

## Electrochemical Behavior of Iron in Alkaline Solution in the Presence of Silicate and Sulphate

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Estudos potenciodinâmicos foram realizados com um eletrodo de disco de ferro usando Voltametria Cíclica com Varredura Triangular de Potencial Repetitiva. Foi testada a influência da velocidade de varredura de potencial e da velocidade de rotação do eletrodo em soluções contendo silicato. A velocidade de rotação do eletrodo não apresenta influência nos resultados. Foi analisado o desenvolvimento do perfil E/I ao longo da ciclagem progressiva, assim como o comportamento dos picos anódicos e catódicos e da corrente passiva. Observou-se um comportamento eletroquímico do ferro diferente em soluções contendo silicato se comparado a soluções sem silicato. Esse inibidor parece necessitar da formação prévia de alguns produtos de corrosão do ferro para formar um filme que irá promover uma boa proteção contra o ânion agressivo sulfato.

Potentiodynamic studies were done with an iron disk electrode using Cyclic Voltammetry with a Repetitive Triangular Potential Sweep Program. The influence of the potential scan rate and the electrode rotation rate for solutions containing silicates were evaluated. The electrode rotation rate did not influence the results. The development of the E/I profile along the progressive cycling as well as the behavior of the anodic and cathodic peaks and the passive current were analyzed. Different electrochemical behavior of iron was observed in solutions containing silicate *versus* those not containing silicate. It appears that silicate needs the previous formation of some iron corrosion products to form a film which promotes good protection against the aggressive sulphate anion.

**Keywords:** *silicate, iron passivation*

### Introduction

Sodium silicate is a well known corrosion inhibitor for steel and zinc in aqueous solutions<sup>1,2,3,4,5,6</sup>. It is normally assumed that previous corrosion of the metal is necessary to promote the formation of a protective layer on the surface<sup>2,3,5,6,7,8</sup>.

Most studies with iron in alkaline solutions were carried out at high pH values<sup>9,10,11</sup>. The main corrosion product has been identified as  $\text{Fe}(\text{OH})_2$ <sup>9,12,13,14</sup> which results from Fe(II) dissolution and precipitation as  $\text{Fe}(\text{OH})_2$ <sup>9,11,13</sup>, and its further adsorption on the surface forming a tridimensional film of  $\text{Fe}(\text{OH})_2$  on the metallic substrate<sup>14</sup>. This reaction occurs around the thermodynamic potential Fe/Fe(II)<sup>10</sup>. The Fe(II) easily oxidizes to Fe(III)<sup>9</sup> forming  $\text{FeOOH}$ <sup>12,13,15</sup>. At very positive potentials Fe(III) may be formed directly on the electrode surface as  $\text{Fe}_2\text{O}_3$ , and possibly as  $\text{Fe}_3\text{O}_4$ , or it dissolves and precipitates as  $\text{FeOOH}$ <sup>9,13</sup>.

There has been a lot of discussion about the nature and the mechanism of this formation of protective layers on iron<sup>1,6</sup>, but nevertheless the kinetic data are insufficient to explain the exact mechanism of the reactions<sup>14</sup>.

The solid corrosion products of iron, according to Shuldener *et al.*<sup>6</sup>, react with silicate removing it from the solution. The film formed on iron in the presence of silicate used to be described as a two-layered deposit, the inner layer being composed of corrosion products and the outer one of a conglomerate of adsorption compounds of silica, metal hydroxide and silica gel<sup>8</sup>. The variety of experimental conditions such as sodium silicate concentration, pH, temperature,  $\text{Na}_2\text{O}:\text{SiO}_2$  ratio, presence or absence of air or other ions, and potentiodynamic or steady state conditions, do not allow a consensus to emerge on the nature and mechanism of the formation of these layers.

The objective of this work is to verify the influence of silicate on the electrochemical behavior of iron in alkaline

solutions and to evaluate the protection efficiency of the film formed in these solutions in the presence of aggressive sulphate anions.

