

THE EFFECT OF CARBONATE/BICARBONATE ON THE ELECTROCHEMICAL  
BEHAVIOUR OF MILD STEEL IN ALKALINE MEDIA

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ABSTRACT

The Electrochemical behaviour of mild steel in equimolar carbonate/bicarbonate solutions was investigated by means of cyclic voltammetry.

In the pre-passive region the presence of three anodic peaks (peak I, II and III) indicated the participation of Fe(0), Fe(II) and Fe(III) in the electrochemical processes. The participation of carbonate/bicarbonate species in this region was detected by X-Rays diffraction.

At potentials  $> + 0.800$  V (SCE) the transpassive region begins with a sharp increase in current giving place to a novel peak preceeding oxygen evolution.

This peak is associated to Fe(VI) species, also being observed by the authors in the absence of carbonate/bicarbonate for solutions of NaOH with pH  $> 11.06$ .

The reduction peaks detected in the reverse scan (peaks VI, VIII and IX) correspond to the anodic peaks V, III and II respectively. This characterization was made by sweep

reversal studies. A subsequent chemical reaction is thought to be coupled to the electrochemical processes taking place in the transpassive region.

The present research work aims to contribute to the determination of the mechanism in the transpassive region. Further work related to the characterization of the transpassive peak is in progress.

INTRODUCTION

The electrochemical behaviour of iron and mild steel in carbonate/bicarbonate solutions has been investigated by means of galvanostatic, potentiostatic and potentiodynamic techniques [1-7].

The response of the system in terms of E-I profiles shows generally two anodic peaks when polarization is extended up to the oxygen evolution region [4]. The presence of only one peak is being reported in the literature for dynamic systems [6].

It is anticipated that in the active passive transition range the structure of the film is complex, probably a mixture of iron oxides and ferrous carbonate [4,7,8].

The nature of reaction products produced in the active passive transition have been examined with view to its implications in the behaviour of natural waters and pH also associated to stress corrosion phenomena [9].

The work described here utilizes, basically, cyclic voltammetry. For the transpassive region, the appearance of a conjugated pair in a well defined potential interval is reported for the first time. Data support that a chemical reaction is also part of the complex process taking place in the transpassive region.

EXPERIMENTAL

The working electrode was a cylinder made from mild steel with the chemical composition given in Table 1. The electrode with an exposed area of 0.078 cm<sup>2</sup> was mounted in epoxy resin.

Before each experiment the working electrode was polished with SiC paper of various grit size from 220 to 1000, then washed with double distilled water and degreased with ethanol.

Solutions were prepared from bidistilled water and chemicals of Analar grade. When necessary pH was adjusted by adding concentrated NaOH.

A Greene cell [10] was used in this work. The reference electrode was a saturated calomel electrode (SCE) placed in a separate compartment connected to the cell via an external bridge with a Luggin Harper capillary. As secondary electrodes two cylinders made from Pt were placed symmetrically to the working electrode.

Table 1. Chemical composition of the mild steel used as working electrode.

Element	C	S	P	Si	Mn	Fe
%	0.20	--	--	0.31	0.94	balance

Experiments were performed at room temperature ( $20 \pm 2^\circ\text{C}$ ). Cyclic voltammograms were obtained by running the potential between hydrogen and oxygen evolution regions ( $-1500 \rightarrow +1500$  mV (SCE)). Sweep rates ranging from 40 to 125.  $\text{mV s}^{-1}$  were used. Good reproducibility was always obtained. Most of the experiments were conducted in equimolar solutions of 100 and 600 ppm carbonate/bicarbonate. Concentrations from 50 to 1200 ppm were also used. A conventional equipment from PAR was used throughout.

### RESULTS

Fig. 1 shows a typical voltammogram for mild steel/carbonate/bicarbonate solution of 600 ppm, pH 10 at room temperature and at a scan rate of  $12.5 \text{ mV s}^{-1}$ .

The pre-passive region shows two well defined peaks at potentials  $-0.636$  and  $-0.262$  V(SCE) respectively. When the output is produced in a logarithmic scale a pre-peak and a third peak are also evident.

A considerable increase in current (density) was observed when the potential scan reached the end of the passive region giving place to a well defined peak in the transpassive region, well before oxygen evolution. This peak, identified in fig. 1 as peak V, was observed (by the authors) for the first time.

