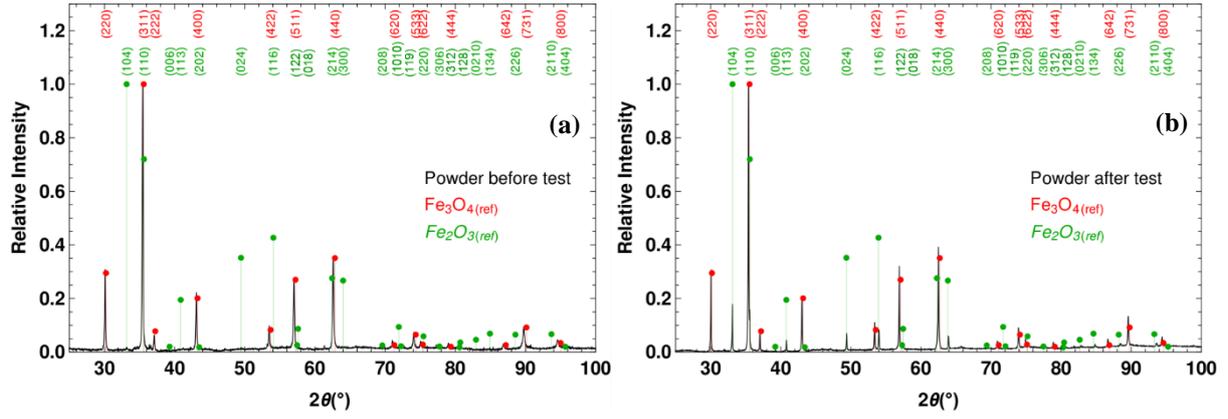
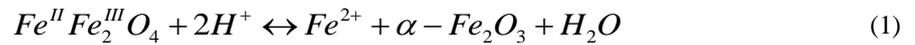


Figure 3 : (a) X-ray diffraction pattern of the tested magnetite powder before interaction with PAA, JCPDS data for magnetite (Fe_3O_4 in red) and for hematite (Fe_2O_3 in green) (b) X-ray diffraction pattern of the tested magnetite powder after interaction with PAA at 275 °C with a 20 min residence time

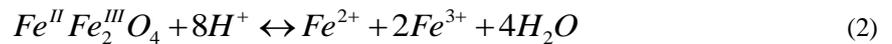
The appearance of hematite is consistent with the results of D'Angelo *et al.* [6] who studied the effect of PAA on magnetite deposits, formed electrochemically, in similar physico-chemical conditions than this study (single liquid phase, same temperature, reducing conditions and $pH_{25^\circ C}$ 9.6). They observed by XRD analyses the formation of another oxide phase than magnetite: hematite, α - Fe_2O_3 for the test with the highest concentration of PAA *i.e.* $10 \times 10^{-3} g.kg^{-1}$.

According to the Pourbaix diagram of iron-water at 25 °C [7], the stable phase of iron is magnetite at pH 9.6 in reducing conditions. The same stable phase is found at higher temperature for the same pH [8]. As a consequence, from a thermodynamic point of view hematite should not form in the SG.

The first hypothesis links the formation of hematite to an interaction of PAA with the iron (II) in water (Equation 1). The iron (II) was complexed by PAA shifting the equilibrium towards the right and thus iron (III) in solution precipitated as hematite which could have been deposited on the surface.



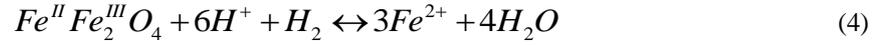
This balanced chemical equation (Equation 1) can be divided in the following steps. First, magnetite dissolution at the oxide/solution interface, leads to the formation of iron (II) and iron (III) according to Equation 2:



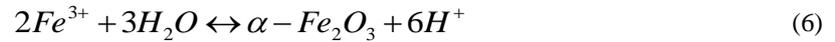
In presence of dihydrogen, iron (III) is reduced in iron (II). The equilibrium is given Equation 3.



Then, the sum of Equations 2 and 3 leads to the equilibrium reaction of magnetite dissolution which occurs in a reduce media (Equation 4).