## Experimental

An iron disk electrode (Gallard - Schlesinger 99.999%) with a diameter of 4.9 mm was embedded in PTFE, and 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 it was electroreduced at -1.6 V (SCE) for 5 min in a three electrode electrochemical cell to obtain reproducible results. The counter-electrode was a platinum wire and the reference electrode was a SCE to which all the potentials in the text are referred.

Cyclic Voltammetry with the Repetitive Triangular Potential Sweep Program was used. The first cycle began at -1.6 V and the following cycles had upper and lower limits of +0.3 V and -1.3 V, respectively. The potential scan rate ( $v$ ) used in the experiments with silicate solutions was in the  $0.01 \text{ V/s} < v < 0.1 \text{ V/s}$  range, and the electrode rotation rate ( $w$ ) was in the  $0 \text{ rpm} < w < 4000 \text{ rpm}$  range.

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

Solutions were prepared using boiled, double-distilled water and p.a. reagents. The silicate composition was 18%  $\text{Na}_2\text{O}$ , 63%  $\text{SiO}_2$  and 18%  $\text{H}_2\text{O}$ . The concentration of silicate solutions varied from 500 ppm to 2000 ppm in  $\text{SiO}_2$ , and the concentration of sulphate solution was 0.025 M  $\text{Na}_2\text{SO}_4$ . The pH was adjusted with 1 M  $\text{NaOH}$  to the values 10.5 or 13 used in this experiment. The temperature was kept at 25 °C and nitrogen bubbling was used to remove oxygen from the solutions.

## Results and Discussion

The first part of this discussion presents the results obtained in solutions containing silicate at  $\text{pH} = 10.5$ .

Figure 1 shows the profile during seventy consecutive scans for the iron disk in 1000 ppm  $\text{SiO}_2$ . As can be observed, the E/I profile is not stable even after 70 cycles. The second anodic scan presents lower currents along the whole potential range studied if compared to the first anodic scan, and the ratio of total anodic charge to total cathodic charge ( $Q_{\text{an}}/Q_{\text{ct}}$ ) is greater than one indicating incomplete reduction of the oxidized products. The last two facts may be explained by the results of other studies which established that silicate needs previous corrosion product formation to react with in order to form a protective film<sup>2,3,5,6,7,8</sup>, that is if the film formed in our experiments can be considered similar to that obtained in previous research.

Three anodic peaks (peaks I, II and III) and one cathodic peak (peak V) are observed in the first scan. An evolution

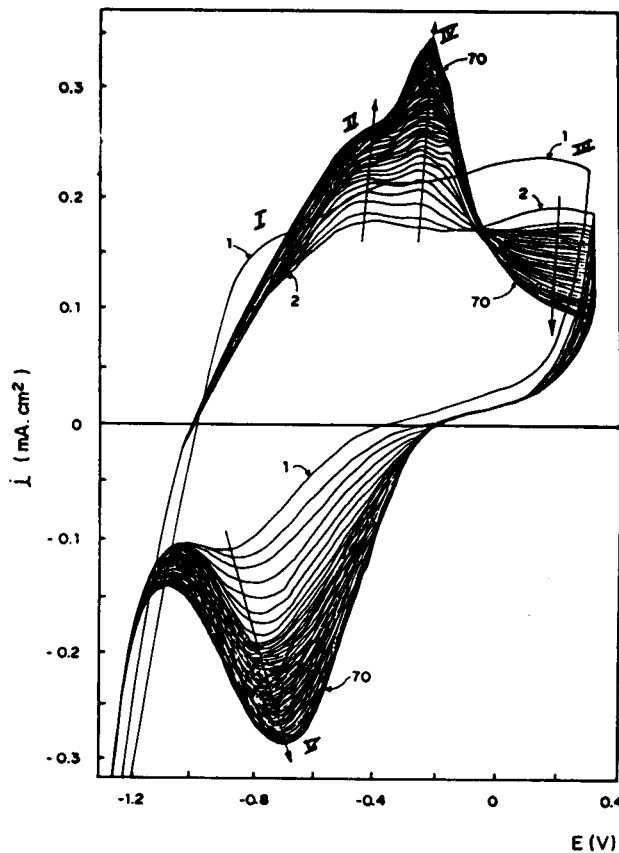


Figure 1. Profile E/I - 70 cycles. Solution: 1000 ppm  $\text{SiO}_2$ ,  $\text{pH} = 10.5$ ,  $v = 0.05 \text{ V/s}$ ;  $w = 1000 \text{ rpm}$

