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Electrochemical Behaviour of Iron in NaOH 0.01 mol/L Solutions Containing Variable Amounts of Silicate

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Ciclos voltamétricos repetitivos do ferro em soluções de NaOH contendo concentrações variáveis de silicato entre 10 ppm e 1500 ppm, mostram comportamentos diferentes da primeira varredura quando comparada com as subsequentes, em todas as soluções testadas. Esta diferença indica uma modificação do processo de formação do filme com a ciclagem. Foi observada uma transição do perfil *i*/E entre 10 ppm e 100 ppm de silicato o que permite formular considerações sobre a incorporação de silicato ao filme.

Repetitive voltammetric cycling of iron in NaOH solutions containing variable silicate concentrations between 10 ppm and 1500 ppm, shows different behaviour for the first scan when compared to the following ones in all studied solutions. This difference indicates a modification on the film formation process. A transition in the *i*/E profile between 10 ppm and 100 ppm of silicate was observed allowing considerations about silicate incorporation to be formulated.

Keywords: iron, cyclic voltammetry, anodic films, passive films

Introduction

Iron passivation in different electrolytes has been extensively studied¹⁻⁴⁴. Many investigations were carried out using highly alkaline solutions²⁻¹⁸ or using buffer solutions as carbonate/bicarbonate¹⁹⁻²⁶ or borate buffer²⁷⁻³² when a constant and not very high pH is desirable. Many products have been identified as resulting from the anodic polarization of iron at different potentials, by different surface analysis techniques^{6-13,22,26,33-45}. Several electrochemical techniques have also been used to investigate the kinetics of the formation of these products and among them cyclic voltammetry is one of the most used^{2-8,14-22}.

The surface analysis techniques that perform *in-situ* analysis have the great advantage of avoiding decomposition and/or dehydration of products formed which is inevitable with *ex-situ* analysis due to the high vacuum conditions and to the heating promoted by electron bombardment^{1,14,28,33-38}.

Although there is no consensus about the nature of products formed on an iron surface during anodic polarization, some ferric products are often mentioned as the passive film components and almost all authors propose that

the ferrous species formed during anodic polarization, which are the precursors of ferric ones, are the species $\text{Fe}(\text{OH})_2$ ^{6,7,18,22,42,43}.

At more anodic potentials, some authors identified β -FeOOH and sometimes Fe₃O₄ using *in-situ* Mössbauer spectroscopy¹², while others based on *in-situ* Raman spectroscopy results proposed a bi-layer structure of γ -Fe₂O₃/ γ -FeOOH⁷ or Fe₃O₄/ γ -FeOOH¹⁰ (or α -FeOOH¹³). *In-situ* UV and visible spectroscopy techniques have also determined such a bi-layer structure¹⁵. Another proposition for the film passive composition based in ellipsometric results⁷, XANES *in-situ*^{27,28} and other optical techniques^{37,39,44}, is a superposition of Fe₃O₄/ γ -FeOOH at the beginning which changes to Fe₃O₄/ γ -Fe₂O₃ after ageing although it was not specified after how long a time and at which potential. Nevertheless some ellipsometric^{9,10,29,41}, Raman²⁹ and Mössbauer⁴⁰ results identified γ -FeOOH as the only passivant species while infrared^{16,17} results identified Fe₃O₄ as the only passivant species.

The *in-situ* analysis results show that the film presents an amorphous character due to water presence which is an

essential factor for passivation and this amorphous character is destroyed if the film is dried^{10,14,34,35}.

When a passive film is described as a double layer film, the inner layer is considered a barrier layer and the outer layer is a substrate for Fe(II)/Fe(III) redox reactions during potential cycling^{6,7,22,42,43}.

The literature shows that the *i*/*E* profile obtained in cyclic voltammetry depends on the potential perturbation program characteristics. The real number of potentiodynamic peaks for iron are still questionable²⁻⁴ and they change with repetitive cycling. Generally three or four anodic peaks and one or two cathodic ones are identified for iron. Although the considered mechanisms may be different, almost all authors agree that the first and second anodic peaks are associated to ferrous species formation^{2-8,11,16,45,46} although these anodic peaks are sometimes attributed to Fe₃O₄ formation^{8,11,15,16}, or the first one to adsorbed hydrogen oxidation^{14,16}. The third and fourth anodic peaks are associated to ferric species formation^{2-8,11,14,15,45,46}. The first cathodic peak is associated with the third and fourth anodic peaks and is attributed to ferric species reduction to ferrous ones^{2-8,14,15} while the second cathodic peak is associated to the first and second anodic peaks and should correspond to ferrous species reduction to metallic iron^{2-7,45,46} or Fe₃O₄ reduction to ferrous species⁸.

The aim of this study is to investigate the iron behaviour during repetitive cycling in NaOH 0.01 mol/L solutions containing variable amounts of silicate ranging from 0 ppm to 1500 ppm in order to evaluate the influence of this anion well known for its inhibitive properties of iron corrosion in aqueous solutions.

