



Study of the effect of deposit of allotropic forms of calcium carbonate and related carbon steel interface behavior

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Abstract

This work reports on the possible protecting role of the calcium carbonate layer against corrosion of carbon steel substrate into synthetic water media. The electrochemical impedance spectroscopy measurements (EIS) of metal-scale-water interface made in the free electrode potential of steel after two hours of stabilization, were used to evaluate the coating performance of calcium carbonate deposits. The (EIS) recorded data during the calcareous deposition were also simulated using equivalent electric circuit (EEC) method. The interpretation of the results of (SIE) is discussed as a function of the morphology of the surface formed on the working electrode found from the SEM picture (Scanning Electron Microscopy). The electrochemical behavior of scaled surfaces was studied by corrosion potential measurements.

Keywords: Corrosion, scaling, carbon steel, chronoamperometry, potentiometry, electrochemical impedance spectroscopy.

1. Introduction

Scaling is the corrosion of carbon steel are two phenomena often encountered when metal is in contact with natural water, or worn distribution. They usually lead to problems both technical and economic. The formation of these deposits causes a malfunction of industrial facilities. It causes a gradual reduction in pipe sections with increased losses, even their obstruction. These problems are observed in a spectacular way, in parts of the North African countries that exploit geothermal water drawn from deep aquifers. These waters are used mostly for irrigation, geothermal, but also for human consumption in certain regions. This is the case in southern Tunisia, where the water table infill Continental operates. The major problem with its use is corrosion and scaling in pipes and cooling towers after a few years of operation. The study of scaling corrosion interaction then seems necessary to understand the mode of action of these two phenomena steel water interface and look for the best conditions to minimize adverse effects on the different types of facilities. The phenomenon of interaction between the process of corrosion and scaling presented below has been little attention from researchers and work on this issue reflect the results and relatively contradictory interpretations. According Bousselmi et al. [1], the presence of the reduction products formed on the carbon steel surface immersed in a drilling water, forms a barrier against the diffusion of oxygen and results in slower corrosion kinetics. These products consist of an adherent deposit of calcium carbonate and a magnesium hydroxide layer. Similar results were observed by Ben Amor et al. [2] which have shown that the corrosion potential of the middle steel charge sulphate ions, the metal surface was covered in part by calcite crystals. This deposit is strongly influenced by the hydrodynamic conditions and composition of the medium studied. Keysar S. et al [3] have shown in their turns as scale acts as a protective layer against the corrosion of steel. M. E. Botello-Zubiate et al. [4] have studied the influence of the magnetic treatment of water of the nature of the crystallographic variety of calcium carbonate formed and the kinetics of the electrochemical corrosion of the carbon steel. The observations showed that calcite is the main form of calcium carbonate formed.

This variety is transformed into aragonite under the action of the magnetic field. The speed of the electrochemical corrosion was evaluated using the polarization curves. The results obtained showed that the

highest corrosion rate is observed in the presence of aragonite. However, H. Moller et al. [5] pointed out that the deposition of scale, particularly aragonite protects steel by reducing the corrosion rate. In a more recent study Y. Ben Amor et al. [6] used the electrochemical impedance spectroscopy to describe the behavior of ordinary steel interfaces water containing Mg^{2+} ions. Whatever the crystallographic variety of calcium carbonate that has been obtained, measurements have mounted that the metal surface was accessible to the diffusion of dissolved oxygen. The corresponding reduction reaction occurs in the pores formed between crystals of $CaCO_3$ and the metal surface. To study the interaction between both corrosion and scaling, deposits are formed on the working electrodes in the chronoamperometric trials. After scaling, the cathodic polarization is stopped and monitor the free potential is recorded during two hours of immersion. Studied interfaces are subsequently characterized by electrochemical impedance measurements at open circuit potential. This latter technique makes it possible to evaluate the steel corrosion rate in carbon coated by the deposition of scale. The protective efficacy of these deposits against corrosion is discussed in terms of the crystallographic variety deposited on the surface of the selected metal.

2. Materials and methods

2.1. Electrolytes

The aim of this work is to study the electrochemical behaviour of ordinary carbon steels cover by calcium carbonate layer during their immersion in synthetic water. Electrolytes were prepared from analytical grade reagents: hydrated magnesium chloride, sodium chloride, and calcium carbonate. They were dissolved in deionized water. The calcium and chloride concentrations were fixed respectively at $2.5 \times 10^{-3} \text{ mol L}^{-1}$ and $1.7 \times 10^{-3} \text{ mol L}^{-1}$. Three magnesium concentrations were examined: $0 \times 10^{-3} \text{ mol L}^{-1}$, $3 \times 10^{-3} \text{ mol L}^{-1}$ and $6 \times 10^{-3} \text{ mol L}^{-1}$. Immersion dept is approximately 10 cm. Water temperature is 25°C and pH is around 8.