After the anodic limit was reached, the scan direction was inverted revealing 3 reduction peaks at potentials of  $+0.800$ ,  $-0.650$  and  $-1.080$  mv(SCE) referred to as VI, VIII and IX respectively.

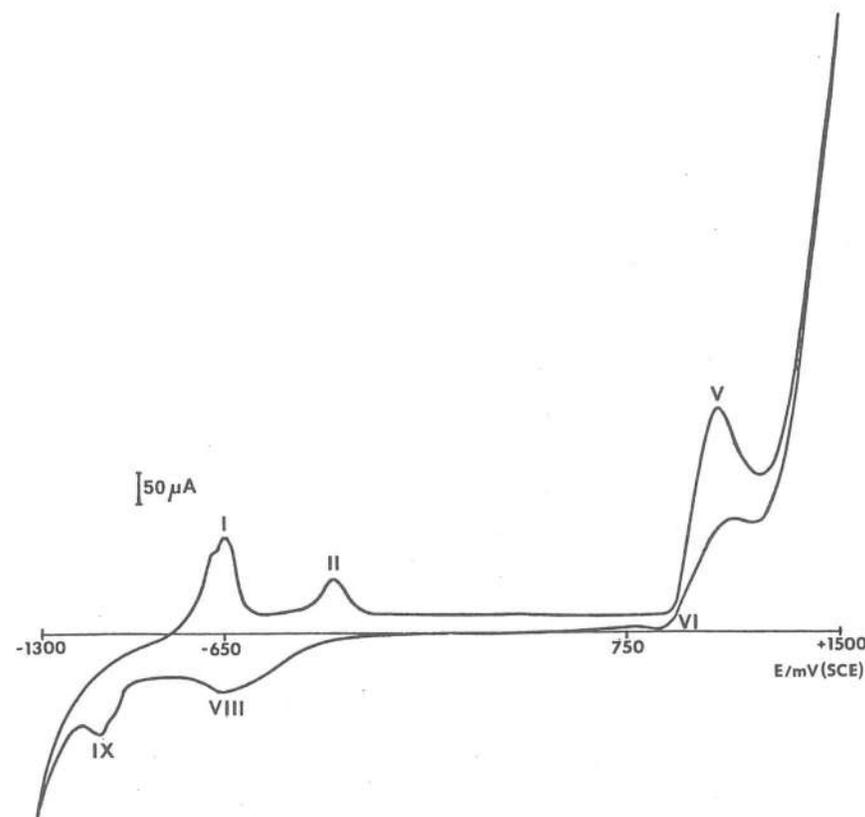


Fig. 1 - Cyclic voltammogram for the system mild steel/carbonate/bicarbonate, 600 ppm,  $v=12.5 \text{ mV s}^{-1}$ .

The possible correspondence between the anodic and cathodic observed peaks was made by the analysis of sweep reversal experiments.

According to fig.2 the correspondance is proposed to be:  
Peak I - Peak IX, Peak II - Peak VIII, Peak V - Peak VI.

If the potential scan is reverted before the formation of peak II, peak VIII is not observed. It is also noticeable that a reduction peak (VI) corresponds to the transpassive peak (V). An increase in the current of peak VIII characteristic of Fe (III) species reduction, is also associated to peak V.