Experimental

An iron disk electrode (Gallard-Schlesinger 99.999 %) with a diameter of 4.9 mm embedded in PTFE served as the working electrode. Its surface was polished with emery paper of grit 400, 600 and 1000 and with 1 micron alumina and washed with double-distilled water and acetone. Before each experiment the disk was electroreduced at -1600 mV (SCE) for 10 min in a three electrode electrochemical cell to obtain reproducible results. The counter electrode was a platinum wire and the reference electrode was a saturated calomel electrode (SCE) to which all the potentials in the text are referred.

Solutions were prepared using boiled, double-distilled water and p.a. reagents. The silicate composition was 18% Na₂O, 63% SiO₂ and 18% H₂O. The silicate concentrations used were: 0, 10, 20, 50, 75, 100, 250, 500, 750, 1000, 1250 and 1500 ppm as SiO₂ and the NaOH concentration was always 0.01 mol/L. The temperature was kept at 25 °C and nitrogen bubbling was used throughout the experiments to remove oxygen from the solution.

The disk electrode potential was scanned repetitively between +600 mV and -1300 mV during ten cycles at a scan rate of 50 mV/s and a constant electrode rotation rate of 1000 rpm was used.

The equipment consisted of a Pine Model AFRDE5 Bipotentiostat, an Analytical Rotor and a BBC Model SE 780 XY Recorder.

Results and Discussion

Figure 1 shows the voltammograms of the first to the fifth cycle and the tenth cycle of iron for solutions NaOH 0.01 mol/L + SiO₂ x ppm (x = 0, 20 and 50) and Fig. 2 the same for solutions NaOH 0.01 mol/L + SiO₂ x ppm (x = 75, 100, 250 and 1000).

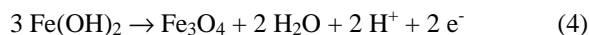
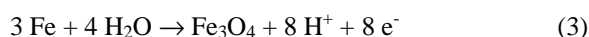
It can be seen that the first anodic scan presents three anodic peaks (a₁, a₂, a₃) and in the solutions containing silicate above 50 ppm an anodic shoulder a'₃ appears. The anodic peak potentials become less negative as the silicate concentration increases. The first cathodic scan, in solutions containing silicate with concentrations above 50 ppm, presents one cathodic peak c₁ that is associated to a₃ and a'₃, as proven by preliminary tests⁴⁷. The solutions without silicate and up to 20 ppm SiO₂, do not present distinguishable cathodic peaks at the first scan and it is probable that ferric and ferrous species reduction may be hindered by the hydrogen evolution reaction.

Based on the literature already mentioned, and in potential-pH diagrams developed by Misawa⁴⁸, it is possible to propose that the processes that probably are occurring during the first anodic scan are:

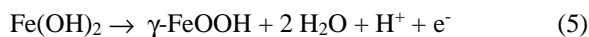
- peak a₁:



- peak a₂:



- peak a₃:



- peak a'₃:



These processes are in agreement with thermodynamic data since the peak potential values are slightly more anodic than the equilibrium potentials predicted by Misawa⁴⁸ for these reactions at pH 12, which are respectively:

$$(1) \quad E_{\text{eq}} = -1,057 \text{ mV} \quad (4) \quad E_{\text{eq}} = -979 \text{ mV}$$

$$(2) \quad E_{\text{eq}} = -1,057 \text{ mV} \quad (5) \quad E_{\text{eq}} = -706 \text{ mV}$$