For the test with PAA, composed a large number of ligands L, the complexation of iron (II) by PAA (Equation 5) shifts the equilibrium (2) to the right. Then, the formation of iron (III) is increased. Since, hematite is formed from iron (III) (Equation 6), this complexation favors the formation of hematite rather than magnetite.



Moreover, the reduction of iron (III) into iron (II) (Equation 3) consumes the dihydrogen in the solution close to the interface oxide/solution. As a consequence, the redox potential increases locally, which enhances the formation of hematite on the oxide surface.

The redox potential can also be modified because of the thermal degradation products of PAA. The main degradation product, acetate and to a lesser extent formate [9], could create localized areas of oxidation, which in turn oxidize the magnetite forming hematite.

3.2. Dispersing and/or complexing effect of PAA on iron oxide and on metallic copper

The results of the six experiments are given in Table 1. The first tests with the matrix (Fe-Test 0) show that in the nominal operating conditions of the secondary circuit, without PAA, the quantity of iron is relatively low (around $6.5 \times 10^{-6} \text{ g.kg}^{-1}$) and the quantity of copper is negligible ($< 0.5 \times 10^{-6} \text{ g.kg}^{-1}$) at the output of the test section. As iron solubility is equal to few $10^{-6} \text{ g.kg}^{-1}$ and is about one order higher than copper in these conditions [10], the obtained values are consistent. However, the iron content is a little higher than the solubility limit

Regarding cationic conductivity and pH measures, they are identical taking into account their uncertainties.

For both iron oxide and metallic copper, tests 1 and 2 evaluate the dispersing/complexing effect of PAA. In the case of iron, 15 % increase of the conductivity is measured between the input and the output of the device. This increase is probably due to the thermal degradation of PAA and to the production of carboxylic acid (mainly acetic and formic acid) in the form of carboxylate ions. Given the uncertainty of the pH, it can be considered constant.

The iron content in the tanks at 25 °C is less than $0.9 \times 10^{-6} \text{ g.kg}^{-1}$. Then no complexing effect of PAA on iron is observed at low temperature. After 20 min of interaction with PAA at 275 °C in a reducing solution, the iron

concentration average is $5,000 \times 10^{-6} \text{ g.kg}^{-1}$ for the two tests. These results mean that **the presence of PAA ($500 \times 10^{-3} \text{ g.kg}^{-1}$) of high molecular weight leads to an iron concentration three orders of magnitude higher than the magnetite solubility at this temperature** [11]. The dispersing and complexing effect of PAA on iron at high temperature is shown.

Table 1: Summary table of the results obtained for the six experiments (3 on Fe_3O_4 and 3 on Cu). The mean value and twice the standard deviation of the total conductivity, the pH, the Fe and Cu concentrations for input and output of the cell are given

	Cell input σ ($10^{-6} \text{ S.cm}^{-1}$)	Cell output σ ($10^{-6} \text{ S.cm}^{-1}$)	Input pH at 25 °C	Output pH at 25 °C	Input [Fe] or [Cu] ($10^{-6} \text{ g.kg}^{-1}$)	Output [Fe] or [Cu] ($10^{-6} \text{ g.kg}^{-1}$)
Fe-Test 0 <i>Matrix NH_4OH</i>	890 ± 60	910 ± 34	9.3 ± 0.1	9.3 ± 0.1	< 0.3	6.5 ± 6.6
Fe-Test 1 <i>0.5 g.kg⁻¹ PAA</i>	145 ± 7	168 ± 9	9.1 ± 0.3	9.2 ± 0.5	0.4 ± 0.5	5299 ± 736
Fe-Test 2 <i>0.5 g.kg⁻¹ PAA</i>	143 ± 8	174 ± 6	9.4 ± 0.1	9.5 ± 0.1	< 0.3	4799 ± 397
Cu-Test 0 <i>Matrix NH_4OH</i>	17 ± 1	18 ± 1	9.6 ± 0.1	9.6 ± 0.1	< 0.3	< 0.5
Cu-Test 1 <i>0.5 g.kg⁻¹ PAA</i>	142 ± 6	231 ± 22	9.2 ± 0.2	8.5 ± 0.3	[3.9 ; 20.7]	[0 ; 2.0]
Cu-Test 2 <i>0.5 g.kg⁻¹ PAA</i>	155 ± 4	213 ± 7	9.4 ± 0.1	8.8 ± 0.1	[1.6 ; 27.2]	[0 ; 0.5]

