# Temporal series micrographs coupled with electrochemical techniques to analysis pit corrosion in carbonate and chloride solutions

Alexsandro M. Zimer, Matheus A.S. de Carra, Lucia H. Mascaro, <u>Ernesto C. Pereira</u> Universidade Federal de São Carlos, LIEC – DQ – UFSCar, São Carlos - SP (e-mail: <u>amzimer@gmail.com</u>)

### Introduction

Considering the corrosion induced by  $CO_2$ , one of the most important parameter is the water chemistry. In this sense, the carbon speciation can change from very simple, with only a few carbonic species, as in the case of condensed water in gas pipelines, to a very complex speciation, for example, in those one found in the water emerging together with crude oil [1]. Corrosion of carbon steel in oilfield brines (as those pre-salt oil wells located Brazil) is mainly related to the presence of dissolved gases: mostly  $CO_2$ , and, in some cases,  $H_2S$ . Dissolved  $CO_2$  hydrates to form carbonic acid, which dissociates to hydrogen and bicarbonate ions. A second dissociation could occur leading to another hydrogen and a carbonate ions. When the solubility of salt is exceeded, it will precipitate and then there is the formation of a protective scale. The most common type of scale encountered in  $CO_2$  corrosion is iron carbonate [1].

In sour corrosion, iron carbonate becomes the secondary corrosive product because it depends on the partial pressure of the system to form iron carbonate passive film rather than sulfide one [2]. Carbonate and chloride solution have been widely studied in the literature in those cases where pitting corrosion occurs [3]. In the case of carbon steel in bicarbonate media, siderite, FeCO<sub>3</sub>, precipitates inside the pits as soon as the anodic dissolution of iron begins [4]. This film is a necessary condition for the growth of pits due to acidification of the surface region, together with the presence of chloride ions which activates the dissolution of iron. The reaction mentioned above is described below:

# $Fe^{2+} + HCO_3^- \rightarrow FeCO_3 + H^+$

Considering the exposed above, this work uses *in situ* optical microscopy aiming at to get local information about pitting corrosion during the constant potential measurements in carbonate solution. The approach was applied to investigate the influence of different chloride concentration during the pit initiation and it evolution under anodic polarization.

## Experimental

**Solutions:** 0.1 mol dm<sup>3</sup> carbonate solution was prepared by the dissociation of NaHCO<sub>3</sub> (Merck) in deionised water, pH 8.3. The chloride influence was investigated using the following percentages of: 1.5, 2.0, 2.25, 2.5, 3.0, 3.5, and 4.5 (wt.%) of the NaCl solution.

**Sample preparation:** Cylindrical AISI 1040 steel (Sanchelli) with 9.5 mm diameter (A =  $0.709 \text{ cm}^2$ ) was used as working electrode (WE). The material composition was determined by Atomic Absorption Spectroscopy analysis: 0.419% C, 0.703% Mn, 0.018% S, 0.007% P, 0.035% Ni, 0.132% Cu and 98.686 % Fe (wt. %). Prior to use, the samples were polished with sandpaper up to 2000-grit and then with diamond paste 1 and 1/4 µm, and degreased in acetone for 3 minutes in ultrasonic bath.

**Equipments and techniques used:** The electrode surface was observed by an inverted optical microscope (Opton - mod. TNM-07T-PL) and the images were collected using Scope Photo<sup>®</sup> 1.0 software. All electrochemical measurements were carried out using an Autolab model PGSTAT 30. As reference electrode (RE) a Ag/AgCl/KCl (Sat.) was used and a Pt wire was as auxiliary electrode (AE). The open-circuit potential ( $E_{oc}$ ) was measured up to its stabilization during 6000 s. Also was utilized the chronoamperometry (CA) technique with an overpotential of 350 mV shift positively from  $E_{oc}$  for 1800 s.

**Methodology:** To perform *in situ* image acquisition, the steel electrode was immersed in the corrosive solution in a home made flat-bottom cell [5] and 680 x 544  $\mu$ m<sup>2</sup> (0.52 %) of the surface electrode were recorded using an acquisition rate of 0.05 and 1 frame s<sup>-1</sup> during E<sub>oc</sub>

and CA measurements, respectively. Fig. 1 shows the flowchart used to convert images into information [6]. From color images (32 bits) up to a cubic matrix of  $f \ge c \le r$ , where: f = number of frames of time series micrographs ( $f = \sum (f_1 + f_2 + ... + f_n)$ ); c = horizontal resolution (columns); and r = vertical resolution (rows). This cubic matrix contains all temporal information of analyzed regions.



Fig. 1 - Flowchart used in digital image processing to converting the image in information resulting in a cubic matrix  $f \ge c \ge r$ .

This matrix can be correlated to the data of CA to create a three-dimensional model of the pit depths evolution. The Faraday's law and same considerations were used to do this: i) the current only flows through pits with a faradaic current efficiency of 100%, and ii) the current flowing through and each pit is proportional to pit's mouth area [6]. Using the molar mass of iron, the AISI 1040 steel density a fraction of total charge (Q<sub>t</sub>) of electrode was used to estimate the volume in cm<sup>3</sup> for each pit. In the final frame ( $f_n$ ), all pits were marked and the centroids for these places are fixed to create the three-dimensional model evolution of pits to estimate his depth (L<sub>pit</sub>). A conical geometry was chosen to represent each pit because it is closer to experimental observed by *ex situ* optical microscopy. For this last one, the pit depth was determined with a micrometer to comparing it with the depth estimated, after removing the porous deposit of pits with 5 % H<sub>3</sub>PO<sub>4</sub> solution.

