



Corrosion inhibition of the 316L stainless steel in sodium hypochlorite media by sodium silicate

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Abstract

The present work relates to the use of silicates as corrosion inhibitor¹ of the stainless steel 316L bleaching process by the hypochlorite of sodium. The aggressiveness of alkaline solutions toward metals is essentially due to the instability of passive films which very often protect the metal of the surrounding environment. Silicates act as an inhibitor of the localized corrosion of 316L stainless steel in bleaching process. They form a film which remains stable even in high potential, by moving the pitting potential towards more noble values. The alkalinity nature of silicates was determining in their choice as inhibitor, their addition does not modify the pH. The Inhibition by silicates depends on their concentrations, immersion time, hydrodynamics conditions and surface corrosion state.

Keywords: Corrosion, Bleaching, Steel, Silicates and Inhibition.

Introduction

The purpose of the bleaching, in the textile industry is to eliminate, among the impurities of the cotton those presence of which would not allow the goods to present required qualities. Bleaching is one of the stages in the manufacture of textiles to obtain a white perfect final product, the processes of bleaching are very varied and require the use of oxidizing chemicals. These bleaching process are aggressive, with complex composition, they contain various oxidizing agents.

Our work is a logical result of our previous published works [1-4] which allowed bringing a contribution to the knowledge of the electrochemical behavior of 316L stainless steel in the bleaching process. In this article we bring solutions of these problems of corrosion by inhibitors silicates.

The complexity of bleaching process, the strong oxidizing power, strongly limited the range choice of the inhibitor, because this one must not have a reaction with the bleaching environment, a lot of inhibitors that we tried, had a more or less important ability to react our bleaching solutions, what changed completely their properties.

We opted in this work for the choice of the silicates which are little expensive, ecological inhibitors (recommended by the American agency of environmental protection EPA), not toxic, and even facilitate bleaching in hydrogen peroxides [5]. Word "Silicates" is a generic term [6] which indicates compound containing the silicon, the oxygen and one or two metals. They exist under natural or synthetic shape (obtained by fusion of silica sand extreme reactionary pure and washing sodas or potassium in the temperature 1000-1500°C to obtain an amorphous glass which one can dissolve in the water and obtain solutions of silicates).

Silicates are classified [7] as inhibitors, in aqueous solutions, silicates [8] form colloidal particles; these particles migrate to anodic sites and form, from the corrosion products, a monomolecular thin film.

The film covers the entire metal surface, but its porosity does not completely stop the oxygen diffusion.

2. Materials and methods

2.1. Materials.

Our study will concern the 316L Stainless steels used in the bleaching installations, the chemical composition is represented in the table 1

Table 1: Chemical Composition of the 316L stainless steel

C	Si	Mn	P	S	Cr	Ni	Mo
0.02	0.71	1.35	0.02	0.02	17.90	12.20	2.30

Solutions are prepared by respecting concentrations used in the bleaching process as shown in table 2.

Table 2: Chemical composition and pH of sodium hypochlorite solutions

Chemical Composition	pH	[Cl ⁻] ppm
ClONa	10.80	785
ClONa + 0.5g NaOH / litr	12.50	650
ClONa + 1.0g NaOH / litr	13.25	500

The surface preparation, condition of the working electrode, is following the same protocol for all tests, namely a polishing on emery paper followed by washing with distilled water and alcohol, and then drying in hot air. The rotation speed of working electrode can vary from 0 to 5000tr.mn⁻¹. The use of such system has the advantage of producing a constant and homogenous agitation in the vicinity of the working electrode and therefore offers the possibility of studying the behavior of the electrode in defined hydrodynamic conditions; the main interest is to allow the study of diffusion phenomena that can partially or completely control the corrosion process.

The electrochemical experiments were conducted in traditional three electrodes system, in which, the working electrode is the 316L stainless steel, the counter electrode was a platinum wire, and the reference electrode was a saturated silver chloride electrode Ag/AgCl at 25 °C, the difference in potential of such electrode with respect to the normal hydrogen electrode (NHE) is of the order of 0.22 V.

For the Electrochemical impedance spectroscopy measurement, the frequency range was 10 mHz to 100 kHz and the amplitude of the sinusoidal voltage signal was 10 mV. Polarization curves were recorded with a scan rate of 1 mV/s.