Figure 4 gathers the results of this study and those from D'Angelo *et al.* [6] who found a linear law between the iron concentration and the one of PAA after interaction of PAA (between $0.1 \times 10^{-3} \text{ g.kg}^{-1}$ and $10 \times 10^{-3} \text{ g.kg}^{-1}$) and with iron oxides deposits in similar conditions than our tests. These comparison shows a clear consistency between the two studies. As a consequence, the proportionality is verified between the iron quantity complexed and/or dispersed by PAA and the introduced PAA concentration over four decades.

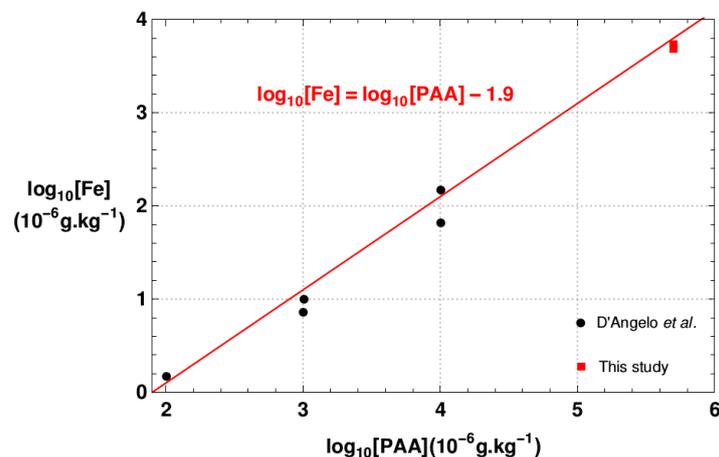


Figure 4 : Evolution of the iron concentration logarithm as a function of the PAA concentration logarithm after interaction at 275 °C with 20 min residence time. The black points are from the study of D'Angelo *et al.* [6] and the red squares are from this study

Regarding the tests on metallic copper, there is more copper detected at the input of the cell at room temperature than after PAA interaction at high temperature and the copper content values are similar to the calculated solubility in the same conditions. **As a consequence, PAA and copper have almost no interaction in the nominal operating conditions of the secondary circuit.**

Moreover, at the cell input, the measured copper concentrations are several orders of magnitude above the copper solubility at 25 °C and pH 9.6 and a large scattering of the copper content values is observed. These two points suggest that copper is in the particulate form.

Several hypotheses have been done about the provenance of these copper particles. It could have come from the chemicals used to prepare the solutions or from a pollution of the device. Nevertheless, a copper titration was performed all along the preparation chain and no copper was detected and given that the matrix test (Cu-Test 0) and the test with the PAA degradation products do not show copper at the input of the cell: the two previous hypotheses are then rejected. The most likely cause is that PAA introduction in the tanks has dispersed copper particles present on their inside wall. **As a consequence, PAA seems to have a dispersing action on copper at low temperature which disappears at high temperature. This result needs to be confirmed by further experiments.**

If it is confirmed, the removal of copper(II) ions in cold conditions is really interesting from an industrial point of view. Indeed, PAA could be used during steam generator wet layup and during sludge lancing to remove impurities, in particular bivalent ions such as copper(II). Reasoning by analogy, it would be possible that at low temperature, PAA had a dispersing effect on zinc(II) ions present in water due to the corrosion of brass condensers but also on lead(II) ions which can promote lead-induced stress corrosion cracking of nickel-base alloy SG tubing [12].

At high temperature, the removal of iron oxide has been showed but the distinction between dispersing or complexing action is not established.