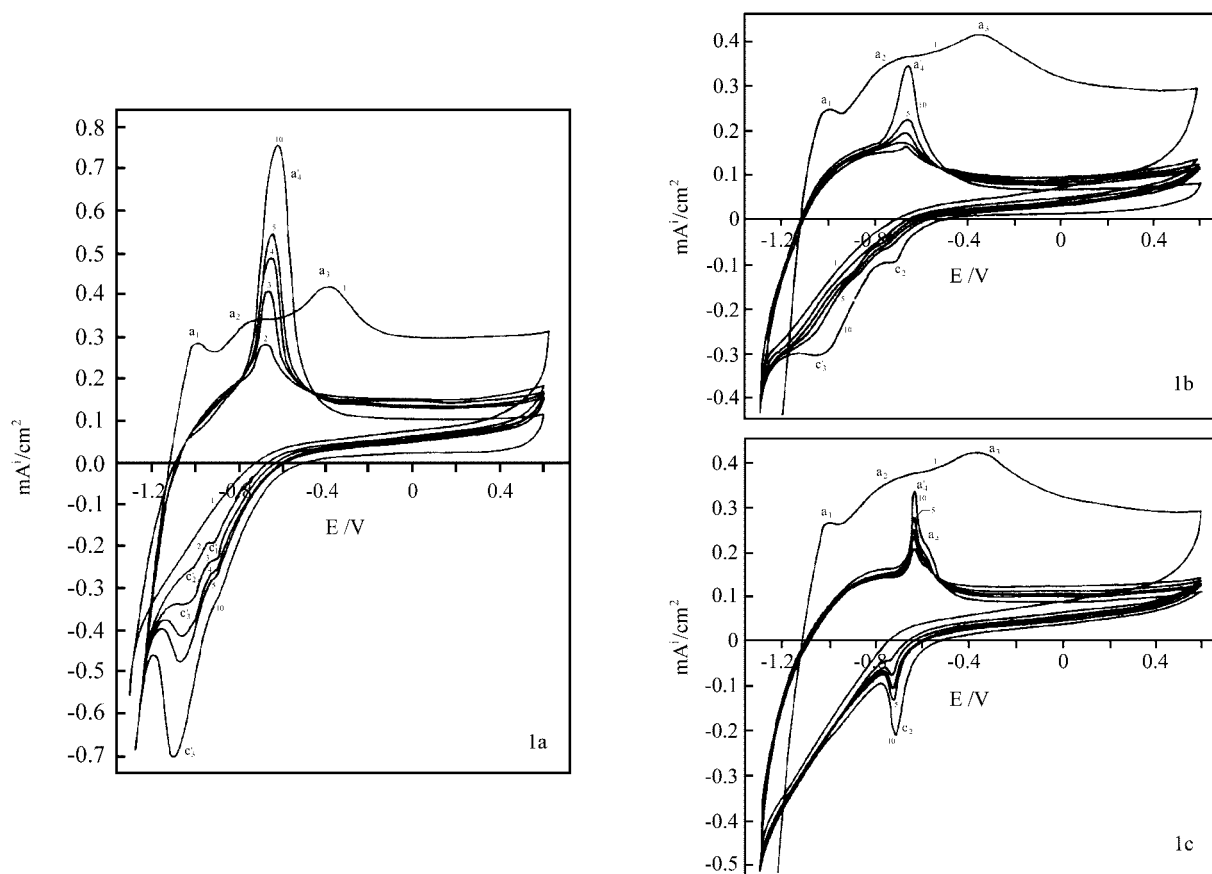


Figure 1. Voltammograms of the first to fifth and of the tenth cycle for solutions of NaOH 0.01 mol/L containing: ($v = 50$ mV/s and $w = 1000$ rpm). 1a: 0 ppm SiO₂; 1b: 20 ppm SiO₂; 1c: 50 ppm SiO₂

$$(3) E_{eq} = -1,038 \text{ mV} \quad (6) E_{eq} = -159 \text{ mV}$$

An experimental separation of the anodic peaks for the first scan, followed by a stoichiometric charge balance⁴⁷, reinforce that the possibility of these processes are occurring is feasible.

The anodic charge density associated with the first anodic scan is bigger than the cathodic charge density associated with the first cathodic scan in all solutions tested and this fact proves that, if no important metal dissolution occurs as has been found⁴⁷, at the end of the first cathodic scan the film is not completely reduced and the electrode surface is probably recovered by Fe(OH)₂. The hydrogen evolution reaction is polarized at the end of this scan which reinforces the proposition that the ferrous species are not completely reduced.

The i/E profile for the first anodic scan is similar for all solutions but the total anodic charge density for the first anodic scan is approximately constant in solutions up to SiO₂ 100 ppm, then decreases until SiO₂ 1250 ppm and remains constant for higher concentrations. Data are shown in Fig. 3 and indicate that, for the film formed at the first anodic scan, the thickness decreases gradually from 100

ppm SiO₂ to 1250 ppm SiO₂ and this thickness reduction reaches about 30 % when SiO₂ concentration in solution is 1250 ppm.

It is important to stress that “thickness” does not mean necessarily the physical thickness of the film. The incorporation of silicate in the film (or other components from solution) could contribute to the increase of its dimension, although the anodic charge involved in its formation could be decreasing. The fact is that in the presence of silicate the film formed is more resistive.

Some interesting facts are observed along the second scan:

Peak a₁ disappears in all solutions, which may indicate that the surface is already recovered by a tridimensional film, probably Fe(OH)₂, formed in the previous cycle.

Peaks a₃ (and a₃') disappear in all solutions which indicates, according to the above proposed processes, that ferric species formation from Fe(OH)₂ is not occurring.

Current density values within the peak a₂ potential range decrease in all solutions and this fact allows the proposition that at this potential range Fe₃O₄ formation preferentially occurs from metallic iron at the metal/Fe(OH)₂ interface and at the same time the oxidation of