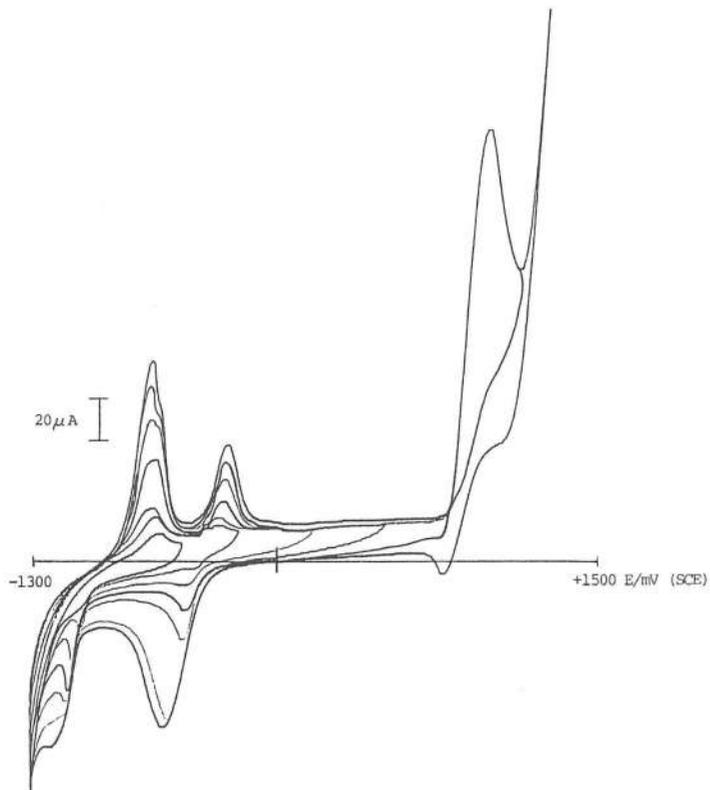


Fig. 2 - Sweep reversal experiment of the system mild steel/carbonate/bicarbonate, 600 ppm,  $v=12.5 \text{ mV s}^{-1}$ .

The E-I curves obtained for scan rates between  $1.25$  and  $125 \text{ mVs}^{-1}$  show well defined peaks for  $v$  values  $< 80 \text{ mVs}^{-1}$ . At low sweep rates peak I is unfolded into two peaks (see Fig.3), one of them probably corresponding to the pre-peak evident at higher sweep rates in both cyclic voltammograms and E-I curves produced in a logarithmic scale. Peak potentials agree well with values obtained from cyclic voltammograms.

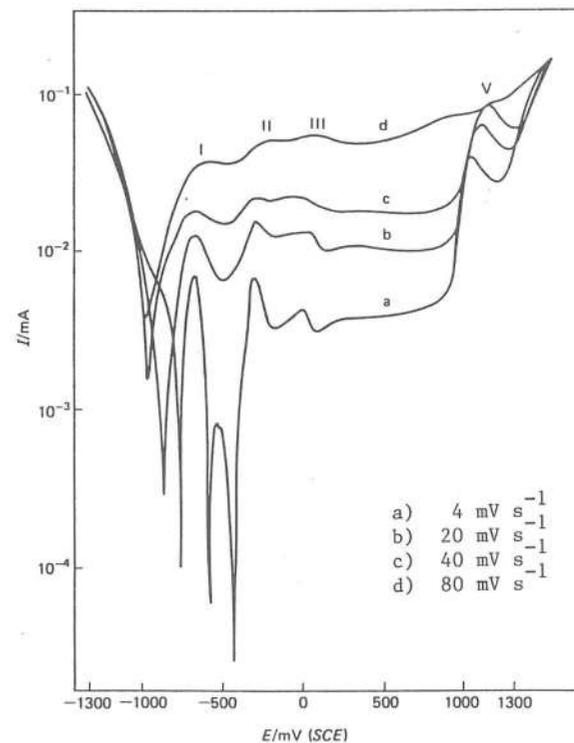


Fig. 3 - Sweep rate effect on the polarization characteristics of mild steel/carbonate/bicarbonate, 100 ppm.

The graphic representation of  $\log I$  vs  $\log v$  defines a straight line of slope  $0.38$  for solutions of  $600$  and  $100$  ppm for peak V.

Table 2 shows the effect of carbonate/bicarbonate concentration on the anodic characteristics of the system.

Table 2 - Potentials and peak currents as a function of carbonate/bicarbonate concentration,  $v=12.5 \text{ mV s}^{-1}$ .

ELECTROLYTE	PEAK I		PEAK II		PEAK III		PEAK V	
	$E_I$ (mV)	$I_I$ (mA)	$E_{II}$ (mV)	$I_{II}$ (mA)	$E_{III}$ (mV)	$I_{III}$ (mA)	$E_V$ (mV)	$I_V$ (mA)
50	-622.9	0.0048	-294.0	0.012	22.7	0.015	1059.7	0.030
100	-640.9	0.011	-289.0	0.012	25.0	0.011	1064.0	0.050
300	-620.3	0.034	-266.9	0.029	-61.7	0.024	1097.0	0.170
600	-621.7	0.0425	-274.1	0.027	+6.6	0.019	1110.4	0.310
900	-610.0	0.027	-260.0	0.011	0.0	0.0074	1070.0	0.185
1200	-622.9	0.021	-281.6	0.0175	16.5	0.012	1084.5	0.165

For all the peaks observed there is an increase in the current that reaches a maximum at a concentration of 600 ppm. This variation is more marked in the case of peak V.

