Corrosion of SA 508 in High Temperature and Pressure Water Containing Silicon Compounds

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Steam generators are crucial components of pressurized water reactors. The failure of the steam generator as a result of components degradation by corrosion has been a major cause of Pressurized Water Reactor (PWR) plant unavailability. Steam generator problems have caused major economic losses in terms of lost electricity production through forced unit out ages and, in cases of extreme damage, as additional direct cost for large-scale repair or replacement of steam generators. Steam generator tubes and tubesheet are susceptible to failure by a variety of mechanisms, the most majority of which are related to corrosion. The feedwater that enters the steam generators under normal operating conditions is extremely pure, but nevertheless contains low levels (generally in the µg/L concentration range) of impurities such as iron, chloride, sulphate, silicate, etc. When water is converted to steam and exits the steam generator, the non-volatile impurities are left behind. As a result, the concentration of the bulk steam generator water is considerably higher than that in the feedwater. When the silicon compounds concentration is higher the localized corrosion appears and can have a catastrophic result consisting in the loss of components integrity and the development of a large quantity of soluble corrosion products and deposits. For low concentration the effect of the silicon compounds on the behaviour of steam generator materials has never been considered adequately. The information available is contradictory, and it is possible to encounter in the literature old results that indicate an inhibition or an aggressive effect of silicon compounds in caustic environment. The purpose of this paper consists in assessment of localized corrosion behaviour of the tubesheet material (carbon steel SA 508 cl.2) at the normal secondary circuit parameters (temperature = 260^0C, pressure = 5.1MPa). The testing environment was the demineralized water containing different silicon compounds, such as silica (SiO_2) and sodium metasilicate (Na_2SiO_3) used separately or together, at pH=9.5 regulated with morpholine and ciclohexilamine (all volatile treatment – AVT). The paper presents the results of metallographic and X - ray diffraction examinations as well as the results of electrochemical measurements.

Keywords: steam generators, feedwater, silicon compounds, demineralized water, morpholine, ciclohexilamine

Silicon compounds are abundant both in the steam generator tube deposits removed from operating plants and in the hideout return analyses performed during plant operation. Despite abundance, the effect of these compounds on the susceptibility to different types of corrosion has not been established clearly by laboratory tests or under operating conditions. Cooling water contains dissolved silicon compounds which have the possibility to form deposits on the tubes surfaces. By evaporation, the quantity of hard deposits increases. The main consequences of deposits generation consist of the increase of pressure, obstruction of the flow holes and a significant decrease of heat transfer. The decrease of silicon compounds deposition rate will result in the life extension of different steam generator components and the mitigation of the costs related to chemical cleaning.

In the case of a low fluid flow rate or of the change of flow direction, it generates the deposits containing silicon compounds.

The effect of the silicon compounds on the behaviour of steam generator tubesheet material has never been considered adequately. The information available is contradictory, and it is possible to encounter in the literature old results that indicate an inhibition or an aggressive effect of silicon compounds in caustic environment. Lack of understanding of the role played by silicon compounds may be caused by the complexity of their chemistry which complicates laboratory tests and interpretation of the analyses of the deposits. High concentration of SiO_2 in the crevices may react with the impurities forming different polymerized species of silicates that show retrograde solubility at the operating temperature of steam generator, which, in turn, precipitate, leaving free SiO_2 and/or impurities in the solution. The present work studies the effect of different silicon compounds, such as silica (SiO_2) and sodium metasilicate (Na_2SiO_3) used separately or together on the corrosion susceptibility of steam generator tubing.

The inhibition effect of silicon compounds was shown in the corrosion tests. Under all corrosion tests conditions, the material of the steam generator tubing (SA 508) demonstrates a great corrosion resistance when compared to its behaviour in other impurities (NaCl, Na_2SO_4). The information obtained from this work was not sufficient to appreciate if the corrosion behaviour observed in the solutions containing silicon compounds was caused by the incorporation of silicon in the oxide layer, making the latter more protective or simply that it had a barrier effect preventing the contact between the solution and the surface of the material. Moreover, it is important to consider the possible effect of silicon compounds on the *p*H of the solutions, [1-5].

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Experimental part

Corrosion experiments included in the present paper have been carried out by autoclaving at specific parameters for the secondary circuit of the CANDU steam generator: temperature - 260°C, pressure - 5.1MPa. The as-received samples, preoxidized for 10 days or preoxidized for 150 days were from the SA 508 steam generator tubesheet material which was sectioned into 20 . 15 . 2 mm pieces. The testing solutions, with *p*H 9.5 had the next composition: 1g/LSiO_2, 10g/LSiO_2, 1g/L Na_2SiO_3; 10g/L Na_2SiO_3; and 1g/LSiO_2 + 1g/L Na_2SiO_3 (table 1).

Table 1

TYPES OF SA508 SAMPLES AND TESTING SOLUTIONS

No.	History	Testing solution
1	as received	1g/l SiO_2
2	preoxidized 10 days	1g/l SiO_2
3	preoxidized 150 days	1g/l SiO_2
4	as received	10g/l SiO_2
5	preoxidized 10 days	10g/l SiO_2
6	preoxidized 150 days	10g/l SiO_2
7	as received	1g/l Na_2SiO_3
8	preoxidized 10 days	1g/l Na_2SiO_3
9	preoxidized 150 days	1g/l Na_2SiO_3
10	as received	10g/l Na_2SiO_3
11	preoxidized 10 days	10g/l Na_2SiO_3
12	preoxidized 150 days	10g/l Na_2SiO_3
13	as received	1g/l SiO_3 + 1g/l Na_2SiO_3
14	preoxidized 10 days	1g/l SiO_3 + 1g/l Na_2SiO_3
15	preoxidized 150 days	1g/l SiO_3 + 1g/l Na_2SiO_3

The testing period was 432 h for every condition, at the specific parameters for the steam generator secondary circuit: temperature 260°C and pressure 5.1MPa. The post-testing examination has been done by metallographic analyses, electrochemical measurements (potentiodynamic and impedance), electronic microscopy and X-ray diffraction, [6] ÷ [12].