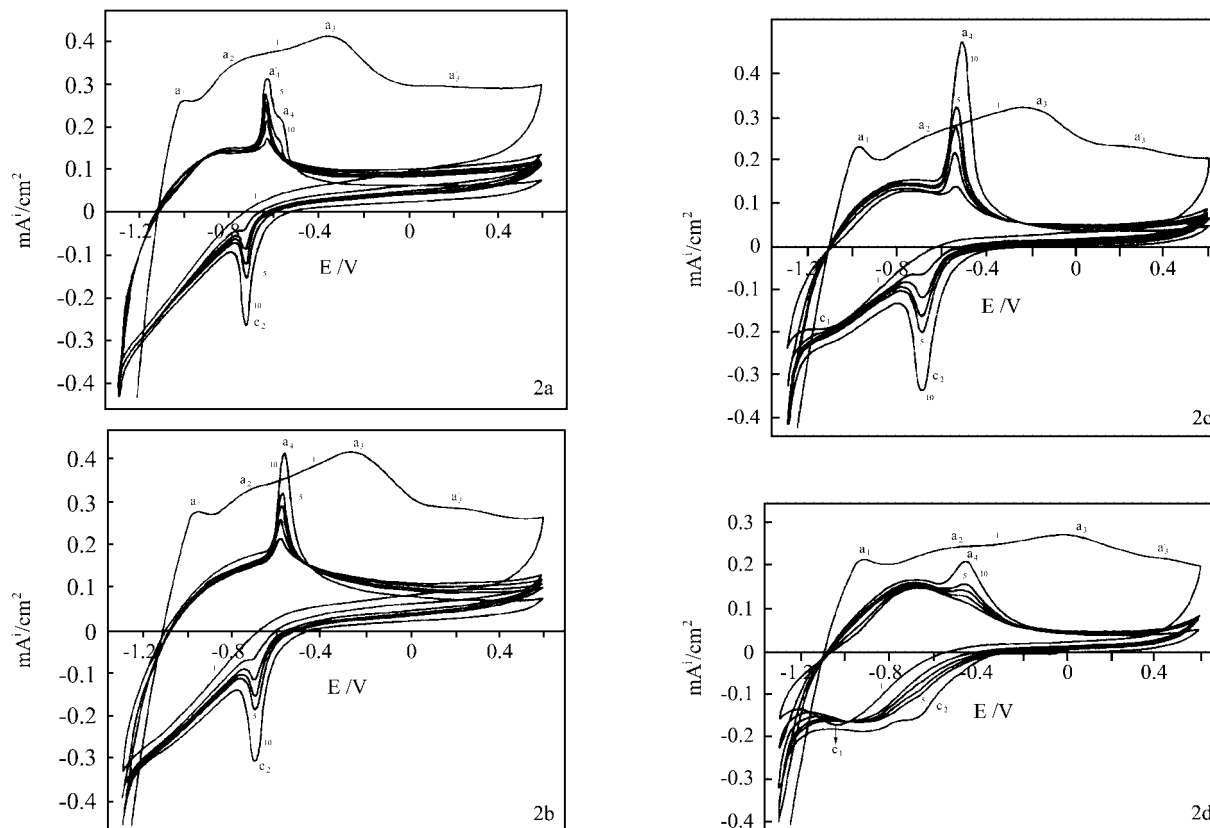


Figure 2. Voltammograms of the first to fifth and of the tenth cycle for solutions of NaOH 0.01 mol/L containing: ($v = 50$ mV/s and $w = 1000$ rpm). 2a: 75 ppm SiO₂; 2b: 100 ppm SiO₂; 2c: 250 ppm SiO₂; 2d: 1000 ppm SiO₂

pre-existent Fe(OH)₂ to Fe₃O₄ at the Fe(OH)₂/solution interface. The peak a₃ disappears and thus, the ferric species formed at peaks a₄ and a'₄ are not the same ones formed at peak a₃ in the first scan. For this reason, it is reasonable to believe that from the second anodic scan another species preferentially formed that differs from Fe(OH)₂, along the potential range corresponding to peak a₂.

New anodic and cathodic peaks appear and from this point on, the behaviour in solutions: NaOH 0.01 mol/L and NaOH 0.01 mol/L + SiO₂ 250 ppm will be analysed separately. The results of all the other solutions will be compared afterwards.

A new anodic peak a'₄ appears at -675 mV in NaOH 0.01 mol/L solution as well as a new anodic peak a₄ at -515 mV in NaOH 0.01 mol/L + SiO₂ 250 ppm solution. These peaks can be attributed to the oxidation of the outer Fe₃O₄ layer (formed from Fe(OH)₂) to α -FeOOH, since the equilibrium potential for this reaction at pH = 12 is -710 mV⁴⁸. The difference between potential peaks a₄ and a'₄ can be explained if it is accepted that silicate present in solution promotes the polarization of this reaction.

In NaOH 0.01 mol/L + SiO₂ 250 ppm solution a new cathodic peak c₂ appears at -690 mV and is clearly associated with a₄, therefore it should correspond to the reduction

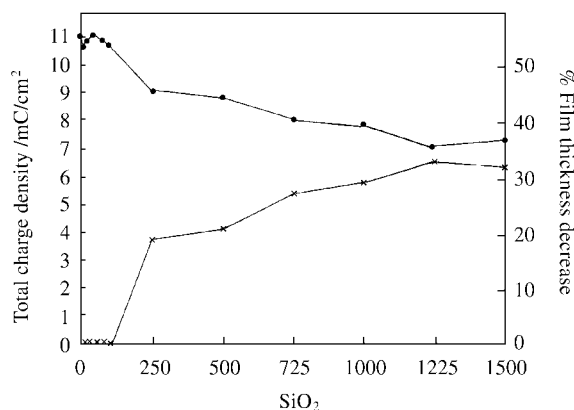


Figure 3. Total charge density for the first anodic scan (●) and % of film thickness decrease in relation to silicate free solution (x) for the SiO₂ concentration range of 0 to 1500 ppm.

of α -FeOOH to Fe₃O₄. The i/E profile is distorted in the peak c₁ potential range and it is possible that at this potential range the Fe₃O₄ reduction to Fe(OH)₂ added to the reduction of other ferric species formed in the passive zone occurs. This correlation can be proved by varying the anodic reversion potential for the tenth cycle and the results are shown in Fig. 4a. Thus it is reasonable to propose that

at the end of the second cathodic scan the film of $\text{Fe}(\text{OH})_2$ is thicker than at the end of the previous scan and it is possible that below this film a thin Fe_3O_4 film has been formed from metallic iron in the second anodic scan which does not participate in the associated electrochemical processes occurring at a_4/c_2 .