#### **Results and Discussion**

Fig.2a presents some frames of time series micrograph for 2.5 % [CI<sup>-</sup>] in carbonate solution, at different times, together with the binarized ones, during the constant potential measurements. As can be observed all pits appear approximately until 50 s on steel surface.

Fig. 2b presents the number of pits vs. all chloride concentration. Initially the pit number follow the same behavior, i.e., increase reaching a plateau up to 50 s. Comparing the different chloride concentrations the number of pits increases until 2.5 % [Cl<sup>-</sup>]. For higher concentrations it is observed a decrease in its number. This occurs because at higher chloride concentration occur fusion of pits by the growth of his mouth, see insert of Fig. 2a.



**Fig. 2** – Time series micrographs with binarized images to Cl 2.5 % versus polarization time (a). Analysis of temporal series micrographs during CA measurements at different chloride concentration (%) to number of pits (b), total pit area (c). Overpotential of 350 mV over the E<sub>oc</sub>.

A different behavior is observed for the total pit area, Fig. 2c, where it is observed a monotonic increase of this parameter as a function of [Cl<sup>-</sup>]. In this case, the tendency a constant value is also observed, except for 3.5 % [Cl<sup>-</sup>]. This behavior occurs because all pits appear until stabilization time (50 s) and after just few pits presents a high increment. Such conclusions are corroborated in Fig. 2a where the insert show a pit evolution from 50 s to 1800 s. In the literature this behavior characterizes the metastable and stable pits growing in a surface, where a pit stabilization criterion must reached during pit growth to avoid it repassivation [7]. The existence of stable pits could be related to the precipitation of FeCO<sub>3</sub>

which induces itself the acidification of the electrolyte inside the pits. Then, there is a subsequent increase of the chloride concentration inside the pits to counter balance the  $H^+$  ions produced [3].



Fig. 3 – Analysis of temporal series micrographs during CA measurements at different chloride concentration
(%) to mean pit depths (a) all versus polarization time. 3D model evolution of pits to estimate each individual pit depths in Cl 2.5 % (b). Over potential of 350 mV on the E<sub>oc</sub>.

Fig. 3a presents the mean pit depths vs. [CI] estimated using the same procedure described before [6]. As can be observed, from 2.5 % chloride the raise of the pit depth is faster with chloride concentration increase. Fig. 3b presents the three-dimensional model for the evolution of pits. This calculation use a fraction of  $Q_t$  proportional to each pit surface area. As described in the literature [8] there is a distinct distribution on pit depths on metal surface during the pitting corrosion, Fig. 3b. To confirm these values, *ex situ* optical microscopy measurements were performed before and after to remove the porous deposit of pits (5 % H<sub>3</sub>PO<sub>4</sub>). It was found that there are a large number of pit on the surface with almost the same depth together with very deep pits generally 3-4 times deeper than the mean distribution. This qualitative behavior is also observed in Fig. 3b. The same behavior is found for the other experiments performed.

#### Conclusions

Here is presented a method to the study of corrosion reactions in real time by the analysis of a temporal series of micrographs. During the constant potential measurements it is observed that the number of pits increase and then stabilize for the [Cl<sup>-</sup>] studied. A different behavior is observed for the highest [Cl<sup>-</sup>] studied, i.e. [Cl<sup>-</sup>] = 3.5 % where a decrease in the number of pits was found. Besides, a monotonic increment of pit's mouth as a function of chloride concentration occurs. Finally, based on the normalized charge for a pit's mouth area and in Faraday's law, it was possible to calculate a 3D model of pits growth on the metal surface during the progress of pitting corrosion to predict his depth and distribution.

#### Acknowledgements

The authors would like to thank FAPESP, CNPq and CAPES for their financial support.

#### References

- [[1] S. Nesic, Corrosion 49 (2007) 4308-4338.
- [2] C. Ren, D. Liu, Z. Bai, T. Li, Mater. Chem. Phys. 93 (2005) 305-309.
- [3] M. Reffass, R. Sabot, M. Jeannin, C. Berziou, P. Refait, Electrochim. Acta 54 (2009) 4389-4396.
- [4] M. Reffass, R. Sabot, C. Savall, M. Jeannin, J. Creus, P. Refait, Corros. Sci. 48 (2006) 709-726.

[5] A.M. Zimer, E.C. Rios, P. de Carvalho Dias Mendes, W.N. Gonçalves, O.M. Bruno, E.C. Pereira, L.H. Mascaro, Corros. Sci. 53 (2011) 3193-3201.

- [6] A.M. Zimer, E.C. Rios, L.H. Mascaro, E.C. Pereira, Electrochem. Commum. 13 (2011) 1484-1487.
- [7] Y. Cheng, Electrochimica Acta 44 (1999) 4795-4804.
- [8] R.E. Melchers, Corrosion 61 (2005) 766-777.