Results and discussion

SA 508 tested in 1g/L SiO_2 solution

For the samples as received, the aspect of the surface is influenced by the presence of the SiO_2 in the solution, the thickness of the layer being between 3.0μm ÷ 3.5μm and the aspect of the superficial layer shows the deviation from the normal conditions of the CANDU steam generator secondary circuit operation due to the presence of the impurity (SiO_2) in excess in comparison with the normal values (1ppm).

At the preoxidized samples for 10 days we can observe the presence of a layer with a fine and uniform granulation, the initial presence of the oxide having a great contribution in the achievement of the uniform film. The thickness of the continuous and uniform superficial layer is between 3.0μm ÷ 3.8μm.

The testing environment for the electrochemical measurements was demineralized water with *p*H=9.5 (All Volatile Treatment), 25°C.

Comparing the potentiodynamic curves for SA 508 samples as received, preoxidized 10 days and preoxidized 150 days, in the case of the sample preoxidized 150 days the value of the current density is less than others and the electrochemical potential tends to more positive values. That means a great corrosion resistance for the sample which has an initial layer of oxides consisting principally in magnetite and/or nickel and chromium oxides.

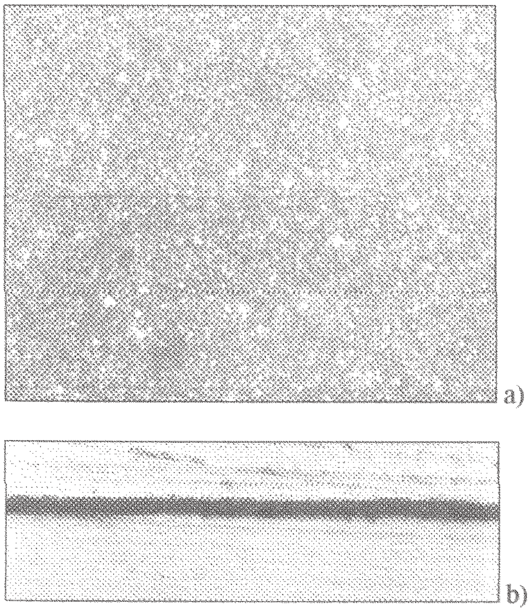


Fig.1 Surface morphology (x200) (a) and aspect of the superficial layer (x1000) (b) for SA508 preoxidized 150 days, tested in 1g/l SiO_2

Significant results concerning the inhibition properties of SiO_2 were obtained while comparing a sample preoxidized 10 days with a sample preoxidized 10 days and then tested in 1g/l SiO_2 solution. For the second sample the values of the electrochemical potential are higher than for the first one and the current density value is lower. It is possible that the presence of SiO_2 in the solution will determine the inhibition of corrosion process and this fact is evident on the samples initially covered with a magnetite layer.

A sample preoxidized for 150 days and then tested in 1g/l SiO_2 solution is more susceptible to corrosion as compared to a sample preoxidized for 150 days. In this case the SiO_2 from the testing solution cannot inhibit the corrosion due to the properties of the layer formed after 150 days. If this layer, by its structure, allows the access of the solution in the vicinity of metallic surface, the attack becomes inherent.

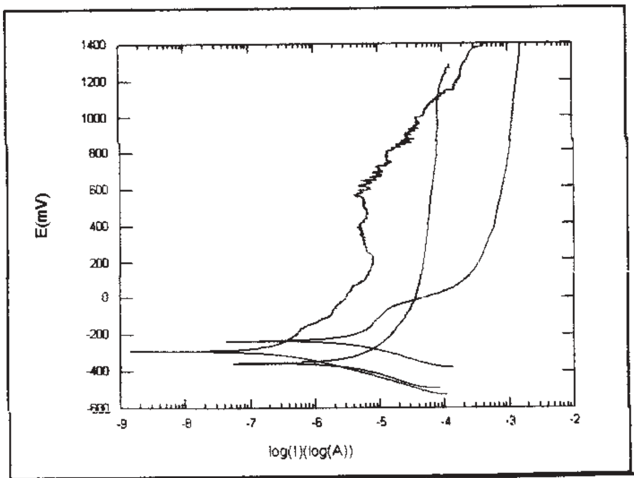
When comparing three samples tested in a solution of the same concentration (1g/lSiO_2) but with a different initial status (as-received, preoxidized for 10 days, preoxidized for 150 days), the sample preoxidized for 150 days has the best corrosion behavior demonstrated by the values of current density (fig. 2).

Figure 3 and figure.4 show the results of electrochemical measurements which give the possibility to characterize the superficial layers formed on the SA 508 samples.

SA 508 tested in 10g/l SiO_2 solution

For the as-received sample, the surface is altered as compared to a sample exposed in demineralized water without SiO_2. The superficial layer shows discontinuities and, sometimes, it is absent. The average thickness of the superficial layer has values in the range 8.0÷10.0μm. For the sample preoxidized for 10 days the surface morphology shows a fine granulation and the superficial layer is uniform, continuous and adherent. The properties of the layer obtained during preoxidation determine the corrosion behaviour in the presence of SiO_2. The film formed is unstable and initially it ensure, for the solution with SiO_2, the possibility to attaint the metallic surface and, in this way, the properties of the layer are held sometimes at appreciable values, 9.0÷12.0μm.