3. Results and discussion

3.1. Gravimetric measurements

The inhibition efficiency is defined by the following expression:

$$E(\%) = \frac{i_{\text{ocorr}} - i_{\text{corr}}}{i_{\text{ocorr}}} \times 100 \quad (1)$$

Table 3: inhibition efficiency depending on the inhibitor concentration at the pH 10.80 for sodium hypochlorite solution

Silicate concentrations [mol/L]	E ₁	E ₂
0		
10 ⁻⁴	44	51
10 ⁻³	69	79
10 ⁻²	96	90

Figure 1 and Table 1 presents variation of inhibition efficiency of 316L stainless steel upon using different inhibitors' concentrations. Aggressiveness of alkaline solutions is primarily due to instability in these environments, weakness protection films that often protect the metal from the surrounding environment. A major difficulty in finding an inhibitor is the fact that in basic media, the corrosion process takes place at low potential, an area where most of the organic compounds are removed from the double layer [9]. The basic nature of silicates was decisive in their choice as an inhibitor, adding them to the bath laundering by sodium hypochlorite does not change the basic pH of the solution. The weight loss experiments for 316L Stainless steel in the test solutions without and with the concentrations of silicates confirm that the presence of inhibitors decreases the corrosion rate and increases corrosion resistance see Figure 1.

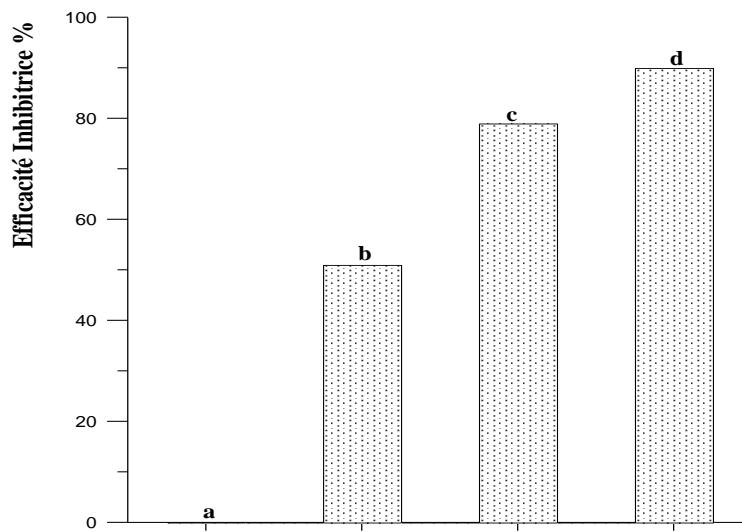


Figure 1: Inhibitive efficiencies of silicates in sodium hypochlorite a: 0 M, b: 10^{-4} M, c: 10^{-3} M, d: 10^{-2} M

3.1 stationary electrochemical techniques

3.1.1.Cathodic curves

The cathodic behavior of the 316L steel in presence and in absence of various silicates concentrations is represented in the figure 2. These curves are drawn after a preliminary stabilization 30minutes at free corrosion potential. A first analysis of the obtained curves shows a light movement of the corrosion potential towards positive values. This movement is more marked in the cases of concentrations 10^{-3} mol/l and 10^{-2} mol/l. The cathodic current decreases in the presence of silicates. The Efficiency of inhibition grows with the increase of the inhibitor concentration. This behavior can be attributed to the increase of the surface covered with the silica molecules.

