Temporal series of micrographs coupled with electrochemical techniques to analyze pitting corrosion of AISI 1040 steel in carbonate and chloride solutions

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ABSTRACT

This work presents a method to study corrosion reactions in real time by the analysis of a temporal series of micrographs using in situ optical microscopy coupled to electrochemical techniques. The approach was applied to study the pitting corrosion of AISI 1040 steel during chronoamperometric measurements, in carbonate and chloride solutions. Using this coupled approach, it was possible to measure different pit parameters as well as to estimate the mean pit depth. The number of pits and the total pit area presented different behaviors as the chloride concentration increased and active and passive pits were detected.

Corrosion in carbonate and bicarbonate solutions in the presence of Cl− ions has been widely studied in [7,11–13] because the dissolution products are the same as those found in CO2 dissociation and hydration in aqueous media. Additionally, steel pitting corrosion has been described in these solutions [7,11–13]. During the corrosion of carbon steel in bicarbonate media, siderite (FeCO3) could precipitate inside the pits as soon as the anodic dissolution of iron begins [11], as follows:

\[ \text{Fe}^{2+} \text{(aq)} + \text{HCO}_3^- \text{(aq)} \rightarrow \text{FeCO}_3(s) + \text{H}^+ \text{(aq)} \]

In some cases, instead of a passive layer formation its breakdown occurs, promoting the initiation of pitting corrosion [14–16]. This film is a necessary condition for the growth of pits due to the acidification of the surface region along with the presence of Cl− ions, which activate dissolution of the iron. Then, Cl− ions tend to accumulate to counterbalance the H+ produced during the reaction [11] and, as a consequence, pits grow on the metal surface. In this context, Cl− ions could have an important role in pit growth and stability [13]. Regarding investigations of CO2 corrosion, the detrimental influence of Cl− ions on passivation phenomena probably results from the competitive adsorption between HCO3− and Cl− ions [13]. Thus, studies of the pitting corrosion of carbon steel in HCO3−/Cl− solutions will improve understanding of this corrosion process frequently observed in oil and gas fields.

1. Introduction

The corrosion of carbon steel in oilfield brines (such as those found in pre-salt oil wells) is mainly related to the presence of dissolved gases such as CO2 and H2S [1–4]. In sour corrosion, iron carbonate becomes one of the most important corrosion products and its presence depends on the CO2 partial pressure in the system [5]. This substance could lead to the formation of an iron carbonate passive film.

The consequences of the presence of CO2 corrosion must be investigated because it acts as an initiator of pit formation on the metal surface of steel pipelines [6,7]. In this case, the most common type of film found is iron carbonate, FeCO3 [1,8]. When its solubility is exceeded, precipitation of the compound over the metal [1] occurs, forming, in some cases, protective scales [9]. The protective aspect of this layer depends on the pH of the solution as well as the composition, temperature, and pressure [10]. Besides, other solid corrosion products can be formed in the presence of different chemical species in solution such as, Cl−, S2−, or O2 [5].

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The evolution of pitting corrosion in Cl⁻ solutions has been studied in the literature by following a single pit [17–19], multiple pits [20–22], or using combined techniques [23–26]. Recently, the evolution of pit size, the pit-to-crack transition, and the early stages of crack growth were studied by Turnbull et al. [27,28] and Horner et al. [29]. Under those conditions where pitting corrosion occurs, the pit depth distribution is the most important characteristic of the damage [30]. In this sense, Merchers [31–33] has worked on successive determinations of pit depth in steel coupons (calculated under oblique lighting and with a digital dial gauge) that had been exposed to marine conditions for many years. In those papers, a distinct distribution of pit depths was found. Melchers and Jeffrey [34] also described a probabilistic model for total corrosion loss and maximum pit depth distribution based on their previous studies. The distribution of pit depth has been a subject of research over many years. The dissolution kinetics of the pits has been studied and related to the transition in real pits from metastability to stability [35]. Cheng and Luo [36] showed that metastable pit growth is mainly controlled by the ohmic potential drop across the deposit over the pits’ cavities. According to Pistorius and Burstein [37,38], the oxide cover serves as an additional barrier to diffusion and thus maintains the anolyte at a sufficiently aggressive concentration. Thus, this special condition sustains the growth of stable pits [39]. Moreover, pit stability could be also associated with sufficient growth such that the pit depth acts as a diffusion barrier [15,37–39]. Uncertainty regarding the depth of a pit can be one of the most important factors in determining the time period until pipeline failure [40]. In this sense, in a previous paper [41] we developed an in situ method to estimate pit depth in an electrochemical experiment using a time series of micrographs of the surface employing this information together with Faraday’s law. Using the aforementioned method in another paper [42], it was possible to obtain three-dimensional information with spatial coordinates using the two-dimensional data from the micrographs together with the three-dimensional non-localized data from electrochemical measurements to estimate pit depths and, additionally, different parameters associated with them. In bicarbonate solutions, such method can be employed to follow pitting corrosion, allowing quantification of the contributions of passive and active pits, in addition to providing the mean depth distribution of pits under the detrimental influence of chloride ions.