during the cycling can be observed: in the second anodic scan, only peaks II and III appear, then peak II grows, peak III disappears gradually and another anodic peak (peak IV) appears and grows with the cycling. In previous experiments carried out in our laboratory, but not presented in this paper, it was observed that cathodic peak V is associated with anodic peaks II and IV. Anodic peak I is not well defined, virtually disappearing after the first scan and does not present any associated cathodic peak. This means that either the corresponding cathodic reaction occurs in the same potential range as the hydrogen evolution reaction, or that there is no reduction of the products formed at this potential because the process could not be in equilibrium and the species could undergo a subsequent chemical process<sup>12</sup> (or diffuse to the bulk solution if they are soluble).

Some authors believe that anodic peak I is due to the oxidation of adsorbed hydrogen<sup>9,14</sup>, but others claim that it is related to the initial stages of iron oxidation<sup>12</sup>. It is not the purpose of this work to elucidate this fact, but as this anodic peak in the first scan is much larger than in the following ones it could in part be attributed to the oxidation of hydrogen formed at the initial reduction procedure.

Peak II should be related to the electrooxidation to  $\text{Fe(II)}$  species directly from metallic iron<sup>12</sup>, and these  $\text{Fe(II)}$  species are probably responsible for the film formation in

the presence of silicate, because the latter reacts with ferrous species to form a film<sup>2,3,5,6,7,8</sup>. We have already said that we consider the film formed in our experiments to be similar to that obtained in previous research.

Peak IV should correspond to the oxidation of Fe(II) to Fe(III) species. This peak, and the associated cathodic peak V, gradually increase with successive scans, which may be related to the increase in surface roughness, in variation of porosity, and structural modification in the film, because the density of trivalent products is greater than that of bivalent ones. This could promote a rupture in the film structure<sup>12</sup> or even an accumulation of corrosion products and film thickening if not completely reduced<sup>16</sup>. As the total anodic charge is always greater than the total cathodic charge this last reason must be taken into account.

The current after anodic peak IV diminishes with successive scans (and was therefore considered a passive current) which may indicate that the protection is increasing because the film is probably thickening, as has already been suggested.

The attribution of the peaks in this study was based on the equilibrium potentials reported by Misawa<sup>17</sup> for the Fe-H<sub>2</sub>O system at 25 °C. The experimental values of the anodic peak potentials are a little more positive than the ones reported in the literature, which means that the attribution is appropriate. Besides this, such consecutive reactions should occur because their products have been experimentally confirmed by X-Ray Diffraction Techniques and SEM for the Fe/alkaline solution interface by Anderson and Öjefors<sup>13</sup> in studies with concentrated KOH solutions.

Anodic peaks II and IV are associated with the process of film formation and are analyzed in the following figures. The data were obtained from the sixteenth cycle.

Figure 2 shows the influence of silicate concentration on the results of experiments in solution with pH = 10.5. Straight lines are obtained when a plot of  $\log i_p$  vs.  $\log$  silicate concentration is done for peaks II and IV. The slope is negative in both cases, indicating an inhibition of the electrochemical processes, but is more negative for peak IV suggesting that Fe(II) species react with silicate, as has already been potentiometrically verified<sup>18</sup>, and so its oxidation to Fe(III) species is hindered. This may be one of the aspects of the inhibitive properties of silicate.