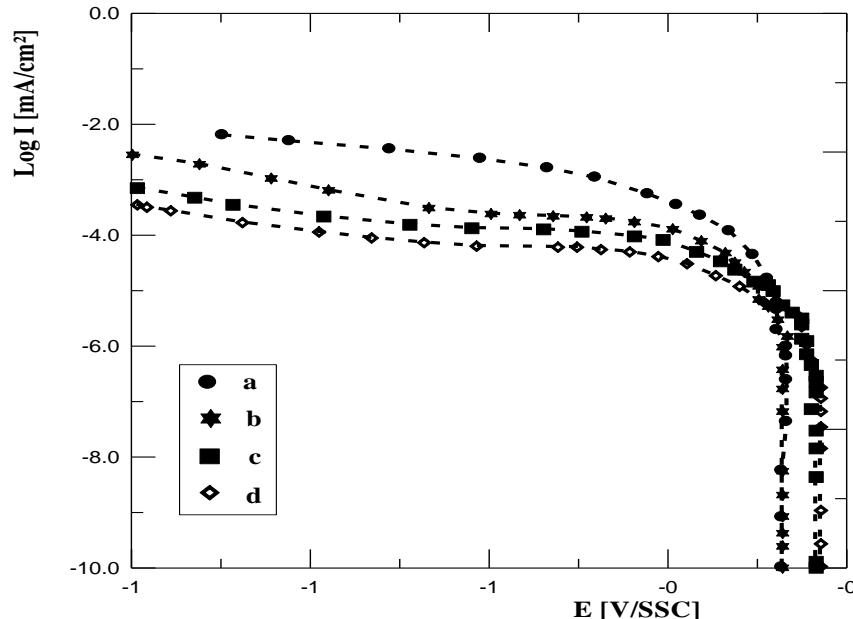


Figure 2: The concentration influence in silicate on the cathodic Curves in the sodium hypochlorite baths pH 10.80 a 0 M, b 10^{-4} M, c 10^{-3} M, d 10^{-2} M.

3.2. Anodic curves.

To study the silicates inhibition towards corrosion of the steel 316L in the sodium hypochlorite solution, we drew the polarization curves of the metal in the solution at pH: 10.80 with silicates concentrations of 10^{-4} , 10^{-3} , and 10^{-2} mol / liter. Obtained results are represented on the figure 3.

We represented in Figures 4 the evolution of the pitting potential according to the logarithm of the silicates concentration. Figures 3 and 4 show the evolution of the pitting potentials towards anodic potential when the concentration of silicates increases. We explain this phenomenon by the competitiveness of adsorption between the corrosive anion Cl^- and $(\text{SiO}_3)^{2-}$, on the metal surface to delay the destructive action of chloride anions [10].

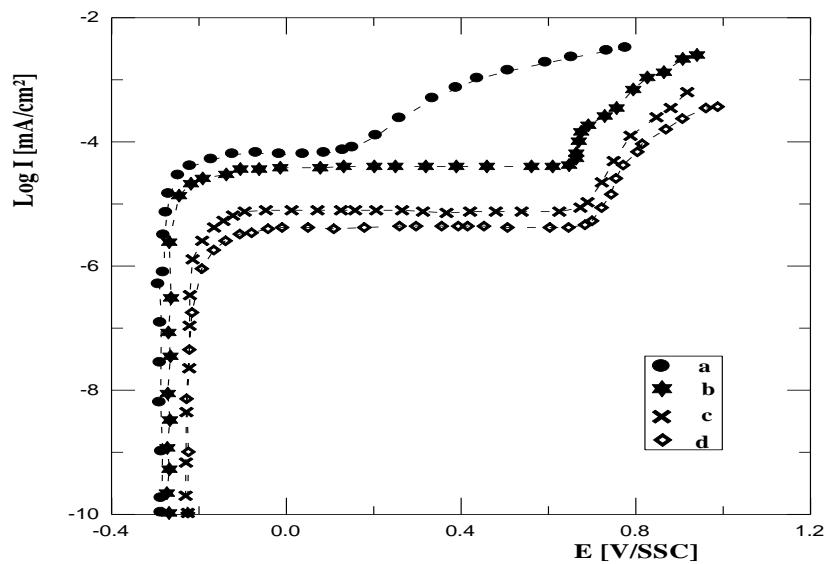


Figure 3: Influence of the silicate concentration on anodic Curves of 316L stainless steel in the sodium hypochlorite baths pH 10.80: **a** 0 M, **b** 10^{-4} M, **c** 10^{-3} M, **d** 10^{-2} M

For the concentration 10^{-4} mol / l in silicates, efficiency remains weak; it means that the film defender is not completely formed. In 10^{-3} mol / l we notice an important increase of the efficiency, we can say that from this concentration a good part of the active surface is covered but efficiency is not still for its maximum and the surface is not covered in 100%.