Figure 5 shows the surface morphology and the aspect of the superficial layer for SA 508 preoxidized for 150 days,



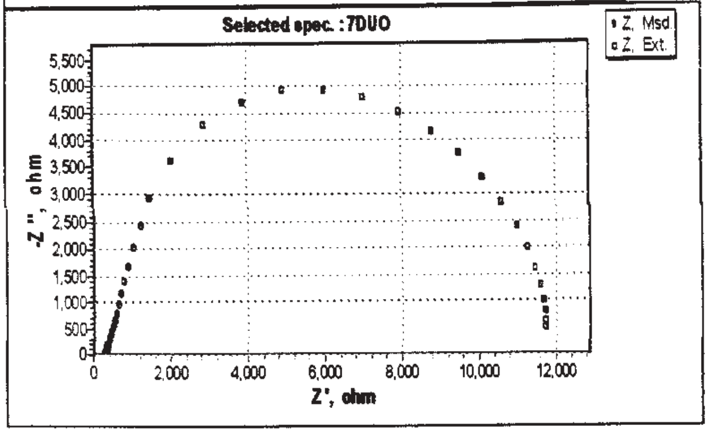
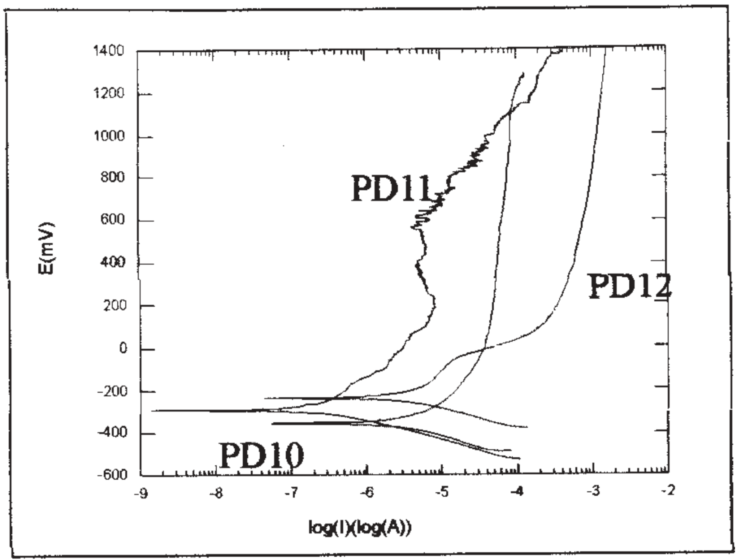


Fig. 2 Potentiodynamic curves for SA508 in demineralized water *p*H=9,5 (AVT): PD10 – as received, tested in 1g/L SiO_2; PD11 - preoxidized 10 days, tested in 1g/L SiO_2; PD12 – preoxidized 150 days, tested in 1g/L SiO_2



tested in 10g/L SiO_2, the thickness of the film being 6.0 ÷ 16.0μm.

If two as-received samples of SA 508 are tested in 1g/L SiO_2 and 10 g/L SiO_2, respectively, the latter has a bad corrosion behaviour. The solution containing 10g/L SiO_2 displays a higher aggressiveness on the base material and the protective characteristics exist only for a concentration below 10g/L SiO_2. The exact limit of concentration which can play the role of an inhibitor for the SA 508 may be established after further experimental research. The corrosion rate decreases for the samples tested in 10g/L SiO_2 solution: preoxidized for 150 days, preoxidized for 10 days and as-received, respectively (fig. 6).

The increase of SiO_2 contained in the testing solution determines the increase of the corrosion rate for the samples with the same initial status.

Figure 7 shows the Nyquist curve and Fig.8 shows Bode and angle curves for SA 508, preoxidized 10 days, tested in 10g/L SiO_2. For a sample preoxidized 10 days and then tested in a solution containing 10g/L SiO_2, the polarization resistance has the same value with that of a sample tested in a solution containing 1g/L SiO_2, but the value of the angle phase is lower, the layer is porous and has a capacitive behaviour.

Potentiodynamic curves for SA 508 in demineralized water *p*H = 9,5 (AVT) for a sample preoxidized for 10 days and a samle preoxidized for 10 days, tested in 10g/L SiO_2,