The influence of the electrode rotation rate was also tested in a 1000 ppm SiO<sub>2</sub> solution, pH = 10.5. The results are shown in Fig. 3. The figure shows a slight dependence between  $i_p$  and  $w^{1/2}$  for both peaks II and IV, but it is possible to neglect this fact and consider a linear relationship between  $i_p$  and  $w^{1/2}$  with an almost zero slope because other tests carried out in solutions with a different silicate concentration and/or a different pH did not show any dependence between these variables. The  $i_p$  values vary very little around an average value. This fact suggests that

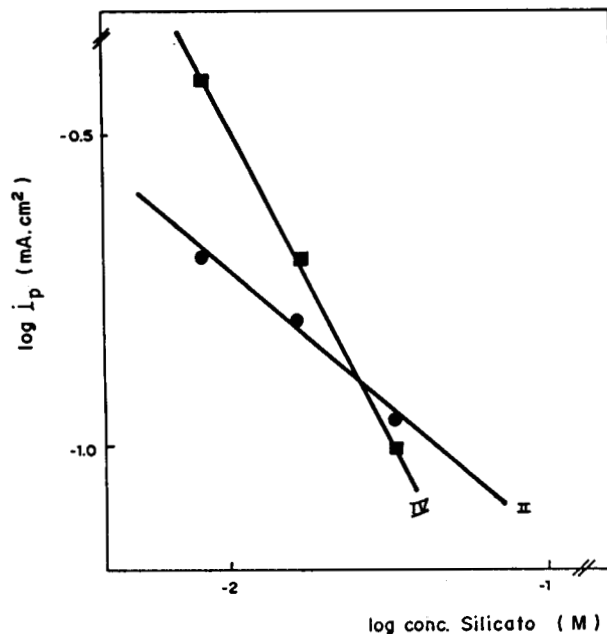


Figure 2. Influence of SiO<sub>2</sub> concentration. Solutions: 500 ppm and 2000 ppm SiO<sub>2</sub>, pH = 10.5,  $v = 0.05$  V/s;  $w = 1000$  rpm sixteenth cycle.

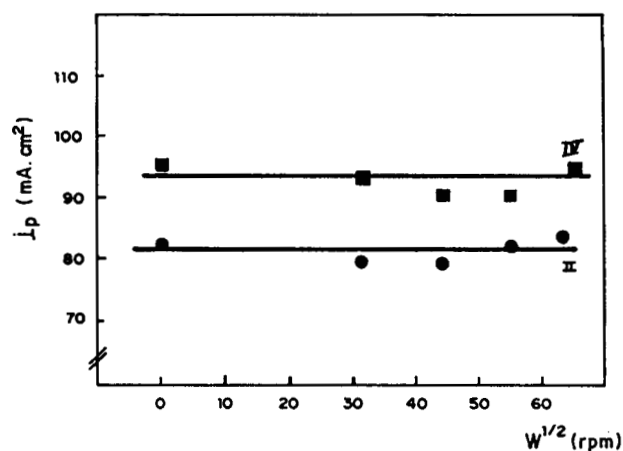


Figure 3. Influence of electrode rotation rate. Solution: 1000 ppm SiO<sub>2</sub>, pH = 10.5,  $v = 0.05$  V/s,  $w = 0, 1000, 2000, 3000, 4000$  rpm; sixteenth cycle.

the film is formed by a solid state reaction mechanism instead of a dissolution/precipitation mechanism.

The influence of the potential scan rate was also tested in the 1000 ppm SiO<sub>2</sub> solution, pH = 10.5. Figure 4 shows a linear relationship between  $i_p$  and  $v^{1/2}$  for anodic peaks II and IV with correlation coefficients of 0.9896 and 0.9884, respectively. This suggests that the respective electrochemical processes occur under ohmic control<sup>19,20</sup>, which means that the mass transport across the film is more dependent on the electric potential gradient than on the concentration gradient. The experimental straight line obtained for anodic peak II crosses the origin, and the same happens to anodic peak IV if the first experimental point is ignored (dashed line). This would indicate that there is no