Considering the above, this work uses an electrochemical technique coupled to in situ optical microscopy aimed at obtaining local information about pitting corrosion during chronoamperometric measurements in alkaline carbonate solutions containing chloride ions. This approach was also applied to investigate the influence of chloride concentration during pit initiation and evolution.

2. Experimental

The carbonate solution (0.1 mol dm⁻³) was prepared by the dissociation of NaHCO₃ (Merck) in deionized water at pH 8.3. The influence of chloride ions was investigated using the following weight percentages of NaCl (JT Backer) in the solution: 1.5, 2.0, 2.25, 2.5, and 3.5 wt.% (0.26, 0.34, 0.38, 0.43, and 0.6 mol dm⁻³). Prior to data acquisition, the solution was deaerated for 10 min with N₂.

Cylindrical AISI 1040 steel (Sanchelli) with a diameter of 9.5 mm (A = 0.7 cm²) was used as the working electrode (WE). The material composition was determined by Atomic Absorption Spectroscopy (AAS) analysis: 0.41% 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 WEs were abraded with sandpaper up to 2000-grit and then polished with diamond paste (1 and 1/4 μm). Finally, they were degreased in acetone for 1 min in an ultrasonic bath. As the reference electrode (RE) and auxiliary electrode (AE), Ag/AgCl/KCl (sat.) and a Pt wire were used, respectively.

An Autolab model PGSTAT 30 was utilized to carry out the electrochemical measurements. The open-circuit potential (Eₒ) was measured up to its stabilization during 6000 s. After stabilization, chronoamperometric measurements (CA) were performed with an overpotential (η) 350 mV more positive than Eₒ for 1800 s. The optimization of the η to be applied during the chronoamperometric measurements was investigated in the lowest chloride concentration, i.e., 1.5 wt.%. The value of 350 mV was chosen because it allowed us to observe the first pitting nucleation when the in situ image of the electrode surface was compared with many others investigated values of η, i.e., 200, 250, 300, 350, 400 and 450 mV. Then, this aforementioned η was applied in the experiments performed for all the investigated solutions. The η was chosen for optimal use of the technique and thus differed from the standard approach. It is important to stress, therefore, that any other experimental conditions can also be chosen.

During Eₒ and CA measurements, the electrode surface was observed in situ by an inverted optical microscope, OM (Opton model TNM-07T-PL). A temporal series of micrographs was collected using the Scope Photo® 1.0 and MCDE (AMCAP) software in a homemade flat-bottom cell. An area of 680 μm x 544 μm, 0.52% of WE, was recorded using an acquisition rate of 0.05 and 1 image s⁻¹ during the Eₒ and CA measurements, respectively. We were careful to follow different positions of the electrode in order to assure that this small part of the surface was representative of the whole process occurring during the measurement. This was performed by starting from the center of the WE and by following towards the corner of the sample in orthogonal directions. Thus, several in situ micrographs were collected in these new positions and were compared with the last frame of the temporal series. For each experimental condition, the pit dispersion was similar over the entire electrode surface. The temporal series of micrographs were collected at the center of the electrode during a CA measurement.

Fig. 1 shows the flowchart used to convert the images (frames) from the temporal series of micrographs into quantitative information [43]. In this figure, all steps in the image analysis are presented, i.e., from color images (32 bits) to a three-dimensional matrix where all temporal information is preserved.