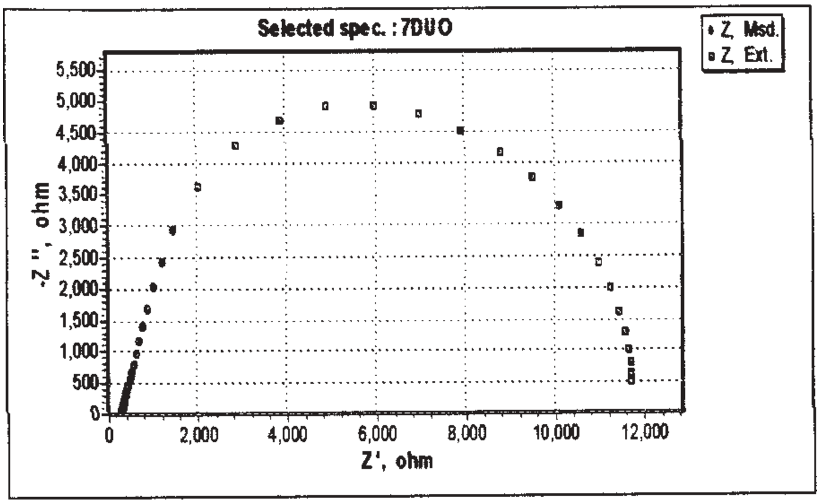


Fig. 3. Nyquist curve for SA 508, preoxidized 10 days, tested in 1 g / L SiO_2

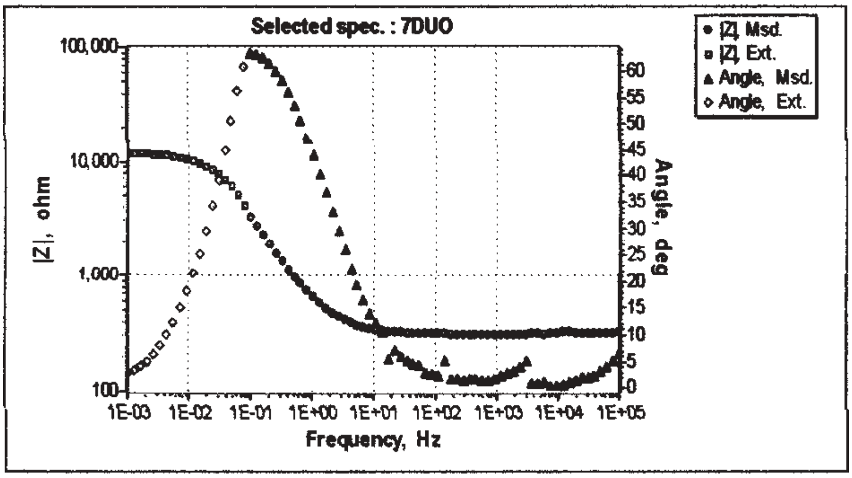


Fig. 4. Bode and phase angle curves for SA 508, preoxidized 10 days, tested in 1g/L SiO_2

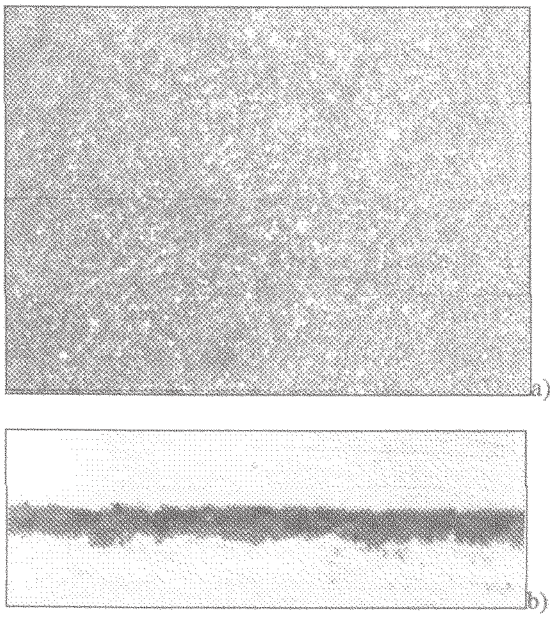


Fig.5 Surface morphology (x200) (a) and aspect of the superficial layer (x1000) (b) for SA 508 preoxidized 150 days, tested in 10g/L $LSiO_2$

(fig. 9) show again the aggressivity of the solution which contains SiO_2.

The analysis achieved by electronic microscopy on the SA 508 sample preoxidized for 150 days and then tested in solution containing 10g/L SiO_2, shows the presence of the dendrites (fig. 10). The elements maps show the qualitative presence of the elements on the surfaces of the samples. The silicon compounds are present on the surfaces samples.

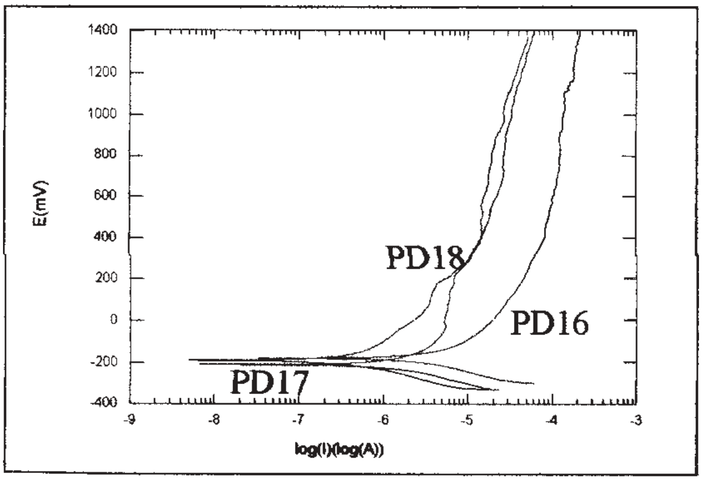


Fig. 6 Potentiodynamic curves for SA 508 in demineralized water pH=9,5 (AVT): PD16 – as received, tested in 10g/L SiO_2; PD17 - preoxidized 10 days, tested in 10g/L SiO_2; PD18 – preoxidized 150 days, tested in 10g/L SiO_2

SA 508 tested in 1g/L Na_2SiO_3 solution

The as-received samples have a 1.5÷2.0μm thickness layer and the superficial film is discontinuous. The sample preoxidized for 10 days has a surface irregular aspect, with great discontinuities and an average thickness of the oxide layer of 1.5-2.5μm. Between the aspect of surface and superficial layer for the samples having the same history of testing there is a similarity when they are tested in solutions containing SiO_2 or Na_2SiO_3. The samples preoxidized for 150 days have a fine granulation on the surface, the oxide layer is uniform and continuous while the thickness mean value is approximately 3.0μm.