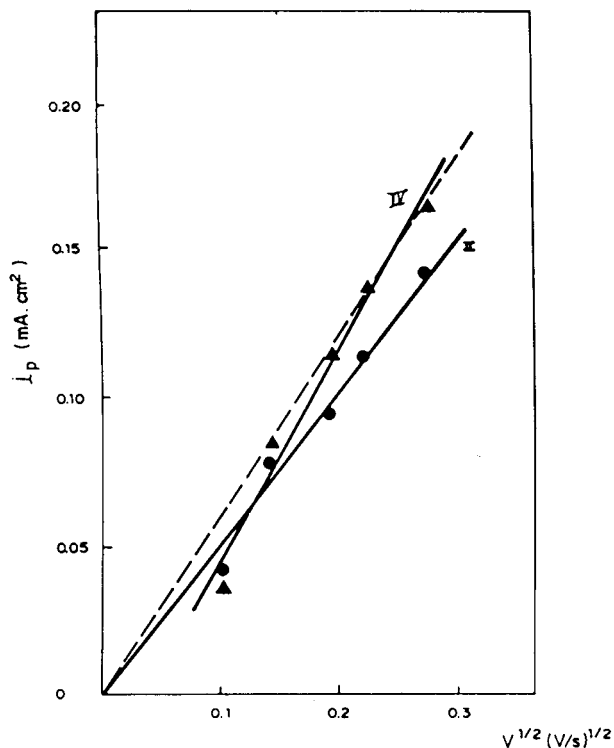


Figure 4. Influence of potential scan rate. Solution: 1000 ppm  $\text{SiO}_2$ , pH = 10.5,  $v = 0.01; 0.02; 0.035; 0.05; 0.75$  and  $0.1$  V/s;  $w = 1000$  rpm; sixteenth cycle.

dissolution, just solid state reactions. If more attention were to be given to the first experimental point, it would be possible that at low potential scan rates the system changes because the mechanism of film formation may be a different one. It is necessary to investigate this much more deeply, and carry out more experiments.

The second part of this discussion presents results obtained in a solution without silicate at pH = 13 (0.1 M NaOH solution), in a solution containing silicate at pH = 13

(1000 ppm  $\text{SiO}_2 + 0.1$  M NaOH solution), and in a solution containing silicate and sulphate at the same pH (1000 ppm  $\text{SiO}_2 + 0.025$  M  $\text{Na}_2\text{SO}_4 + 0.1$  M NaOH solution).

Figure 5 shows the E/I profile during eight consecutive scans for the iron disk in 0.1 M NaOH solution. The E/I profile is not stable after eight cycles and the anodic peak II is very ill defined.

Figure 6 shows the E/I profile during eight consecutive scans for the iron disk in 1000 ppm  $\text{SiO}_2 + 0.1$  M NaOH solution. At this pH anodic peak II is large and not clearly defined, and another cathodic peak (peak VI) appears which is large and not well defined and is associated with anodic peak II.

Figure 7 presents the results of the same sort of experiments in 1000 ppm  $\text{SiO}_2 + 0.025$  M  $\text{Na}_2\text{SO}_4 + 0.1$  M NaOH solution. The behavior is very similar to that shown in Fig. 6, but a slight increase in the passive current is detectable, although this value is lower than the passive current obtained in solution without  $\text{SiO}_2$  at the same pH in the eighth cycle, according to Fig. 5.

Comparing Figs. 5, 6 and 7, some interesting facts can be observed.

The anodic peak IV current density at the eighth cycle in the solution containing  $\text{SiO}_2$  (with and without sulphate) is much lower than the corresponding current density in the solution without  $\text{SiO}_2$  at the same pH. As was already proposed in the discussion of Fig. 2, the silicate ion probably reacts with Fe(II) species stabilizing them in the film, and the oxidation to Fe(III) species is therefore hindered.