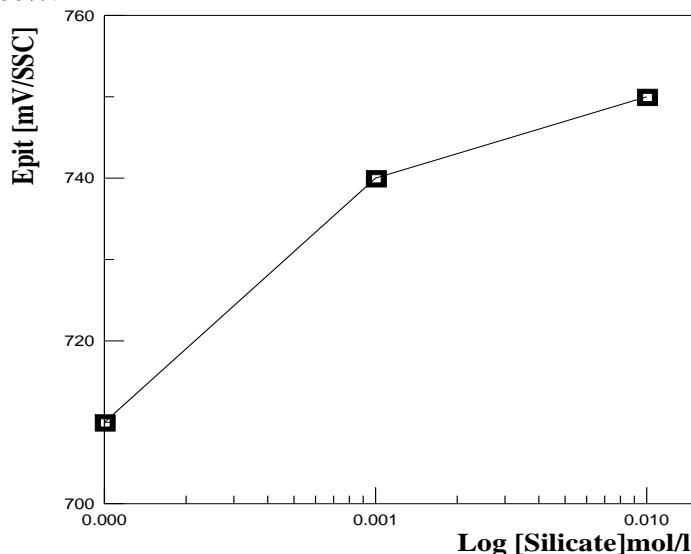


Figure 4: Pitting corrosion potential as a function of the logarithm silicates concentration

3.2 Electrochemical techniques

3.2.1 Silicates concentration effects

Electrochemical impedance spectroscopy has been used in this study of the 316L Stainless steel corrosion in sodium hypochlorite solution.

Figure 5 shows the impedance digraph obtained on the 316L stainless steel in the sodium hypochlorite solution pH: 10.80 for inhibitor concentrations of 10^{-4} M after 30 minutes immersion time at the corrosion potential. In the same figure, we represent, for comparison, the relative diagram obtained with 0M of inhibitor. We are seeing the disappearance of the inductive loop control medium in favor of second loop capacitive. The Semi Circles diameters of the two capacitive loops obtained, increases with the concentration of the inhibitor.

Determining the ability associated with high-frequency loop gives a value of $5.6\mu\text{F} / \text{cm}^2$. This value is very low; so we can not assign it to a double layer. This reflects an important dielectric character; and allows us to attribute the high frequency loop to a protective film effect

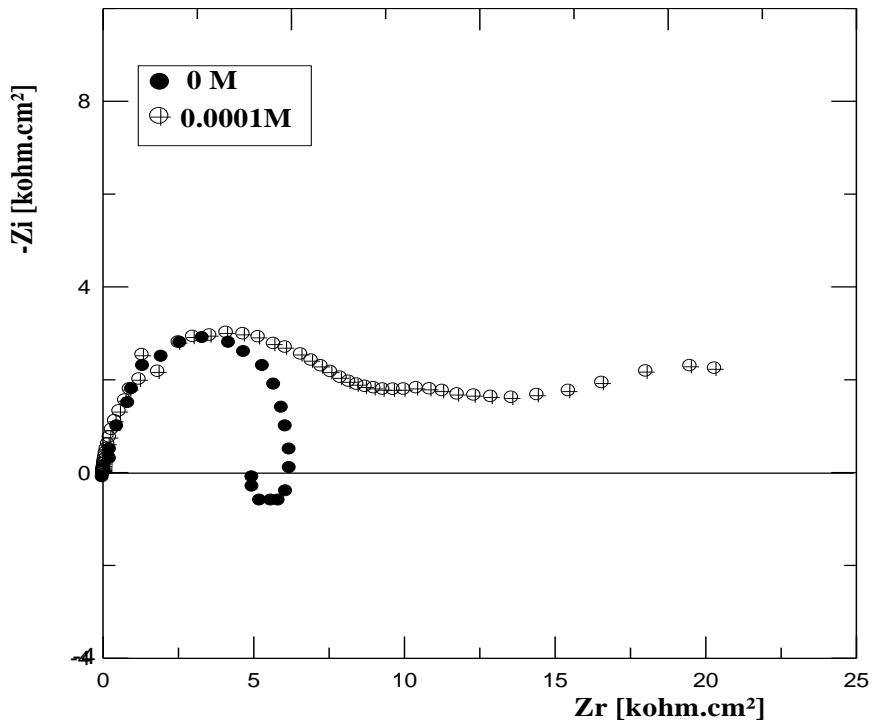


Figure 5: Nyquist plots recorded on the 316L in the sodium hypochlorite solution pH: 10.80 with inhibitor concentration of 10^{-4} M