In the pure NaOH solution two cathodic peaks appear, c'_1 (at -890 mV) and c'_2 (at -970 mV) being well distinguished from the hydrogen evolution reaction which increase, if compared with the first scan. One possibility that can be pointed out is that at c'_1 reduction of $\alpha\text{-FeOOH}$ to Fe_3O_4 occurs and at c'_2 reduction of Fe_3O_4 to $\text{Fe}(\text{OH})_2$ occurs simultaneously with the reduction of ferric species, formed along the passive potential range, to $\text{Fe}(\text{OH})_2$. Likewise it is also possible to suggest that at the end of the second cathodic scan the film of $\text{Fe}(\text{OH})_2$ thickens covering an inner thin film of Fe_3O_4 that does not participate in electrochemical processes occurring at a'_4/c'_1 and is only partially reduced at c'_2 . Figure 4b shows the results of tests varying the anodic reversion potential in the tenth cycle and the results prove this peaks correlation.

The repetitive cycling shows:

In the NaOH 0.01 mol/L + SiO_2 250 ppm solution, the current densities of peaks a_4 and c_2 increase significantly. The suggestion is that at the end of each complete cycle, the outer film of $\text{Fe}(\text{OH})_2$ thickens as well as the inner film

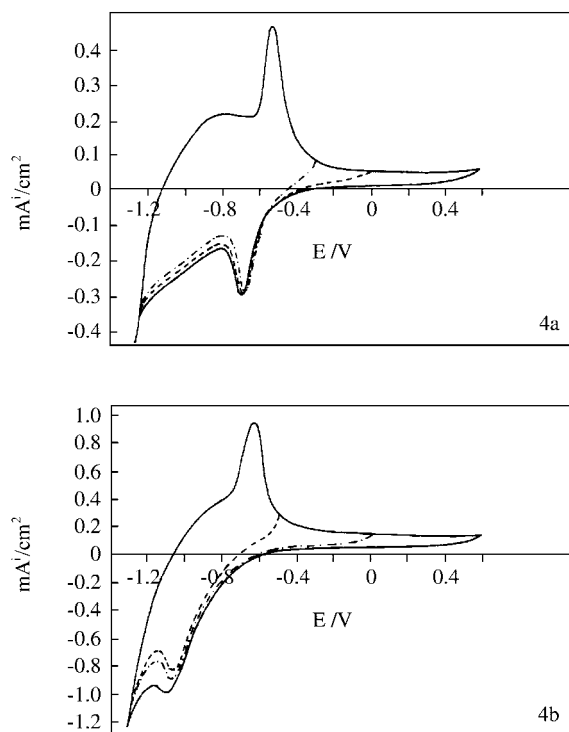


Figure 4. Correlation between anodic and cathodic peaks for voltammograms of the tenth cycle in solutions:

4a: NaOH 0.01 mol/L + 500 ppm SiO_2 ; 4b: NaOH 0.01 mol/L

of Fe_3O_4 which allows an increasing formation of $\alpha\text{-FeOOH}$ in the next anodic scan.

In the NaOH 0.01 mol/L solution, the current density of anodic peak a'_4 increases more significantly than peak a_4 in the silicate containing solution, but cathodic peaks c'_1 and c'_2 are substituted, from the third cathodic scan on, by another cathodic peak c'_3 (at -1090 mV) which increases during the following scans more significantly than the cathodic peak c_2 in the silicate solution. Cathodic peak c'_3 may be attributed to reduction of ferric species directly to $\text{Fe}(\text{OH})_2$ and thus, at the end of each complete cycle the outer $\text{Fe}(\text{OH})_2$ layer should thicken over an inner layer of Fe_3O_4 which does not participate in electrochemical processes occurring at a'_4/c'_3 and is not completely reduced. This Fe_3O_4 film, which thickens at each new cycle, may promote an increasing formation of $\alpha\text{-FeOOH}$ at a'_4 in the next anodic scan.

These considerations suggest that in both solutions the film formed after ten consecutive cycles is composed of an inner layer of Fe_3O_4 that thickens in each cycle and by an outer layer of $\alpha\text{-FeOOH}$ that participates in oxidation/reduction processes also thickening in each cycle. Similar results for i/E profiles during cycling have already been detected for different alkaline solutions^{2-7,42,43} and similar propositions for film composition after cycling have also been advanced^{2-8,11-13,15,42,43}. As the anodic peak a_4 increase is smaller than that of peak a'_4 , it is plausible that the inner film of Fe_3O_4 oxidizes to a smaller intensity and becomes thicker in the presence of silicate than in absence of silicate. This means that the inner layer (barrier layer) in the tenth cycle should be thicker when silicate is present in solution.