The potential of peak IV does not change significantly in the solution containing  $\text{SiO}_2$  during the cycling, suggesting that the pH near the electrode surface is almost constant, which can be attributed to the absence of pores in the film. If pores were present,  $\text{H}^+$  ions would accumulate inside them due to the hydrolysis of iron ion oxides and the

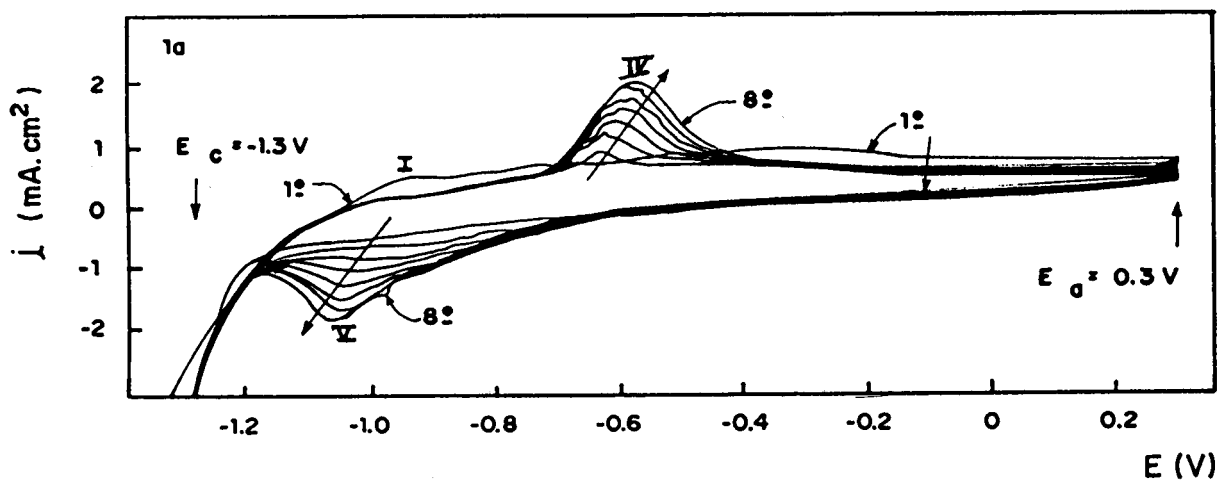


Figure 5. Profile E/I - 8 cycles. Solution: 0.1 M NaOH;  $v = 0.1$  V/s;  $w = 1000$  rpm.

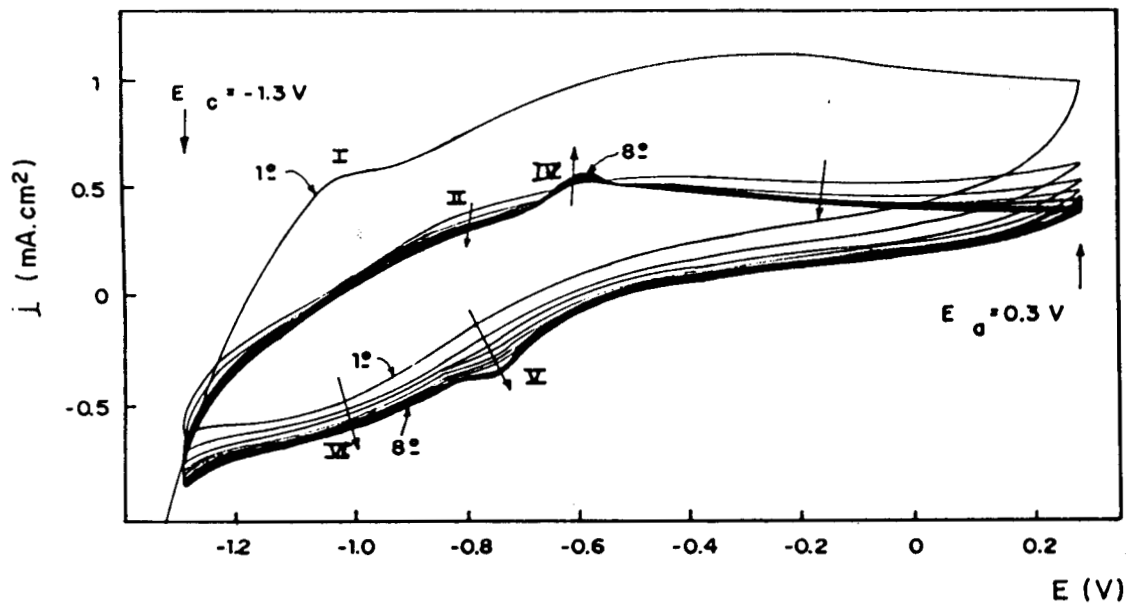


Figure 6. Profile E/I - 8 cycles. Solution: 1000 ppm SiO<sub>2</sub> + 0.1 M NaOH;  $v = 0.1$  V/s;  $w = 1000$  rpm.