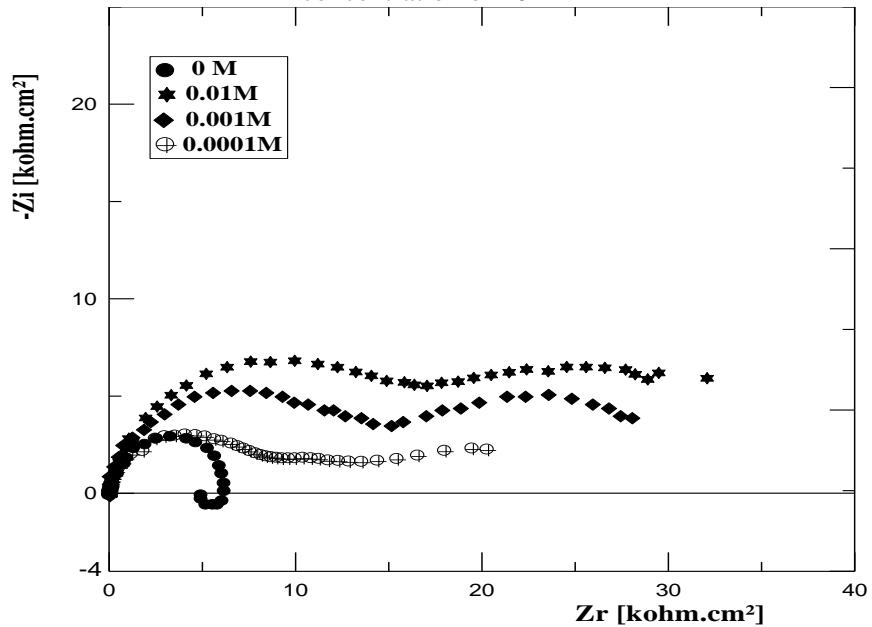


Figure 6: The inhibitor concentration effect impedance diagrams pH: 10.80 Sodium hypochlorite

Inhibitor concentrations of 0, 10^{-4} , 10^{-3} and 10^{-2} M media in the passive region of the Open circuit Potential OCP at stationary and rotating electrodes. The spectra exhibit high frequency and low frequency capacitative loops, with an inductive loop at intermediate frequencies, Figure 5 and 6. This behavior may be assigned to the reactions at silicate/electrolyte and silicate /metal interface. The first behavior at high-frequencies is related to silicate film resistance (R_f), and the second one at the middle and low-frequency region is attributed to charge transfer resistance. We can explain the form of the spectra by a multistep dissolution mechanism, including high field ionic migration through the stainless steel oxide layer, and oxide film relaxation effects.

The diameter of the semicircles is equal to the polarization resistance R_p , It is clearly seen from the spectra that the R_p increases with increasing the film thickness. The spectra confirm that thicker film provides better corrosion protection of 316L stainless steel in full agreement with the linear polarization studies.

3.2.2 Influence of the speed rotation electrode

The corrosion behaviour of 316L stainless steel has been studied under dynamic condition by rotating cylinder electrode (RCE) at rotation speed of 1000, 2000 and 3000 rpm, in the sodium hypochlorite solution pH: 10.80 for inhibitor concentrations of 10^{-2} M after 30 minutes immersion time at the corrosion potential, Figure 7 shows the impedance diagram obtained, the size of the two loops decrease when the rotational speed increases, the diffusion phenomenon is due primarily to the diffusion of species relating to the electrode surface.

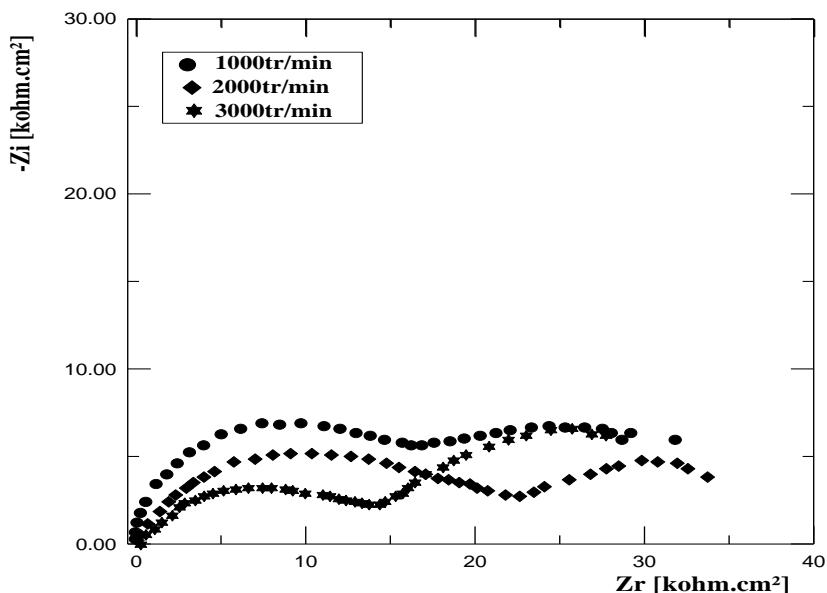


Figure 7: Effect of rotational speed on the impedance diagrams for 316L Stainless steel in sodium hypochlorite with a concentration of 10^{-2} silicates

3.2.2 Effect of immersion time

Figure 8 shows the impedance diagram obtained on the 316L pH in the sodium hypochlorite solution: 10.80 for inhibitor concentrations of 10^{-2} M at different time prior maintaining the corrosion potential.