First, the definition of dispersing agent is considered. In general, a dispersant is a negatively charged natural organic or synthetic polymer that is added to boiler feedwater in order to attempt to maintain the particulate species

in suspension so that they can be removed via blowdown. Polymeric dispersants also act as crystal modifiers, changing the size, shape and properties of crystals [13]. In our study, iron seems to be in the soluble form at the device output: the magnetite grains are not small enough to go through the filter (0.45×10^{-6} m). The presence of this filter does not allow to conclude on the dispersing effect of PAA. Indeed if clusters of magnetite are formed, they probably could not pass through the filter.

Secondly, D'Angelo *et al.* [6] performed a test with coupons of alloy 690TT and 600TT with a thick magnetite (Fe_3O_4) deposit in the same conditions as the magnetite powder with a lower PAA content. Their results showed that the iron concentration is about 200 times higher after interaction with PAA at high temperature. As a consequence, PAA seems to be effective on compact surfaces (magnetite deposits) but also on solid iron oxide suspension (magnetite powder). In case of compact deposit, magnetite and PAA must react together to lead to the presence of soluble iron in the solution at the device output. Dissolution of magnetite forming the deposit and then a complexation reaction between PAA and iron(II) ions (reducing conditions) would seem to be the most likely mechanism. This mechanism is consistent with the formation of hematite observed on the magnetite powder (this study) and on the magnetite deposits [6].

Moreover, dispersant action at high temperature would lead to non-reproducible iron concentrations from one test to another in the same conditions, which is not the case for the two performed tests (see Table 1, Fe-Test 1 and Fe-Test 2).

3.3. Dispersing and/or complexing effect of formic and acetic acids on iron oxide and on metallic copper

Tests with the main degradation products of PAA, Fe-Test 3 and Cu-Test 3 for iron and copper respectively, were performed. The goal of these experiments is to compare the interaction of the PAA of high molecular weight contained in the OptiSpurse PWR6600 with iron at high temperature and with copper at room temperature, and the interaction of the degradation products of this PAA with the same elements in the same conditions. The results, presented in Table 2, are similar for both tests on iron and copper.

First, at low temperature, iron and copper are very weakly dispersed by the degradation products of PAA ($[\text{Fe}] = 0.3 \times 10^{-6} \text{ g.kg}^{-1}$ and $[\text{Cu}] = 0.4 \times 10^{-6} \text{ g.kg}^{-1}$). Then at high temperature, the iron and copper contents in the solution

are $2.0 \times 10^{-6} \text{ g.kg}^{-1}$ and $0.2 \times 10^{-6} \text{ g.kg}^{-1}$ respectively. These values are close to the solubility limits of these elements at the same temperature and same pH [14]. As a consequence, the main PAA degradation products do not have a complexing or dispersing effect at high temperature.

Table 2: Experiments with the main degradation products of PAA (formic and acetic acids) in presence of monoethanolamine. The mean value and the standard deviation of the cationic conductivity, the pH, the Fe and Cu concentrations for input and output of the cell are given

	Cell input σ ($10^{-6} \text{ S.cm}^{-1}$)	Cell output σ ($10^{-6} \text{ S.cm}^{-1}$)	Input pH at 25 °C	Output pH at 25 °C	Input [Fe] or [Cu] ($10^{-6} \text{ g.kg}^{-1}$)	Output [Fe] or [Cu] ($10^{-6} \text{ g.kg}^{-1}$)
Fe-Test 3						
Degradation products	34 ± 2	36 ± 2	10.1 ± 0.1	9.9 ± 0.1	0.3 ± 0.5	2.0 ± 2.5
Cu-Test 3						
Degradation products	27 ± 1	31 ± 1	9.9 ± 0.1	9.6 ± 0.1	0.4 ± 0.9	0.2 ± 0.1

The intermediate degradation products could have a complexing and dispersing effect on iron and copper. Further experiments would be needed to study the effect of the PAA monomer (acrylic acid) on iron and copper and PAA of different molecular weights in order to study the impact of the length of the PAA chain on the complexing and dispersing effect.

Amjad [15], [16] reported that the molecular weight of PAA plays an important role in the inhibition of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ crystal growth from aqueous solution. The author tested the interaction of several PAA molecular weights between 800 and 25,000 with these crystals. PAA was found to have optimum effectiveness on calcium(II) ions at a molecular weight around 2000. As a consequence, it could be interesting to determine the minimum number of monomers of acrylic acid needed in order to observe a complexing effect on iron(II) ions at high temperature and the amount needed to have a dispersing effect on copper(II) ions at low temperature.