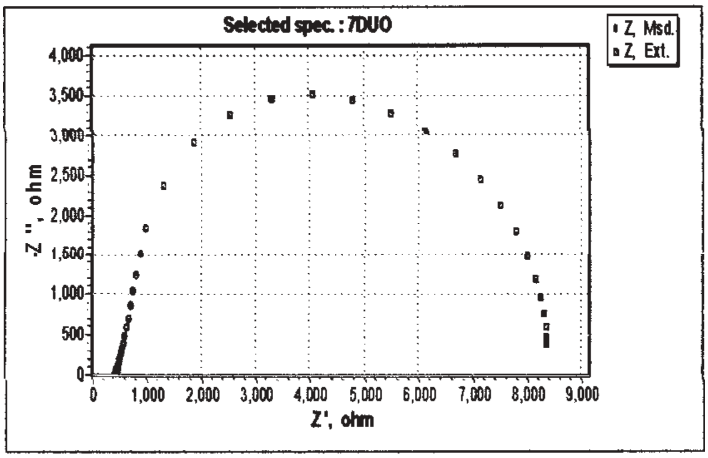


Fig. 7 Nyquist curve for SA 508, preoxidized 10 days, tested in 10g/L SiO_2

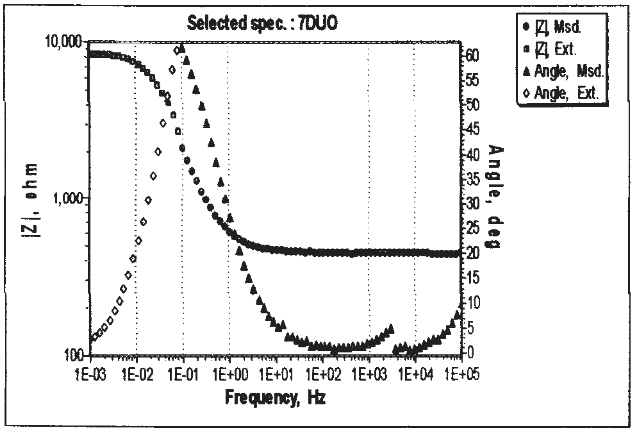


Fig.8 Bode and phase angle curves for SA 508, preoxidized 10 days, tested in 10g/L SiO_2

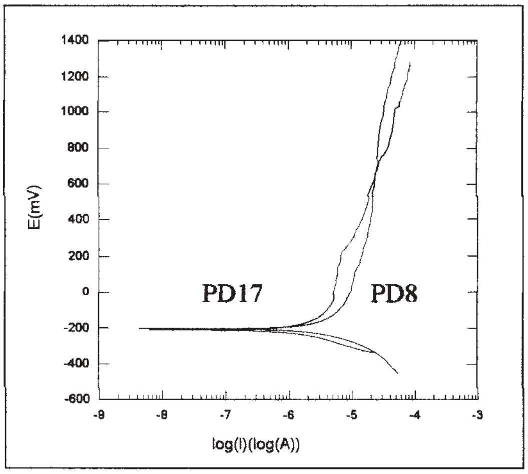
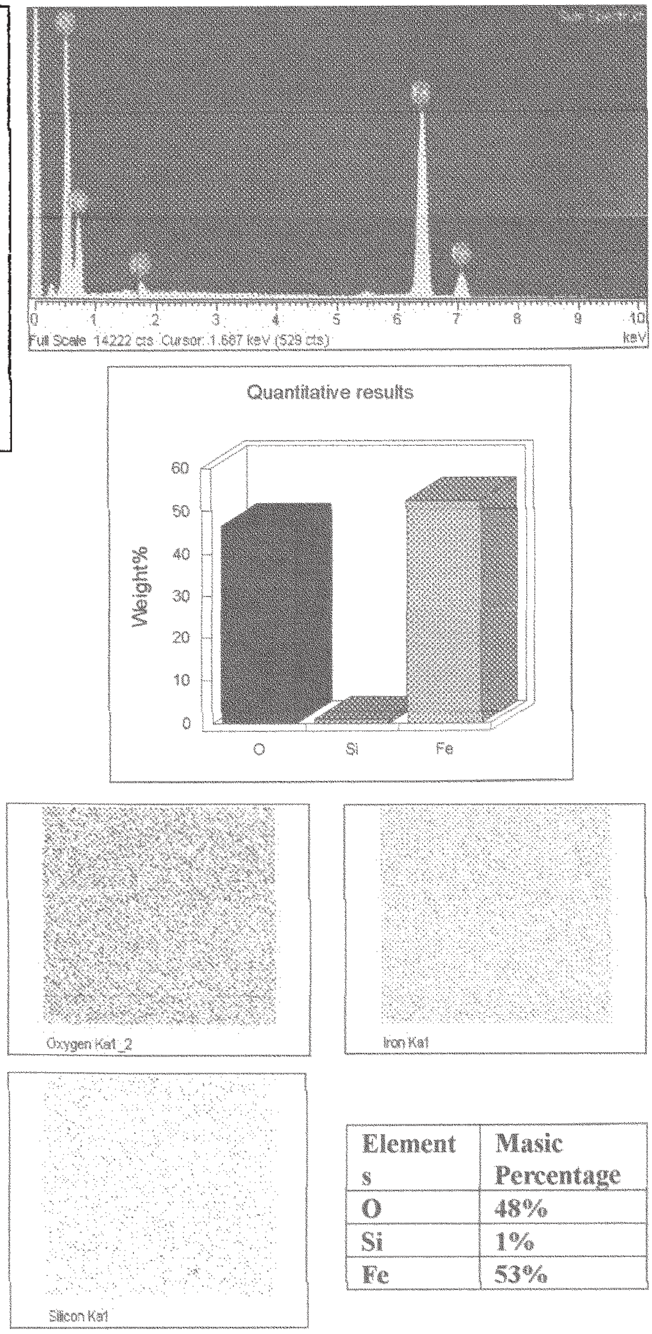


Fig. 9 Potentiodynamic curves for SA 508 in demineralized water *p*H=9,5 (AVT): PD8 – preoxidized 10 days; PD17 - preoxidized 10 days, tested in 10g/L SiO_2

The solution containing 1g/L Na_2SiO_3 has not an aggressive action on the SA 508 as-received sample. The current densities and electrochemical potential values confirm this hypothesis. The samples tested in 1g/L Na_2SiO_3 preoxidized for 150 days have a great corrosion resistance.