Analyzing the voltammograms for the other solutions, it is clear that a transition in the i/E profile is occurring between concentrations of SiO_2 10 ppm and SiO_2 100 ppm:

For SiO_2 10 ppm: The i/E profile behaviour along progressive cycling is the same as the solution without SiO_2 , but the current density values are smaller.

For SiO_2 100 ppm: The i/E profile behaviour along cycling is the same for the solution containing SiO_2 250 ppm, but the current density values are smaller.

For concentrations of SiO_2 between 10 and 100 ppm: Analyzing the tenth cycle, it is possible to notice a transition: a'_4 decreases when SiO_2 concentration increases until 75 ppm and a_4 appears when SiO_2 concentration is 50 ppm and increases with higher concentration. At 100 ppm, a'_4 disappears and only a_4 is observed. The cathodic peak c_2 is observed from SiO_2 20 ppm on and it increases with SiO_2 concentration.

These facts suggest that the silicate present in solution not only polarizes the anodic reactions but is also responsible for some differences between the $\alpha\text{-FeOOH}$ formed at a'_4 when compared to that one formed at a_4 . This differ-

ence may be attributed to a gradual silicate incorporation in the outer film as its concentration in solution increases which may modify the film composition and/or structure. This modified species can be denoted by α -FeOOH*.

For SiO₂ concentrations greater than 250 ppm, the anodic peak a₄ as well as the cathodic peak c₂ decrease with increasing SiO₂ concentration practically disappearing for concentrations greater than 1500 ppm. It is possible to suggest that for SiO₂ concentrations from 250 ppm on, the silicate interferes in the kinetics of α -FeOOH* film formation decreasing the process rate and consequently decreasing α -FeOOH* film thickening during cycling.

It is well known that cycling promotes the ageing of the film⁵. The fact that the *i*/*E* profile is very similar during the first anodic scan in solutions containing or not SiO₂ and changes during cycling showing different peaks in the absence and presence of SiO₂, indicates that time is very important in silicate actuation. The aged passive film seems to be more protective if SiO₂ is present in solution. Previous experiments⁴⁷ showed that the corrosion potential for iron electroreduced in each solution lies, after some time, at a passive zone and coincides with peak a₄ potential in solutions containing SiO₂ and with peak a'₄ potential in solutions without SiO₂. This demonstrates that the species formed during cycling is probably the same as formed in open circuit conditions after ageing.

Figure 5 shows the variation of peak potential (*E_p*) and peak current density (*i_p*) with SiO₂ concentration for anodic peaks a'₄ and a₄ and for cathodic peaks c'₃ and c₂ for the tenth cycle. The results for *E_p* variation may be explained admitting that the α -FeOOH* composition changes gradually as SiO₂ concentration in solution increases which promotes changes in $\Delta G^{\circ}_{\text{formation}}$ for α -FeOOH*. Previous experiments⁴⁷ showed that the variation of peak potential (*E_p*) with potential scan rate (*v*) is significant at the first cycle but it is almost negligible at the tenth cycle which means that species formed at the tenth cycle (aged species) are more stable than the ones formed at the first cycle^{2,5}.

Figure 6 shows the potential at which the line of zero current is crossed (*E_{Flade}*). This potential varies from the first to the tenth cycle which indicates that the film formed in the first anodic scan is not the same as that formed in the tenth scan. Both potential values (1st and 10th) become gradually less negative as SiO₂ content in solutions increases, for concentrations greater than 100 ppm.

The variation of peak a₄ potential (*E_{pa4}*) with the potential scan rate (*v*) for the tenth scan is not significant: not more than 20 mV when comparing *v* = 5 mV/s and *v* = 150 mV/s in NaOH 0.01 mol/L + SiO₂ 500 ppm. On the other hand, in the same solution, the potential peak values for the peaks observed along the first scan present a significant variation with *v*: 150 mV for a₂, 275 mV for a₃ and 270 mV for a'₃ when comparing *v* = 5 mV/s and *v* = 150 mV.

