REVISIÓN DE "LAS PRIMERAS ETAPAS DE LA CRISTALIZACIÓN DE LA SIDERITA DURANTE LA CORROSIÓN POR CO2 DEL ACERO, EVALUADA MEDIANTE DISPERSIÓN IN SITU DE RAYOS X DE PEQUEÑO Y GRAN ÁNGULO".

REVISITING "FIRST STAGES OF SIDERITE CRYSTALLIZATION DURING CO2 CORROSION OF STEEL EVALUATED USING INSITU SYNCHROTRON SMALL AND WIDE ANGLE X-RAY SCATTERING."

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RESUMEN

Las primeras etapas de la cristalización de la siderita son de suma importancia para desarrollar un mejor modelo de corrosión por CO_2. En la literatura, se ha informado de un gran esfuerzo experimental en el que se siguió la formación de siderita cristalina mediante difracción de rayos X, durante la aplicación de un potencial anódico constante en un electrodo de acero al carbono. Las condiciones permitieron la formación de escamas de siderita. Sorprendentemente, los transitorios de corriente obtenidos tenían la forma distintiva de un proceso de nucleación electroquímica. Sin embargo, tras revisar sus datos experimentales, se descubrió que, como se esperaba, la nucleación de siderita no es electroquímica. El carbonato de hierro se nuclea con unas tasas de frecuencia de nacimiento comparables a las de la nucleación proteica y mucho más lentas que las de la nucleación electroquímica. También se descubrió que la cinética de disolución del hierro (velocidad de corrosión) se ve afectada por dos procesos 1) la producción de una película de gel amorfo de carbonato de hierro y 2) la nucleación de siderita y el crecimiento de cristales.

Palabras clave: Corrosión por CO_2, nucleación de siderita y crecimiento de cristales, cronoamperometría.

ABSTRACT

The first stages of siderite crystallization are of a paramount importance to develop a better CO_2 corrosion model. Literature has reported a tremendous experimental effort where they followed the formation of crystalline siderite by X-ray diffraction, while a constant anodic potential was applied on a carbon steel electrode. The conditions were for siderite scale to be formed. Surprisingly, the current transients obtained did have the distinct shape of an electrochemical nucleation process. However, after reviewing their experimental data, it was found that, as expected, siderite nucleation is not electrochemical. Iron carbonate nucleates with a birth frequency rates comparable to protein nucleation and far slower than electrochemical nucleation. It was also found that the kinetic of iron dissolution (corrosion rate) is affected by two processes: 1) the production of an iron carbonate amorphous gel film and 2) siderite nucleation and crystal grow.

Key words: CO_2 corrosion, siderite nucleation and crystal growth, chronoamperometry

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1. INTRODUCTION

CO_2 corrosion of mild steel in the oil and gas industry has been widely investigated. In those investigations, the experimental work on iron carbonate nucleation and scale formation has been performed. Williams et. Al[1]. speculates that the possible reactions occurring are:

$$Fe + CO_3^{2-} \rightarrow FeCO_3(crystalline) + 2e^- \qquad (1)$$

$$Fe \rightarrow Fe^{2+} + 2e^- \qquad (2)$$

$$Fe^{+2} + CO_3^{2-} \rightarrow FeCO_3(colloid) \qquad (3)$$

Reaction (1) claims that the crystallization of siderite is an electrochemical process, which produces two electrons. Also, reaction (3) is an independent reaction, which produces iron carbonate in a colloidal form.

The experiments supporting these reactions were performed after imposing different constant potentials on carbon steel in 0.5 M NaCl, at 80 °C and pH 6.5. Due to the imposed constant anodic potential, the current is only due to reaction (2). Surprisingly, the current transients presented the distinct shape of an electrochemical nucleation process. Given that Fe^{2+} is not nucleating and it is the product of the only electrochemical reaction occurring. Why did those currents showed that behavior?

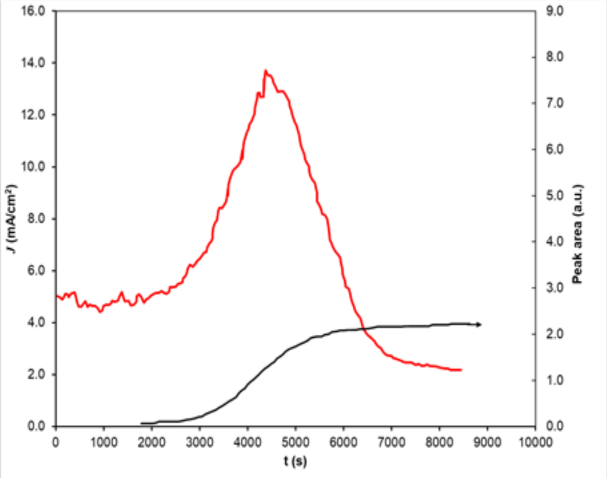

Figure 1 Digitized Figure 11³ from [Ko 2015]. The main axis is the current density of an electrochemical experiment with CO2-saturated 0.5 M NaCl, pH=6.8 at 80°C under potentiostatic control at -500 mV (vs. Ag/AgCl). The corrosion products were followed by X-ray diffraction, only crystalline iron carbonate (siderite) was detected and the peak area of the siderite signal is presented in the secondary axis.