SA 508 tested in 10g/L Na_2SiO_3 solution

For the as-received sample the superficial film with a 2.0µm thickness is continuous, uniform and adherent. The oxide layer thickness and heights of deposits on the surface has 21.0µm values for a sample preoxidized 10 days.



Elements	Masic Percentage
O	48%
Si	1%
Fe	53%

Fig.10 EDX spectrum and quantitative composition of the layer formed on the SA 508 surface sample preoxidized 150 days and tested in 10g/L SiO

The sample preoxidized for 150 days shows an oxide layer having a 15.0÷22.0µm thickness (fig. 13).

A sample preoxidized for 150 days and then tested in 10 g/L Na_2SiO_3 has a good corrosion behaviour consisting of low values for the current density by comparison with the as- received samples and preoxidized for 10 days and then tested in solutions of the same concentration (fig. 14).

Figure 15 and figure 16 display the results of electrochemical measurements.

SA 508 tested in 1g/L SiO_2 +1g/L Na_2SiO_3 solution

The oxide layer for the as-received sample is uniform, continuous and adherent. The thickness value varies between 0.2 µm and 0.3 µm. For the sample preoxidized for 10 days, the general aspect of the film is discontinuity. In the case of the silicon compounds presence the film has 1 µm thickness value.

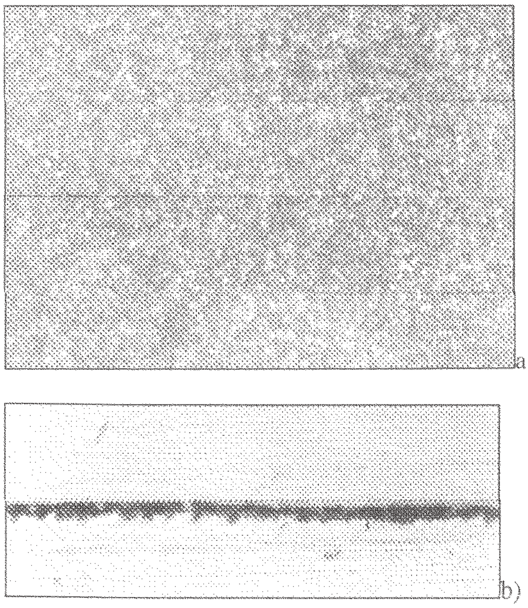


Fig.11. Surface morphology (x200) (a) and aspect of the superficial layer (x1000) (b) for SA 508 preoxidized 150 days, tested in 1g/L Na_2SiO_3

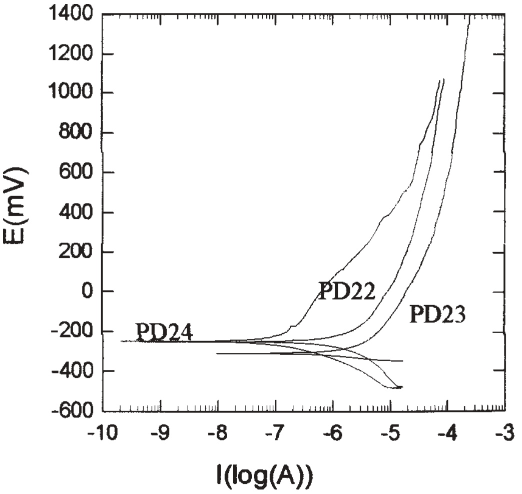


Fig. 12 Potentiodynamic curves for SA 508 in demineralized water *p*H=9,5 (AVT): PD22 – as received, tested in 1g/L Na_2SiO_3; PD23 - preoxidized 10 days, tested in 1g/L Na_2SiO_3; PD24 – preoxidized 150 days, tested in 1g/L Na_2SiO_3

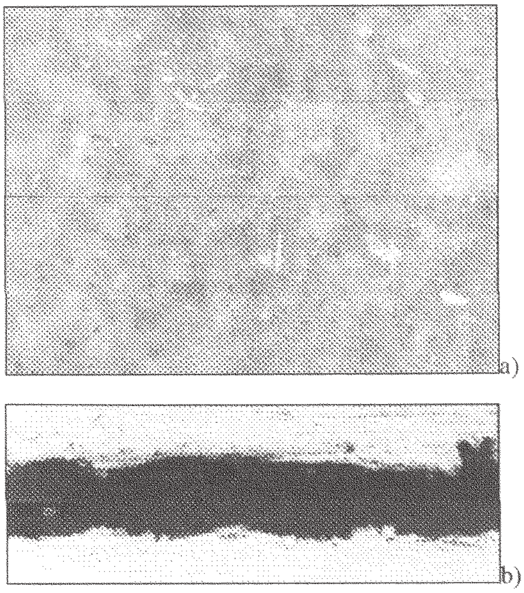


Fig.13. Surface morphology (x200) (a) and aspect of the superficial layer (x1000) (b) for SA 508 preoxidized 150 days, tested in 10g/L Na_2SiO_3