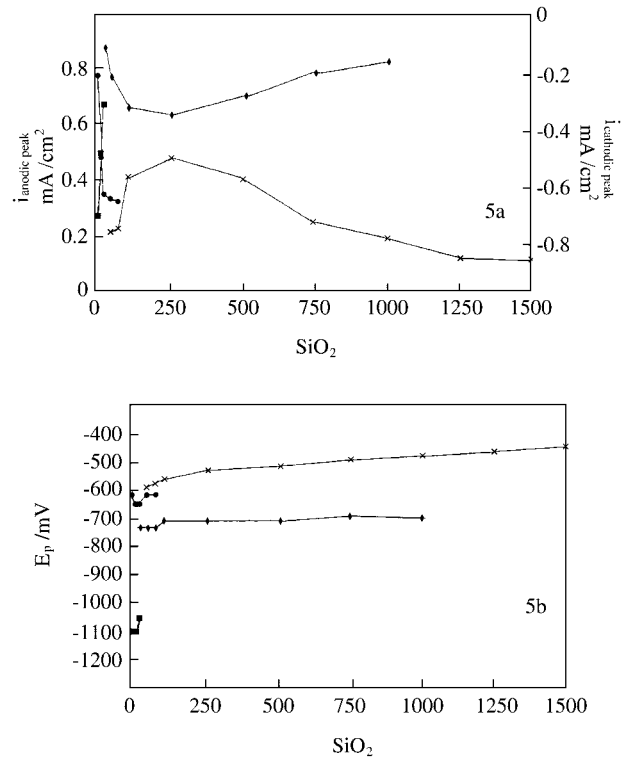


Figure 5. Peak current density (*i_p*) vs. [SiO₂] (5a) and peak potential (*E_p*) vs. [SiO₂] (5b) for:

- peak a'₄
- peak c'₃
- x peak a₄
- ◆ peak c₂

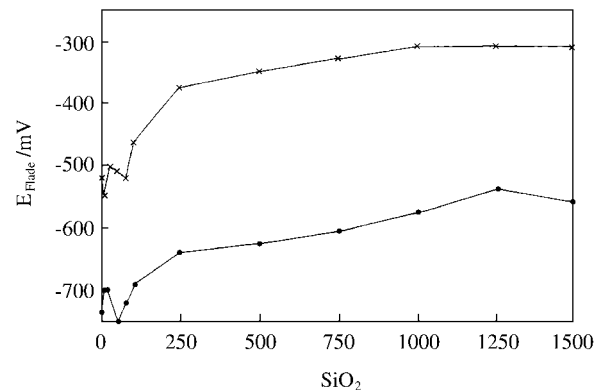


Figure 6. *E_{Flade}* vs. [SiO₂] for first (●) and the tenth (x) cycle.

The facts mentioned above indicate that the species formed during cycling are more stable than those formed during the first scan.

Some important facts should be emphasized:

- The capacitive current (*i_{DL}*), that can be estimated by: $i_{DL} = C_{DL} \cdot v$ (C_{DL} = double layer capacitance and *v* = sweep rate), can be neglected at the sweep rate of 50 mV/s. According to the literature^{2,38,46,47} double layer capacitance is generally within a range of 20 - 40 $\mu\text{F}/\text{cm}^2$, or lower when a film is recovering the metallic surface, and consequently the value of the capacitive current at 50 mV/s is

around 1 - 2 $\mu\text{A}/\text{cm}^2$. For this reason almost all of the total current may be considered as a faradaic current.

- Although adsorption processes were not specially investigated, it is believed that silicate does not adsorb on electrode surface because previous studies⁴⁷, showed that the total current increases as the electro-reduction potential becomes more negative, suggesting a "cleaner" surface and the tests of the present study were carried out after an electro-reduction at -1600 mV. Furthermore, the same study⁴⁷ proved that silicate promotes an increase of the electrolyte ohmic resistance, probably due to a colloidal consistency of the solution in the region near the electrode, and also promotes an increase of the charge transfer resistance affecting the film growth kinetics.

- The electrode rotation rate was chosen as being constant because previous studies⁴⁷ using ring-disk rotating electrode and variable electrode rotation rates, proved that at pH 12 neither soluble species were formed, neither mass transport processes in the solution nor were important for the process kinetics.

Conclusions

Although this study is essentially qualitative it shows that the passive film formed on iron in NaOH 0.01 mol/L solutions, changes during ageing leading to a different composition and/or structure if SiO_2 is present in solution in concentrations greater than 50 ppm, the last one being more protective than that formed in pure NaOH 0.01 mol/L.