In general the anodic characteristics evidenced in the presence of carbonate/bicarbonate are also reproduced in its absence eventhough higher values of pH solutions have to be used as seen in fig. 4. Peak V, as observed, is markedly affected by pH changes.

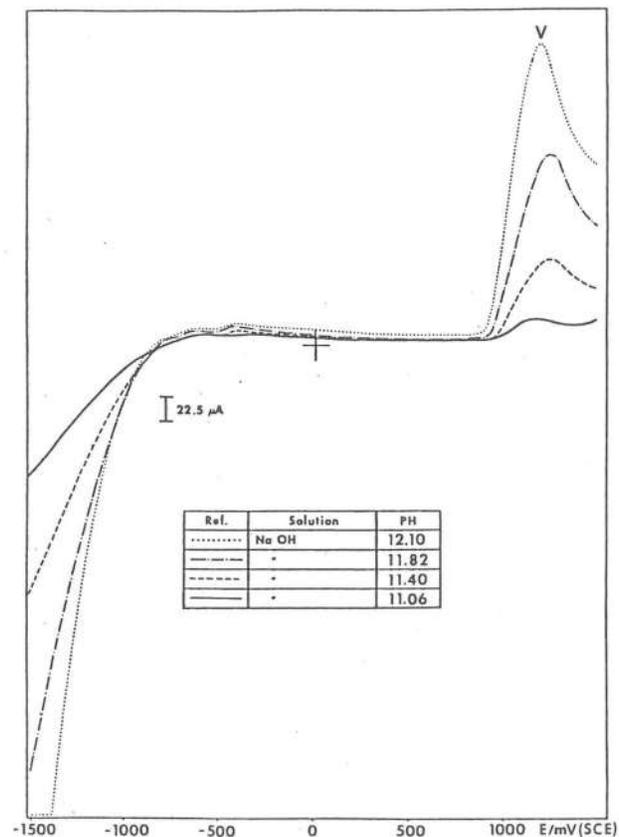


Fig. 4 - Effect of pH on the anodic characteristics of mild steel in NaOH solutions,  $v=12.5 \text{ mV s}^{-1}$ .

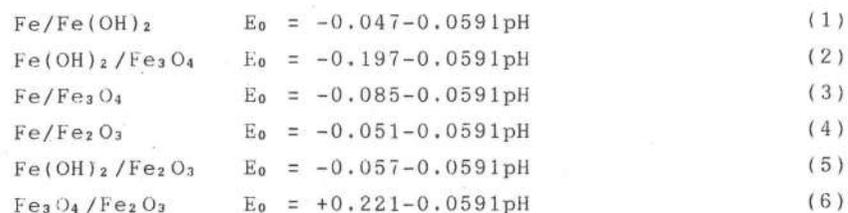
DISCUSSION

Active-passive

The last decades have seen a considerable development in the field of optical techniques applied to the elucidation of the composition and structure of the passive film on iron. Techniques such as Elipsometry [12] and Auger spectroscopy [13,14] have been used to identify the constituent species of the passive film on iron. To that respect and depending on the experimental conditions,  $\text{Fe}(\text{OH})_2$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$  and  $\text{FeOOH}$  are some of the identified species.

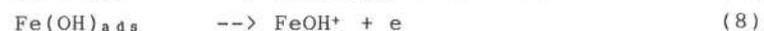
Eventhough there is abundant literature data available, there are still discrepancies on the identification of the oxide/hydroxide phases on iron produced during anodic dissolution.

According to Pourbaix [15] (in the range of potentials used in this work) the equilibrium potentials for the possible redox couples involved in film formation in the active-passive region can be evaluated using the following equations:



The peak frequently identified in the literature as peak I is not observed in alkalyne solutions of pH = 10. At potentials of  $\approx -1000$  mV (SCE) the peak in question is observed as a pre-peak [16]. The reproducibility of this peak is not satisfactory so that it does not allow quantitative analysis as is also referred in the literature [17].