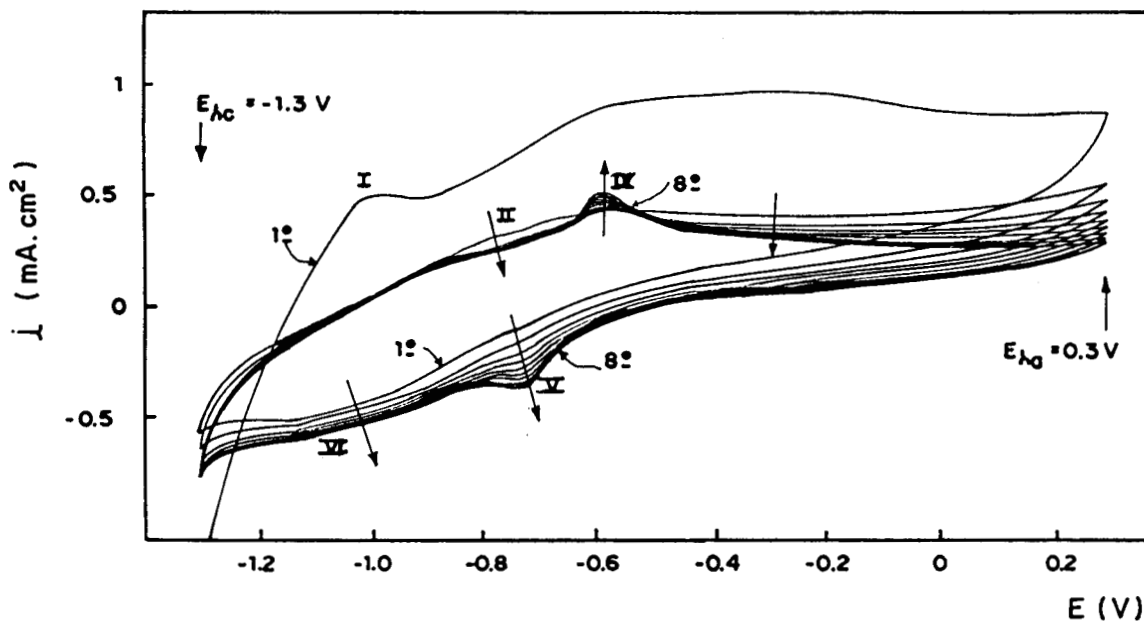


Figure 7. Profile E/I - 8 cycles. Solution: 1000 ppm SiO<sub>2</sub> + 0.025 M Na<sub>2</sub>SO<sub>4</sub> + 0.1 M NaOH;  $v = 0.1$  V/s;  $w = 1000$  rpm.

potential of peak IV potential would shift to more anodic values along the cycling.

The similarity between the E/I profiles in Figs. 6 and 7 indicates that the film formed in these experiments promotes an effective protection for iron against the aggressive sulphate anions. If this were not true some alteration of the E/I profile would be observed in the presence of sulphate, because the values of current densities recorded in the literature for alkaline solutions (pH = 13) containing only sulphate are much higher<sup>14</sup>.

## Conclusions

1) The protective film formed on iron in silicate solutions in these experiments is probably pore-free and formed by a solid state reaction mechanism. The dissolution/precipitation mechanism is not important in this case.

2) Silicate solutions present an additional inhibiting effect besides the alkaline pH effect, and silicate concentration is an important factor in the degree of protection.

3) The proposition that silicate reacts with Fe(II) species inhibiting its oxidation to Fe(III) species should be studied further.

4) Sodium silicate acts as an efficient corrosion inhibitor for iron in the presence of aggressive sulphate anions in these experiments.

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