3.4. Chemical conditioning influence on the PAA effectiveness

Since the PAA effectiveness was showed at high temperature on iron oxide (magnetite) but not on copper, the chemical conditioning influence was conducted on magnetite only. The device, the experimental conditions and the PAA content were the same as in the previous tests. The only difference was the chemical conditioning. Indeed, instead of monoethanolamine (use of the OptiSpense PWR6600), the chosen amine volatile treatment was morpholine (use of the OptiSpense PWR6610). The results obtained for both amine volatile treatments are shown on Figure 2.

After about 20 h of test, the measured iron content stabilizes for both tests. For pH value equal to 9.2 ± 0.1 , the iron removal with PAA conditioned in ethanolamine ($5300 \pm 736 \times 10^{-6} \text{ g.kg}^{-1}$) seems to be slightly higher (about 10 %) than the one with PAA conditioned in morpholine ($4700 \pm 600 \times 10^{-6} \text{ g.kg}^{-1}$). However, given the standard deviation of the iron concentration values, the effectiveness of the two OptiSpense products are similar which means that the choice of the PAA conditioning (ethanolamine or morpholine) should have no impact on the PAA effectiveness on iron oxide.

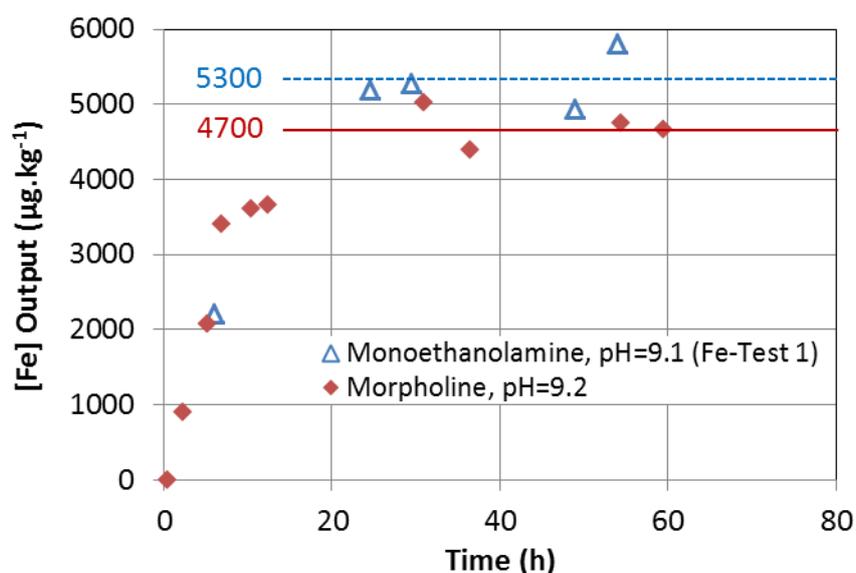


Figure 5: Evolution of iron content for the two different chemical. The samples were realized at the output of the device for a residence time equal to 20 min.

3.5. pH influence on the PAA effectiveness

In order to study a possible influence of the pH solution on the PAA effectiveness over the range from pH 9.2 to 9.6, an additional test was conducted with a morpholine conditioning at pH 9.6 (pH of secondary circuit of the nuclear power plant Golfech 2). The results obtained with the two amine volatile treatments, morpholine (*i.e.* OptiSpense PWR6610) and monoethanolamine (*i.e.* OptiSpense PWR6600) are put together in Figure 6.