References

- Vilche, J.R.; Arvia, A.J. *Anal. Acad. Nac. Cs. Ex. Fis. Nat.* **1981**, 33.
- Guzmán, R.S.S.; Vilche, J.R.; Arvia, A.J. *Electrochim. Acta* **1979**, 24, 395.
- Guzmán, R.S.S.; Vilche, J.R.; Arvia, A.J. *J. Appl. Electrochem.* **1981**, 11, 551.
- Guzmán, R.S.S.; Vilche, J.R.; Arvia, A.J. *Anales Asoc. Quím. Argentina* **1982**, 70, 999.
- Vilche, J.R.; Arvia, A.J. *Acta Cient. Venezolana* **1980**, 31, 408.
- Albani, O.A.; Zerbino, J.O.; Vilche, J.R.; Arvia, A.J. *Electrochim. Acta* **1986**, 31, 1403.
- Albani, O.A.; Gassa, L.M.; Zerbino, J.O.; Vilche, J.R.; Arvia, A.J. *Electrochim. Acta* **1990**, 35, 1437.
- Hugot-Le-Goff, A.; Flis, J.; Boucherit, N.; Joiret, S.; Wilinski, J. *J. Electrochem. Soc.* **1990**, 137, 2684.
- Szklarska-Smialowska, Z.; Kozłowski, W. *Corrosion* **1984**, 40, 595.
- Zakroczyński, T.; Fan, C.-J.; Szklarska-Smialowska, Z. *J. Electrochem. Soc.* **1985**, 132, 2862.
- Flis, J.; Oranowska, H.; Szklarska-Smialowska, Z. *Corros. Sci.* **1990**, 30, 1085.
- Geronov, Y.; Tomov, T.; Georgiev, S. *J. Appl. Electrochem.* **1975**, 5, 351.
- Huang, Z.Q.; Ord, J.L. *J. Electrochem. Soc.* **1985**, 132, 24.
- Burke, L.D.; Lyons, M.E.G. *J. Electroanal. Chem and Interfacial Electrochem* **1986**, 198, 347.
- Zhang, H.; Park, S.M. *J. Electrochem. Soc.* **1994**, 141, 718.
- Zou, J.; Chin, D. *Electrochim. Acta* **1987**, 32, 1751.
- Zou, J.; Chin, D. *Electrochim. Acta* **1988**, 33, 477.
- Armstrong, R.D.; Baurhoo, I. *J. Electroanal. Chem. and Interfacial Electrochem.* **1972**, 40, 325.
- Valentini, C.R.; Moina, C.A.; Vilche, J.R.; Arvia, A.J. *Anales Asoc. Quím. Argentina* **1983**, 71, 555.
- Valentini, C.R.; Moina, C.A.; Vilche, J.R.; Arvia, A.J. *Corros. Sci.* **1985**, 25, 985.
- Castro, E.B.; Valentini, C.R.; Moina, C.A.; Vilche, J.R.; Arvia, A.J. *Corros. Sci.* **1986**, 26, 781.
- Castro, E.B.; Vilche, J.R.; Arvia, A.J. *Corros. Sci.* **1991**, 32, 37.
- Davies, D.H.; Burstein, G.T. *Corrosion* **1980**, 36, 416.
- Rangel, C.M.; Fonseca, I.T.; Leitão, R.A. *Electrochim. Acta* **1986**, 31, 1659.
- Rangel, C.M.; Fonseca, I.T.; Leitão, R.A. *Electrochim. Acta* **1989**, 34, 255.
- Gui, J.; Devine, T.M. *Corros. Sci.* **1995**, 37, 1177.
- Davenport, A.J.; Bardwell, J.A.; Vitus, C.M. *J. Electrochem. Soc.* **1995**, 142, 721.
- Davenport, A.J.; Sansone, M. *J. Electrochem. Soc.* **1995**, 142, 725.
- Ohtsuka, T.; Ju, J.-C.; Ito, S.; Einaga, H. *Corros. Sci.* **1994**, 36, 1257.
- Kozłowski, W.; Flis, J. *Corros. Sci.* **1988**, 28, 787.
- Kozłowski, W.; Flis, J. *Corros. Sci.* **1991**, 32, 861.
- Rubim, J. *J. Electrochem. Soc.* **1993**, 140, 1601.
- Gui, J.; Devine, T.M. *Corros. Sci.* **1994**, 36, 441.
- Kuroda, K.; Cahan, B.D.; Nazri, Gh.; Yeager, E.; Mitchell, T.E. *J. Electrochem. Soc.* **1982**, 129, 2163.
- Debnath, N.C.; Anderson, A.B. *J. Electrochem. Soc.* **1982**, 129, 2169.
- Kruger, J. *Corros. Sci.* **1989**, 29, 149.
- Bockris, J.O'M. *Corros. Sci.* **1989**, 29, 291.
- Searson, P.C.; Latanision, R.M.; Stimming, U. *J. Electrochem. Soc.* **1988**, 135, 1358.
- Rauscher, A.; Konno, H.; Nagayama, M. *Electrochim. Acta* **1977**, 22, 823.
- Vértes, Cs.; Varsányi, M.L.; Vértes, A.; Meisel, W.; Gütllich, P. *Electrochim. Acta* **1993**, 38, 2253.
- Szklarska-Smialowska, Z.; Zakroczyński, T.; Fan, C.-J. *J. Electrochem. Soc.* **1985**, 132, 2543.
- Juanto, S.; Zerbino, J.O.; Miguez, M.I.; Vilche, J.R.; Arvia, A.J. *Electrochim. Acta* **1987**, 32, 1743.

43. Juanto, S.; Schrebler, R.S.; Zerbino, J.O.; Vilche, J.R.; Arvia, A.J. *Electrochim. Acta* **1991**, *36*, 1143.
44. Takahashi, K.; Bardwell, J.A.; MacDougall, B.; Graham, M.J. *Electrochim. Acta* **1992**, *37*, 477.
45. MacDonald, D.D.; Roberts, B. *Electrochim. Acta* **1978**, *23*, 557.
46. MacDonald, D.D.; Roberts, B. *Electrochim. Acta* **1978**, *23*, 781.
47. Amaral, S.T. *Iron Electrochemical behaviour in Alkaline Solution Containing Sodium Silicate*, Dr. Thesis, UFRGS, Brasil, 1996.
48. Misawa, T. *Corros. Sci.* **1973**, *13*, 659.

Received: June 3, 1998