In this paper it is shown that indeed, the only electrochemical reaction is reaction (2). However, the non-electrochemical iron carbonate nucleation and crystal growth affects its kinetics.
All efforts in achieving a clear understanding on the fundamentals on CO_2 corrosion are of a paramount importance to get a better CO_2 corrosion model.

2. RESULTS and DISCUSSION

Figure 11[3] was digitized to gain the experimental data on the current density and the Peak area of the X-ray diffraction signal for the siderite crystal growth. Figure 1 presents those results, it presents the behavior of the corrosion current of carbon steel by CO_2. The current remains constant at 5.0 mA/cm² for 2000 seconds. Then, it increases to arrive to a maximum current of 13.7 mA/cm² around 4500 seconds and then, it decreases to 2.0 mA/cm². Co-occurring with the increase of the current, the Peak area of the X-ray diffraction signal due to the formation of crystalline iron carbonate increases. It presents a slow beginning, then it accelerates and over time reaches a maximum constant value, which also coincides with the 2.0 mA/cm² relatively constant current.

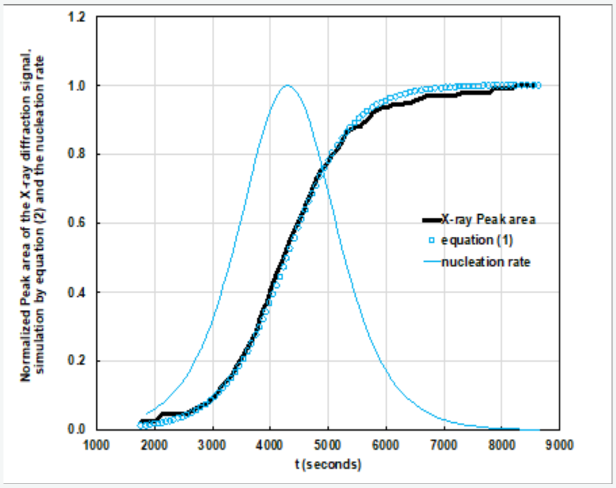

Figure 2 Comparison of normalized Peak area of the X-ray diffraction signal with the behavior predicted by equation (2). The nucleation rate is also shown.

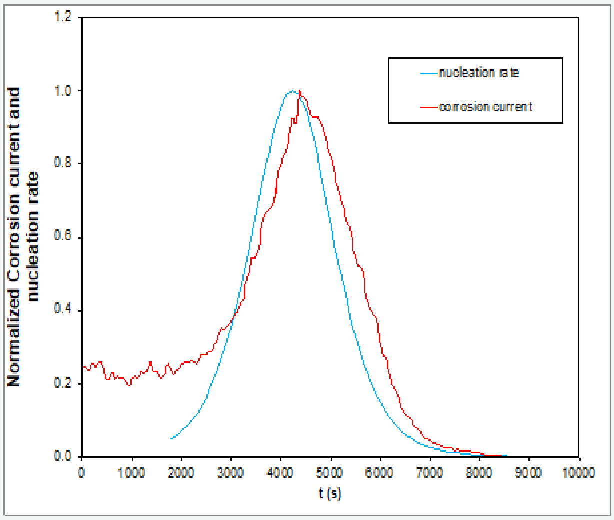

Figure 3: Normalized corrosion current and nucleation rate.

Experimental studies under constant supersaturation have indicated that after some initial time lag, the early crystal nucleation stage is slow, then speeds up gradually (nearly exponential upside), and slows down by approaching the final stage where saturation is established, i.e. a nucleation rate of zero[4]. This is precisely what the corrosion current is showing in Figure 1. During the initial time lag, the current remained constant for 2000 seconds and then, it increased and slowed down exponentially. The problem is that Fe^{2+} is not nucleating. Then, why is this current following a clear nucleation pattern?

The S-shaped progression presented by the Peak area of the X-ray diffraction signal (see Figure 1) can be described by the following logistic function[4] .

$$n = \frac{n_s}{1 + \exp\left[-k(t - t_c)\right]} \qquad (4)$$

Where n is the iron carbonate nuclei number density, ns is the saturated nuclei number density, k is the "birth" frequency and tc is the time when the maximum nucleation rate is reached. Figure 2 presents the fitting of the experimental Peak area of the X-ray diffraction signal to equation (4). Also, Figure 2 presents the nucleation rate, dn/dt , which is just the time derivative of equation (4).

The "birth" frequency, k, obtained for iron carbonate (see Figure 2) was 0.0018 s^{-1}. This is way lower than, for example, the electrochemical silver crystal nucleation measured by Milchev[5], which renders k = 9130 s^{-1}; or for the electrochemical mercury droplet nucleation6, k = 1384 s^{-1}. Therefore, as expected, iron carbonate nucleation is not an electrochemical process. This iron carbonate "birth" frequency is comparable to ones found for protein nucleation, such as insulin and bovine β-lactoglobulin[4].