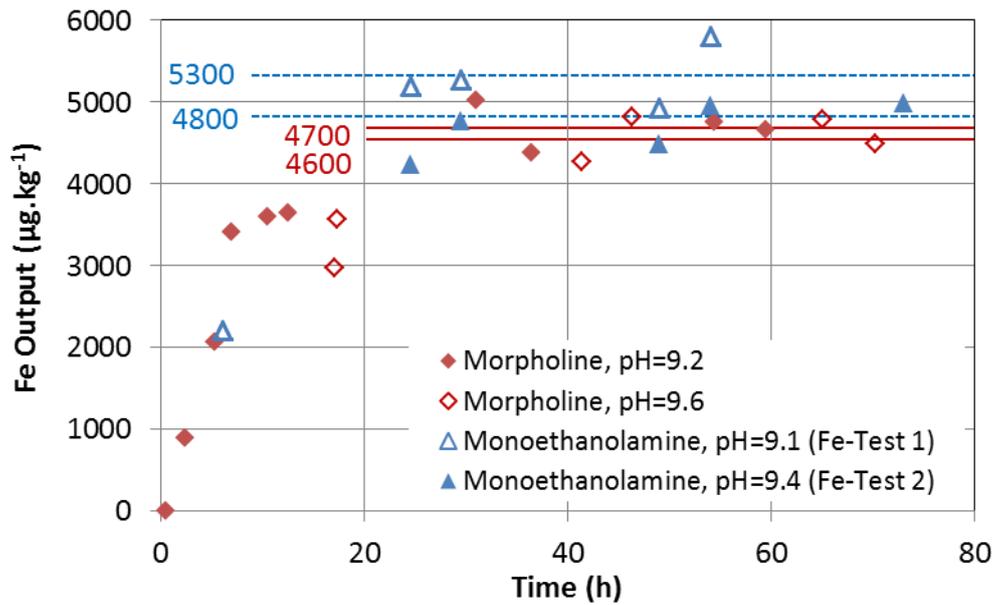


Figure 6: Evolution of iron content in the solution for the monoethanolamine and morpholine chemical conditionings. The samples were realized at the output of the device for a residence time equal to 20 min.

In one hand, when the solution is conditioned with morpholine, the mean iron content is $4700 \pm 260 \times 10^{-6} \text{ g.kg}^{-1}$ for the pH 9.2 and $4600 \pm 260 \times 10^{-6} \text{ g.kg}^{-1}$ for the pH 9.6. Given the standard deviation of the iron content for each test, we can conclude that the PAA effect on iron oxide is similar for both pH. In the other hand, for the ethanolamine conditioning, the observed iron content difference of 10 % between pH 9.1 and pH 9.4 is only due to the dispersion of the results (see Table 1).

In an EPRI study [17], it is shown that the solution pH does not affect the effectiveness of PAA (OptiSpere PWR6600) over the range from pH 9.3 to 10.5 during steam generator wet layup. Therefore, a pH increase up to 10.5 at higher temperature, such as 275 °C, should be possible without modifying the PAA effect.

4. Conclusion

The interaction of a high molecular weight PAA with iron oxide and metallic copper was studied through a number of tests in simulated nominal operating conditions of SG.

At 275 °C, the presence of PAA leads to an iron concentration by two up to three orders of magnitude higher than the magnetite solubility. The dispersing and/or complexing PAA effect on iron oxides was then demonstrated.

As a result of these experiments, the chemical conditioning influence (ethanolamine or morpholine) and the solution pH influence on the PAA effectiveness have been studied. It has been showed that changing the amine volatile treatment or modifying pH over the range from 9.2 to 9.6 seems to not affect the PAA effectiveness on iron oxide.

Then, the discussion on the PAA action mechanism on iron oxide leads to think that magnetite, in the particulate form or in the deposit form, is complexed at high temperature. The nature of the conducted tests and the operating principal of the experimental device, do not allow to conclude on the dispersant effect of PAA. Concerning copper, at low temperature, PAA seems to have a dispersing action on metallic copper that disappears at high temperature.

Finally, no effect of the main PAA degradation products (acetic and formic acids) is observed on copper at room temperature and on iron at high temperature. This conclusion seems to show that only PAA present in the commercial products has an impact on magnetite. For a residence time equals to 20 min, 50 % of PAA are degraded at 275 °C **Erreur ! Source du renvoi introuvable.**, so it seems important to take into account the initial molecular weight of the used PAA and the residence time of the solution to determine the appropriate PAA concentration to inject in the feedwater.

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