The peak identified in this work as peak I for the system carbonate/bicarbonate, occurs in the potential region corresponding to Fe(II) species. The recent detection of the electroformation of FeOH species leads to the formulation of the following sequence of reactions for the formation of the Fe(OH)<sub>2</sub> hydrated film:



In the potential region corresponding to peak I the following experimental facts were evident:

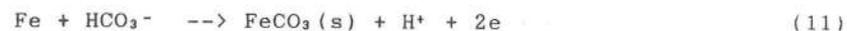
- an increase in the charge with carbonate/bicarbonate concentration [18];
- splitting of the peak at lower scan rates ( $v = 4 \text{ mV s}^{-1}$ );
- presence of FeCO<sub>3</sub> in the reaction products (X-Ray Diffraction).

Considering that for the system Fe-CO<sub>2</sub>-H<sub>2</sub>O the FeCO<sub>3</sub> is a stable phase [15], we can conclude that in the indicated potential region the film includes ferrous hydroxide and ferrous carbonate.

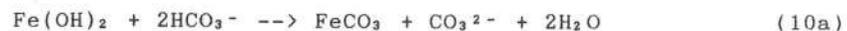
According to Davies and Burstein [7] for carbonate/bicarbonate solutions of pH 8.8 the formation of FeCO<sub>3</sub> can occur according to:



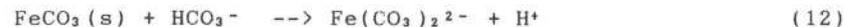
and/or



Due to the fact that a higher pH solution is used in this work, reaction (10a) is proposed to occur instead of reaction (10)



Preliminary studies indicate that in the potential domain of peak I there is a chemical reaction coupled to the electrochemical process (EC mecanism) [18]. The ferrous carbonate phase is attacked by HCO<sub>3</sub><sup>-</sup> and its dissolution occurs according to [7],



Peaks II and III were observed at potentials of -0.260 and 0 V(SCE) respectively being situated in the stability region of Fe(III) species. The formation of films that contain Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub> and FeOOH is being proposed by other authors [12]. Further studies in the pre-passive region might led to the proposal of electrode reactions responsible for peak III.

A passivation region extends from -0.100 V to ≈ 0.800 V (SCE). The peak potential values for peaks I and II are in agreement with published work [12, 19].

#### Transpassive region

The detection of a transpassive peak in alkaline solutions of carbonate/bicarbonate and sodium hydroxide was achieved in the present work by extending the polarization interval up to the end of the passive region in adequate pH conditions. It was possible, then, to establish the experimental conditions so to separate the processes corresponding to the formation of Fe(VI) species and the oxygen evolution reaction.

In the absence of carbonate/bicarbonate and for alkaline solutions of sodium hydroxide of pH > 13 Beck et al [20] detected a transpassive anodic "step" with a corresponding reduction peak that was associated to the couple Fe(III)/Fe(VI). In their experimental conditions the transpassive peak was not observed.

In the potential region corresponding to peak V the following experimental facts were observed:

- The charge under peak VI is very small when compared with the corresponding anodic peak (peak V);

- An increase in the charge under peak VIII is associated to the reduction of Fe(III) species probably resulting from chemical decomposition of Fe(VI) species;

-An increase in the peak current with an increase in temperature [18].

The obtained results are indicative of a process that include apart from the electrochemical process a coupled chemical reaction. The following reactions are admitted as probable,



A similar sequence was proposed by Beck et al [20] for the transpassive region in the absence of carbonate/bicarbonate for NaOH solutions of pH > 13.

It is believed that the main role played by carbonate/bicarbonate is that of lowering the activation energy for the generation of Fe(VI) species. This has also been suggested by Armstrong and Coates [6] for the active dissolution region.

#### CONCLUSIONS

The system mild steel in carbonate/bicarbonate solutions when studied by means of cyclic voltammetry revealed:

#### in the pre-passive region

- three oxidation and two reduction peaks corresponding to the participation of Fe(0), Fe(II) and Fe(III) species in electrochemical reactions together with HCO<sub>3</sub><sup>-</sup> and or CO<sub>3</sub><sup>2-</sup> according to peak potential.

- a chemical reaction coupled to the electrochemical process: the decomposition of Fe(VI) to Fe(III) species probably according to eq. (14).

- an EC mechanism according to evidence produced by cyclic voltammetry.

Research in this field continues with the kinetic characterization of the chemical and electrochemical processes occurring in the transpassive region.

#### ACKNOWLEDGMENTS

This work is partially financed by JNICT under Research Contract n<sup>o</sup> 510.83.87.

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(Received 21 April 1987

In revised form 17 July 1987)