Using the procedure described in previous papers [41,42], a three-dimensional model of pit evolution was created using a fraction of the total charge consumed during the pit formation. Using

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**Fig. 1.** Flowchart used in digital image processing to convert the image into information resulting in a three-dimensional matrix, f x c x r.
Faraday’s law, it was possible to predict the pit depth considering that the pit presented a bullet shaped geometry [28]. It is important to remember that frame acquisition is a linear function of time, and that the fraction of total charge changes in every frame according to the pit mouth area observed during CA. Thus, using this procedure, it was possible to quantitatively analyze different responses from the system during the CA measurements: i) number of pits, ii) total pit area, iii) individual pit area, iv) pit radius, and v) mean pit depth.

3. Results and discussion

A typical $E_{oc}$ measurement is presented in Fig. 2 for the solution containing 2.5% [Cl$^-$]. This curve presents the general shape described in the literature [44]: an induction period (point 1) followed by a fall to more negative values, indicating the beginning of pitting corrosion (point 2), followed by a potential stabilization (point 3). All the $E_{oc}$ data presented the same behavior. Under the conditions employed, few pits grew on the surface at $E_{oc}$ (inset 1 in Fig. 3).

The CA experiments were performed after potential stabilization using an overpotential 350 mV more positive than the measured $E_{oc}$. During CA, Fig. 3, all the pits emerged within 50 s of initiating the experiment (insets 1 and 2, Fig. 3). After this time period, pit growth was observed on the electrode (insets 3-6, Fig. 3). It is important to stress that the number of pits remained constant. This procedure was used for all the solutions investigated. Insets 2 and 6 (Fig. 3) also present magnifications of the regions marked with dotted squares to highlight a group of pits.

Fig. 4 presents the number of pits as a function of the [Cl$^-$]. To make it easy to analyze the data, this figure only shows the first 200 s of each CA. Initially, the number of pits increased, reaching a plateau at 50 s. Comparing the different [Cl$^-$], the number of pits increased until 2.5% [Cl$^-$] (see curves 1-5, Fig. 4) while, at still higher...
concentrations, a decrease in their number was observed (see curve 6, Fig. 4). One possible explanation for this change in behavior for the highest $[\text{Cl}^-]$ studied could be the existence of pit coalescence. This proposition is supported in the magnifications presented in insets 2 and 6 (Fig. 3), where it is possible to observe the coalescence of different pits.

A different behavior was observed for the total pit area, shown in Fig. 5, where an increase in this response occurred as the $[\text{Cl}^-]$
increased. Otherwise, for each solution, a tendency to a constant value was observed when the polarization time was greater than 50 s, except for the 3.5% [Cl−] solution. One possible explanation for this behavior is that, after 50 s, only a few pits continued to grow. Then the total pit area remained approximately constant throughout the experimental run. This hypothesis will be investigated further in the following text.

As discussed above, Fig. 5 can be divided into two distinct regions, indicated by a dotted line in that Figure. The first, region A, occurs up until 50 s, where the pit area presents a sharp increase. The second, region B, occurs after this time, during which the total pit area shows only a slow increase. In order to summarize these data, the slopes of these curves were calculated in each region (Table 1).

From the results presented in Table 1, it is possible to observe that the first slope increased for [Cl−] up to 2.5% but then decreased for [Cl−] at 3.5%. These results are similar to those highlighted in Fig. 4, where for [Cl−] greater than 2.5% there was a decrease in the number of pits compared to lower [Cl−]. One possible explanation for this fact is the coexistence of two phenomena in this region, such as new pit nucleation and pit growth. In other words, pit nucleation could govern the changes observed in slope A until 2.5% [Cl−] (see Fig. 4). On the other hand, in the second region, the changes observed in slope B are only affected by pit growth once the number of pits is constant (see also Fig. 4). Thus, an increase in the number of active pits must be observed on the metal surface as [Cl−] increases. This proposition can easily be confirmed in Fig. 6, where the arrows indicate those pits that continue to grow from 50 s to 400 s.