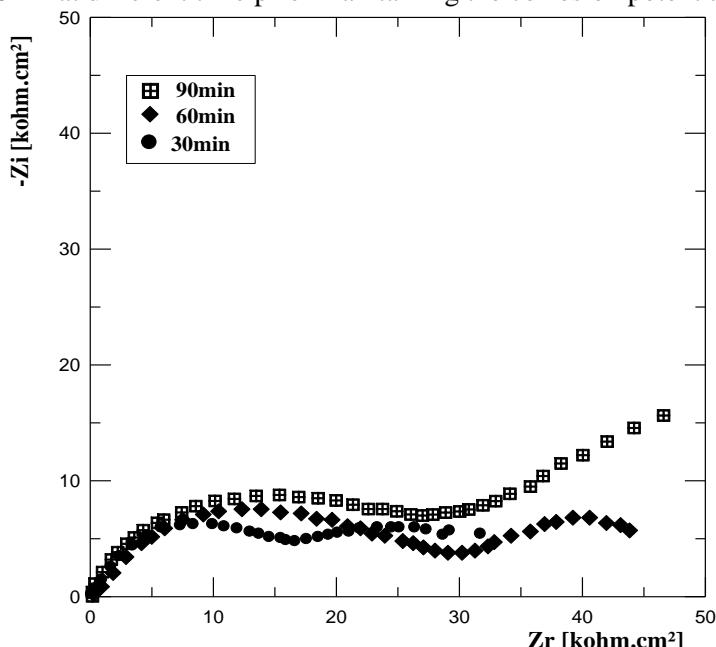


Figure 8 : Immersion time effect on impedance diagrams of 316L steel in sodium hypochlorite with a silicates concentration of 10^{-2} M

The analysis of these spectra shows that the digraphs represented in the complex plane also show two distinct loops.

Arc Nyquist plots of the sodium hypochlorite solution for inhibitor concentration of 10^{-2} M show semicircles at high and low frequencies, Figure 8. This behavior may be assigned to the reactions at silicate/electrolyte and silicate /working electrode.

Determining the ability associated with high-frequency loop after various immersion time gives values that vary between 5 and 6 $\mu\text{F.cm}^2$, these values are very low for that capacity is related to the double layer and thus support a large dielectric character of a protective film formed by the inhibitor on the metal. The results obtained show that it is possible to separate the contributions of the protective film formed by the inhibitor, faradic processes in the corrosion process.

3.3. Mechanism of Corrosion Inhibition

Silicates react with metal anions and the metal surface, this phenomenon is in the base of the mechanism by which silicates inhibit corrosion [11] figure 9 and 10.

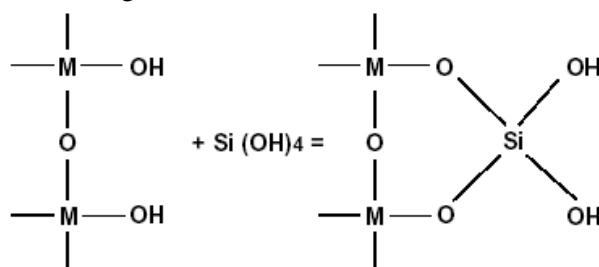


Figure 9: Silicates Interactions with the interface metal.

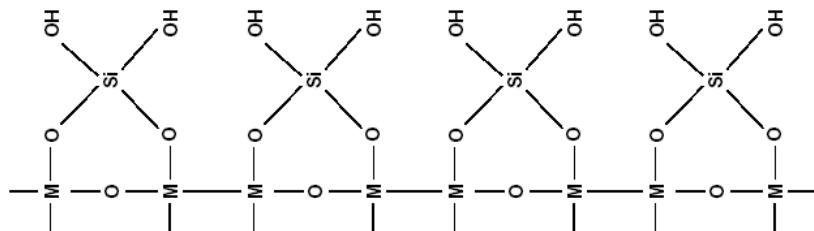


Figure 10: Adsorption silicates on the metal surface of the 316L stainless steel

In solution the $(\text{SiO}_3)^{2-}$ is adsorbed on anodic metal sites by forming a thin mono molecular film which protects the surface. The silica reacts with Fe^{2+} according to the reaction (2), Figure 11, and replace the reaction (4) which would have been able to take place in silica's absence.