Figure 3 compares the nucleation rate, dn/dt , observed in Figure 2 with the corrosion current in Figure 1. The corrosion current indeed follows the shape of the nucleation rate. However, it occurred around 300 s after the iron carbonate crystal formed. This is the iron carbonate crystal happened and, then the corrosion current increased.

As iron dissolution (2) occurs, Fe^{2+} reacts with bicarbonate anions in solution, producing $FeCO_3$ molecules,

$$Fe^{2+} + HCO_3^- \rightarrow FeCO_3 + H^+ \qquad (5)$$

These iron carbonate molecules are in a colloidal form, see reaction (3) and they also accumulate at the interface metal/solution producing an amorphous ferrous carbonate gel layer[7], which blocks the surface,

$$n - FeCO_3 \longrightarrow FeCO_3(AFC) \qquad (6)$$

In this gel layer, a heterogeneous nucleation process is occurring. This involves the formation of a critical nucleus, which is stable enough to allow the formation of the new phase, i.e. the crystal,

$$FeCO_3(AFC) \longrightarrow FeCO_3(Cryst) \qquad (7)$$

As the siderite crystal grows, it will consume the amorphous ferrous carbonate gel layer. This clears the metal surface from blockage.

In turns, a previously covered metal surface is exposed. Metal dissolution[2] enhances and the production of new iron carbonate molecules[5] increases. This feeds the growing crystal[7] directly. The whole process becomes autocatalytic and the corrosion current[2] increases exponentially.

As iron carbonate crystal grows, it covers the surface where the crystal born and it also consumed all extra iron carbonate molecules produced. Therefore, the iron carbonate supersaturation is destroyed and no chance to start another crystal occurs. Hence, all crystal growth stops.

As discussed, reaction (2) is indirectly affected by the production the amorphous ferrous carbonate gel film[6] because it blocked the metal surface and by the nucleation and growth of the siderite crystal, because it destroys the blockage. If this is so, two co-occurring currents should suffice to account for the total corrosion current. One current will decrease progressively to account for the blockage of the surface and the other should follow the nucleation rate. On Figure 4, this result if observed,

The remaining corrosion current occurring after the first nucleation and growth of the iron carbonate crystal is just going back to built a new supersaturation stage. This time with less metal surface to contribute to the formation of the amorphous ferrous carbonate gel layer.

3. CONCLUSIONS

The nucleation and crystal growth[8] of iron carbonate indirectly affect the electrochemical dissolution of iron.

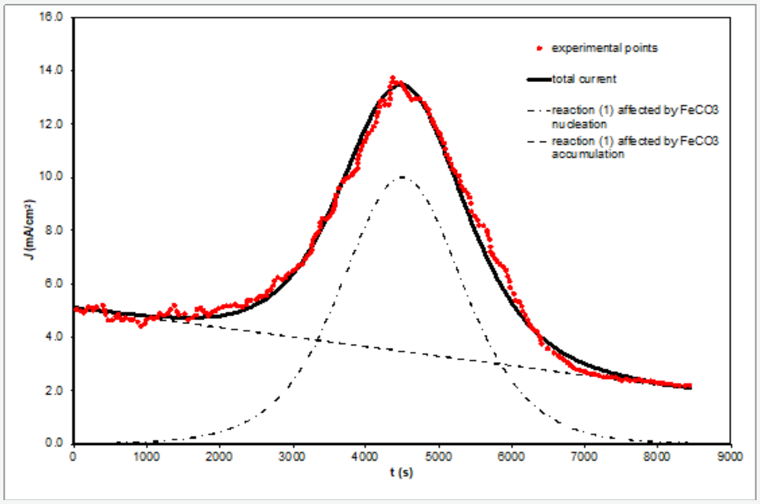

Figure 4: Simulation of the corrosion current, reaction (1), as the sum of two contributions.

(1) It is a process controlled by an energy barrier and this is why such accumulation occurs. The functional form of the nucleation rate is,

$$rate = N_0 \cdot Z \cdot j \cdot f(\theta)\exp(-\Delta F^{*}/kT)$$

where ΔF* is the free energy cost of creating the critical nucleus. By definition the probability of an event occurring is proportional to the exponential of minus the free energy cost of the event over the thermal energy kT. Thus the exponential factor comes from the, very low, probability of forming a nucleus at the top of the energy barrier.

The prefactor is the product of four terms: the number density of active sites for nucleation per unit area No , the rate at which molecules attach to the nucleus causing it to grow, j, a function of the contact angle between the critical nucleus and the surface, f(φ) and the Zeldovich factor Z. This last factor is there as the probability that a nucleus at the top of the barrier will go on to form the critical nucleus. If it is less than one, thus the rate at which a nucleus actually crosses the barrier and grows into a new phase is Z j. The angle φ is the contact angle the nucleus and the bulk phase make with the surface. This angle is determined by the interactions between the surface and the molecules in the nucleus7 .

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