This complex behavior is also observed in Fig. 7, where the mean pit radius ($r_{mean}$) as a function of the time is plotted for all the investigated solutions. In this Figure, it can be observed that until 50 s, there was a strong increase in $r_{mean}$ values, which could be associated with pit growth on the surface after nucleation. After this time point, an evident decrease in this parameter was observed, which could be attributed to the formation of protective FeCO3 scales inside the pits, although some of them still continue to grow. This last proposition can also be clearly observed in Fig. 6.

A second argument to test the latter statement is the behavior verified for several individual pits, which are presented in Fig. 8. This Figure presents an experiment performed in 2.25% [Cl−], which is representative of the general behavior observed in all other studied solutions. As can be observed, some of the pit radii grew continuously while others clearly stopped changing, characteristic of passive and active pits, respectively [37]. In this case, a pit stabilization criterion must be reached during pit growth to avoid repassivation [36]. In the corrosion of carbon steel by CO2, the existence of active pits could be related to the precipitation of FeCO3 inside them, which induces local acidification as described in the literature [1,11]. Therefore, a subsequent increase in [Cl−] occurs to counterbalance the H+ ions produced [11]. Then, the existence of mass transport through the scale inside the pit could determine their activity or passivity [1]. Another point that can sustain the growth of active pits is the behavior of pit depth [15,37,38], which is described in the following paragraphs.

It is important to point out that the interpretation of Fig. 8 corroborates the total pit area behavior presented in Fig. 5, i.e., where two distinct regions were found. As proposed above, pit nucleation probably governs the changes observed in region A, while pit growth governs the changes in region B (Fig. 5 and Table 1). Then, considering all the data combined, most probably the existence of the second slope observed in Fig. 5 is related to the presence of a small number of active pits that are still growing in region B. Therefore, in region B, only these active pits are responsible for the observed behavior. These results are in qualitative agreement with those described by Melchers and Jeffrey [34], who found a distinct depth distribution during pit corrosion of steel coupons in a marine environment. Here, a distinct radii distribution was also observed once active and passive pits were detected on the metal surface.

In this context, Fig. 9 presents the mean pit depth ($L_{pit}$) behavior, calculated using a procedure described previously [41,42]. This model is based on the fraction of the charge for each pit at each time point during electrochemical experiments. Then the pit volume ($V_{pit}$) is calculated using Faraday’s law, considering a bullet-shaped pit to estimate the pit depth ($L_{pit}$). As can be observed in Fig. 9,
for [Cl−] greater than 2.5%, there is a change in the $f_{pit}$ behavior. According to Pistorius and Burstein [37,38], pit stability could also be associated with pit depth, which acts as a diffusion barrier to sustain stable pit growth. This affirmation is corroborated in Fig. 9 along with the in situ binarized images of Fig. 6 (see arrows) that show a high occurrence of active pits in the same experiment (Fig. 6f).

Further work based on temporal series of micrographs coupled with electrochemical techniques [41,42] could also be done to obtain the individual depth of each pit. This would require some modifications to the model described in the previous paragraph in order to estimate the depth of each pit.

In summary, the approach used here allows different parameters associated with pits to be followed as a function of time during an electrochemical experiment. In this sense, substantial information can be provided, which immensely contributes to overall understanding of the pit growth mechanism.

4. Conclusions

This study presents a method to study corrosion reactions in real time by analyzing a temporal series of micrographs coupled to electrochemical techniques. During chronoamperometric measurements, it was observed that the number of pits increased initially and then stabilized at a plateau value at all the [Cl−] studied. Nevertheless, a different behavior was observed for [Cl−] greater than 2.5%, where a decrease in the number of pits was found compared to experiments at lower [Cl−]. Otherwise, a monotonic increment in the total pit area was found that was proportional to [Cl−]. From this last plot, two slopes were calculated where, for the first one, region A, both pit nucleation and growth were observed and there was evidence that pit nucleation governs the process in this region. The pit radius analysis allowed us to infer the existence of two different kinds of pits, i.e. active and passive. Therefore, region B is governed by the growth of active pits in the metal surface. Finally, based on the fraction of the total charge and using Faraday’s law, it was possible to estimate the mean pit depth on the metal surface during the progress of pitting corrosion.

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