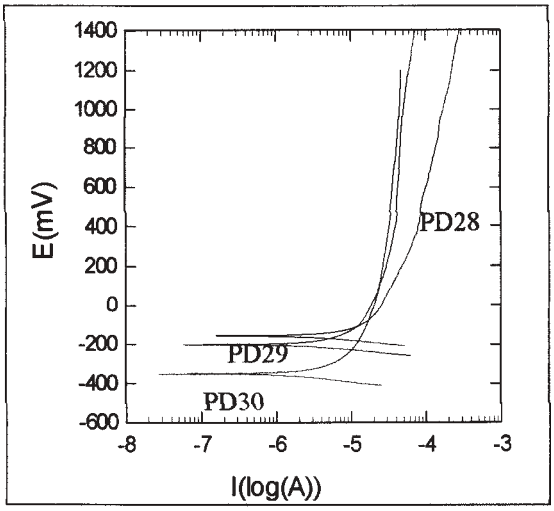


Fig.14 Potentiodynamic curves for SA 508 in demineralized water *p*H=9,5 (AVT): PD28 – as received, tested in 10g/L Na_2SiO_3; PD29 – preoxidized 10 days, tested in 10g/L Na_2SiO_3; PD30 – preoxidized 150 days, tested in 10g/L Na_2SiO_3

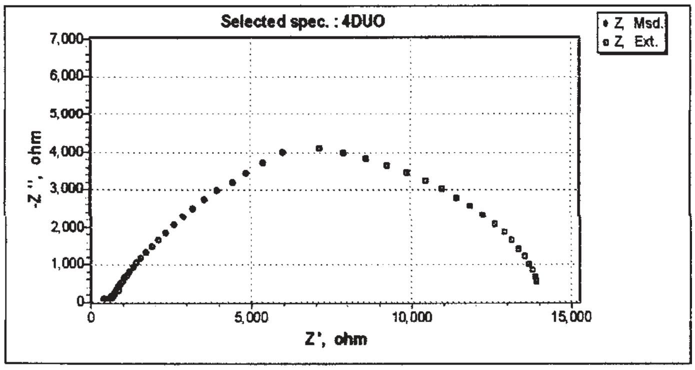


Fig.15 Nyquist curve for SA 508, preoxidized 150 days, tested in 10g/L Na_2SiO_3

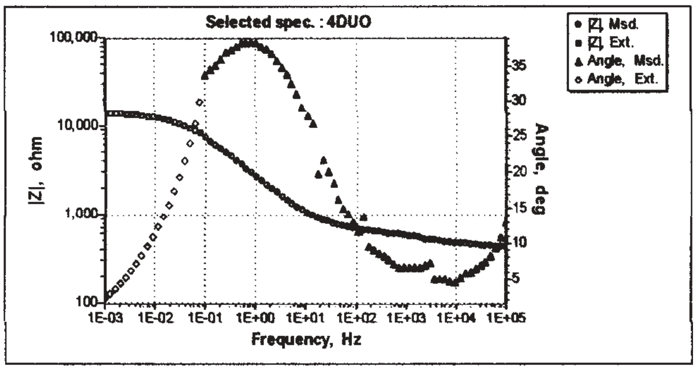


Fig.16 Bode and phase angle curves for SA 508, preoxidized 150 days, tested in 10g/L Na_2SiO_3

For the sample preoxidized for 150 days the film having 1.5÷2.0 µm thickness is uniform, continuous and adherent.

The SA 508 as-received samples tested in a solution containing 1g/L SiO_2+1g/L Na_2SiO_3 have a surface morphology modified comparatively to the samples preoxidated and then exposed in the same conditions. The surface morphology is the same with the surfaces of samples tested separately in 1 g/L SiO_2 or 1g/L Na_2SiO_3. The aspect of the superficial layer having thickness values between 1.5 µm and 2.0 µm is continuous, uniform and adherent.

The SA 508 samples preoxidized for 10 days, tested in 1g/L SiO_2+1g/L Na_2SiO_3, have an irregular aspect with discontinuities and the superficial film has 2.5µm thickness.

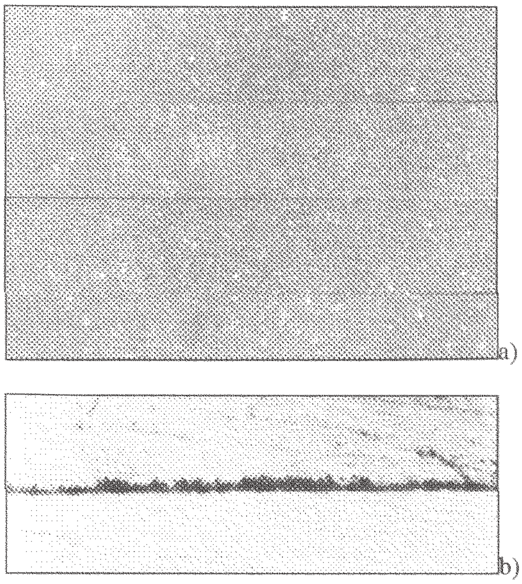
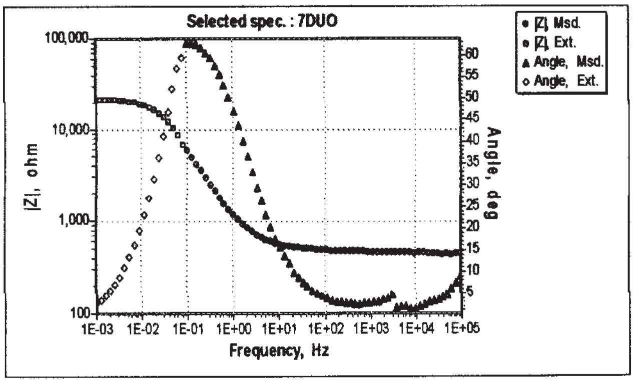