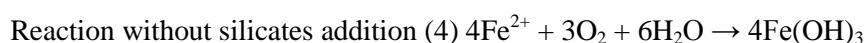
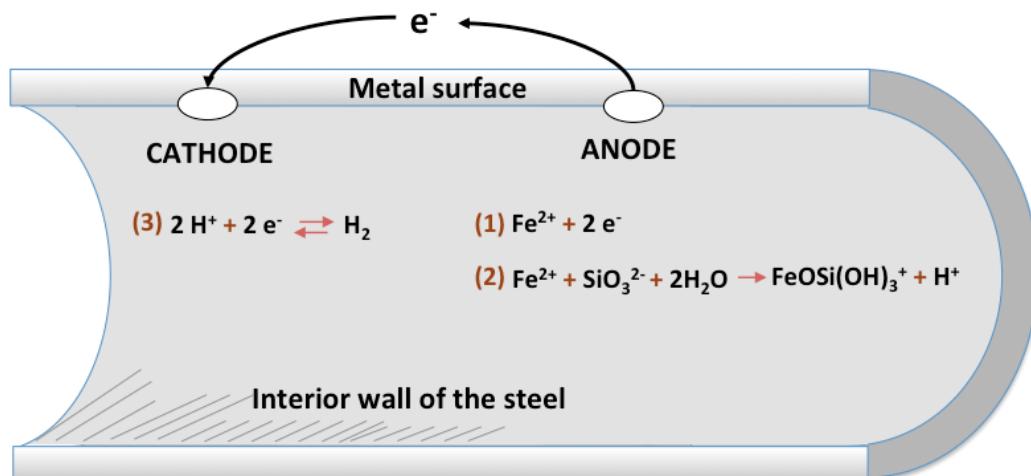


Figure 11: Electrochemical reactions with the metal surface (with and without addition of silicate)

Conclusion

This study highlighted that silicates are effective corrosion inhibition for the 316L stainless steel in the bleaching baths. Silicates have an inhibition effect of the 316L stainless steel localized corrosion in the sodium hypochlorite at pH 10.80, They form a film which remains stable even in high potential by moving so the pitting potential towards more noble values. The level of protection by silicates depends on: Their concentrations, the dumping time, on hydrodynamics conditions and the surface state. Electrochemical measurements allowed concluding that silicates act at the same time on anodic and cathodic reactions. Silicates are anodic inhibitors. In solution the $(\text{SiO}_3)^{2-}$ is adsorbed on anodic metal sites by forming a thin mono molecular film which protects the surface. In the light of these obtained results, we conclude that silicates can be used as corrosion inhibitor in the bleaching process.

References

1. Bäck G., Preet M., *Corrosion Science* 46 (2003) 2159–2182.
2. Tanane O., *PhD Thesis* (2006), *Hassan II University of Casablanca, Morocco*.
3. Prescott R., *Pulp & Paper Canada*. 100 (1999) 84-90.
4. Tanane O., Irhzo A., Pebere N., Chataignier G., Dabosi F., *Journal de Chimie Physique* 90 (1993) 1149-1166.
5. Soluble Silicates: For Protection of Water Systems from Corrosion, *Industrial Chemicals Division Bulletin* 1002 (1992) 37-3.
6. Smallman R. E Bishop R. J, in *Modern Physical Metallurgy and Materials Engineering* (1995).
7. Dietzel M., Usdowski E., *Col. Poly. Sci.* 273 (1995) 590.
8. Hyung Mi Lim, Jinho Lee, Jeong-Hwan J., Seong-Geun, Seung-Ho, *Engineering, Scientific Research* 2 (2010) 998-1005
9. El-Maksoud S.A *Int. J. Electrochem. Sci.* 3 (2008) 528-555
10. Lohdny-Sarc O., Kastelan. L., *Corrosion Science* 16 (1976) 25.
11. Tan Y. J., Bailey S., Kinsella B., *Corrosion Science* 38 (1996) 1545-1561.

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