Fig.17 Surface morphology (x200) (a) and aspect of the superficial layer (x1000) (b) for SA 508 preoxidized 10 days, tested in 1g/L SiO_2 +1g/L Na_2SiO_3



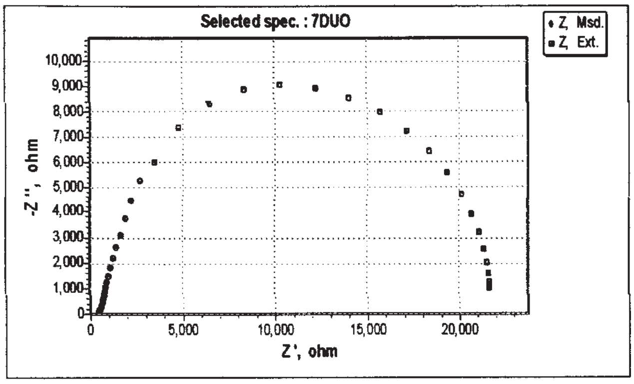


Fig.18 Nyquist curve for SA 508, preoxidized 150 days, tested in 1g/lLSiO_2 + 1g/L Na_2SiO_3

The film keeps the continuity, but the surface morphology shows the discontinuity of the thickness consisting in isolated deposits showing, in some areas, a considerable thickness.

The SA 508 samples preoxidized for 150 days, tested in a solution containing 1g/L SiO_2+1g/L Na_2SiO_3, have an uniform aspect of the surfaces and the superficial layers are uniform, continuous and have less than 1.5µm and 2.5µm thickness, (fig. 17).

The film formed during preoxidation does not allow the access of the testing solution in the immediate vicinity of the metallic surface and, thus, the layer maintains the continuity and uniformity at the end of autoclaving tests.

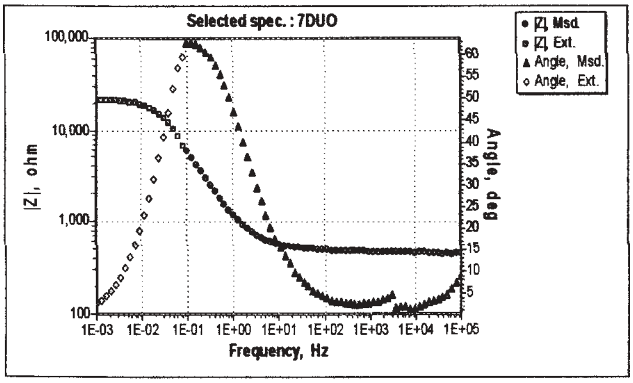


Fig.19 Bode and angle phase curves for SA 508, preoxidized 150 days, tested in 1g/L SiO_2 + 1g/l Na_2SiO_3

Table 2

CORROSION BEHAVIOUR OF SA 508 IN SOLUTION WITH SILICON COMPOUNDS

test samples	1g/l SiO_2	10g/l SiO_2	1g/l Na_2SiO_3	10g/l Na_2SiO_3	1g/l SiO_2 + 1g/l Na_2SiO_3
as received	+	+	+	+	+
preox. 10 days	++	+	++	+	++
preox. 150 days	+++	+++	++	+++	++

The simultaneous presence of SiO_2 and Na_2SiO_3 in the testing solution accelerates the corrosion process of the SA 508 samples, no matter which their initial status was.

The impedance method allows the supplementary characterization of superficial layers formed on the SA 508 samples tested in a solution containing silicon compounds.

Figure 18 shows the Nyquist curve while figure 19 shows Bode and angle phase curves for SA 508, preoxidized for 150 days, tested in 1g/L SiO_2 + 1g/L Na_2SiO_3.

Table 2 shows the corrosion behavior of SA 508 in a solution with silicon compounds, where: (+) – bad corrosion behavior, (+ +) – good corrosion behavior and (+ + +) – very good corrosion behavior.

Conclusions

In the case of SA 508 testing in a solution containing SiO_2 and Na_2SiO_3 the thickness of the superficial layers increase likewise with the increases of the silicon compounds concentration and these have values ranging between 3.0÷ 22.0 µm.

If SA 508 samples are briefly exposed in a solution of 10 g/L SiO_2 and 10 g/L Na_2SiO_3, the surface morphology is predominantly irregular and the silicon compounds deposition occurs.

In the case mentioned above the corrosion is initiated, the oxides films have discontinuities and the corrosion intensity increases with the increase of silicon compounds concentration.

In all cases the operation history consisting of the preoxidation time of the samples has a significant influence, a lower corrosion rates having the samples preoxidized for 150 days.

The corrosion susceptibility and the initiation of pitting are in a close relationship with SiO_2 and Na_2SiO_3 concentration. Generally, the increase of silicon compounds concentration in the testing environment leads to the increase of corrosion rates.

The concomitant presence of the two silicon compounds (SiO_2 and Na_2SiO_3) in the solution has a synergetic effect, the values of corrosion rates being greater than in the case of the presence of only one compound in the testing solution.

The silicon compounds concentration must be monitored with great attention and maintained strictly less than 1ppm in the steam generator secondary circuit.

At higher concentrations the hard deposits are formed and the consequences consist of the blockage of the flow holes, local superheating and an intense pitting corrosion in the case of long time exposition in the contaminated environment.

This paper shows only the influence of the silicon compounds on the SA 508 material but it is very important to investigate the effect of the simultaneously presence of more impurities because it is possible that a synergetic effect will take place.

If the chemical parameters of the cooling water on the secondary side of the steam generator are kept at the imposed values, then corrosion is not a problem for the SA 508 tubing but the corrosion, especially localized corrosion, appears in the case of the presence of impurities and this process has a great contribution to the ageing management of the steam generator as a key component of a nuclear power plant.

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