2.2. Metal

The carbon steel used as working electrode was obtained from well tubing [7]. The working electrode, 0.2 cm^2 in active area, was embedded in inert resin and polished with silicon carbide paper up to 1200 grade before each experiment. A rotating disk electrode (Tacussel, model EDI 101) was used with a rotation speed (ω) which was varied between 300 rpm and 2000 rpm.

2.3. Electrochemical experimentation

A three-electrode cell was used with a rotating disk as working electrode, with a saturated calomel reference electrode, and with a platinum plate as a counter electrode. Electrochemical measurements were carried out with a PGZ 100 Galvanostat potentiostat coupled to a monitored by VOLTMASTER.4 software. EIS data were collected at the scaling potential imposed for a period of 180 min. The impedance measurements were performed at frequencies between 65 kHz and 0.1 Hz. The applied AC voltage was $\pm 10 \text{ mV}$. Chronoamperometry [8] was used to investigate the scaling process. The applied potential ($-1V_{ECS}$) corresponds to the reduction process of dissolved oxygen [9]. The impedance data collected under different experimental conditions were analyzed by a physical model developed from the work of Gabrielli et al. [10].

The SEM pictures were obtained on a JEOL 5410 to characterize the different scaling products deposited on the metallic surface.

3. Results and discussion

3.1. Scaling accelerated measurements

The chronoamperometric measurements were performed in all three environments under a polarization of $-1V_{ECS}$. This potential is optimal for the accelerated scaling test. It corresponds to the process of diffusion of the dissolved oxygen. The speed of rotation of the working electrode is fixed at 1200 rpm. The influence of the latter parameter has been extensively studied and several authors have shown that convection seems to have more effect for higher speeds or equal to 600 rpm [6]. The curves obtained are summarized in Figure 1. The examination of these shows a monotonic decrease of the cathodic current as a function of immersion time.

This decrease is due to the progressive recovery of the active surface of the carbon steel by the calcium carbonate nuclei. These curves show a retarder effect of the kinetics of calcification in presence of magnesium ions. Indeed the fall of the current under $-1V_{ECS}$ is faster in the presence of the solution (S_1) free Mg^{2+} ions. In the latter case the normalized current approaches a value near zero indicating a more significant blockage of the

active surface of the electrode. Extrapolation of chronoamperometric curves allows among other measures to determine two scaling parameters (Table 1).

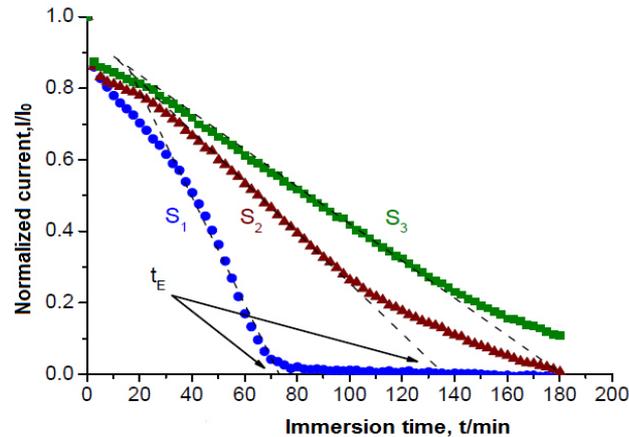


Figure 1: Chronoamperometric curves during formation of deposits at -0.1VSCE , in artificial underground Tunisian water: (S_1) $0 \times 10^{-3} \text{ mol L}^{-1} \text{ Mg}^{2+}$, (S_2) $3 \times 10^{-3} \text{ mol L}^{-1} \text{ Mg}^{2+}$, (S_3) $6 \times 10^{-3} \text{ mol L}^{-1} \text{ Mg}^{2+}$

The first is the time scaling defined as the time required for the current to achieve low and stable value (Figure1). It corresponds to the intersection of the tangent at the point of inflection of the curve with the abscissa axis. The second parameter is the normalized residual current measured at the end of the test.

Table 1: Variation of the scaling parameters studied in the three solutions.

$[\text{Mg}^{2+}]/\text{mol L}^{-1}$	0×10^{-3}	3×10^{-3}	6×10^{-3}
t_E/min	73	135	180
$(I/I_0)_r$	9.6×10^{-3}	1.26×10^{-2}	10.9×10^{-2}

This parameter can provide information relating to the adhesion and the porosity of the deposit formed on the metal surface. Increasing the time scaling is related to the effect of the plating retarder in the presence of Mg^{2+} ions. The slower kinetics is observed in the presence of the solution (S_3) the charged more magnesium ions. The deposit formed in this solution is the less compact with a residual normalized current 10 times greater than that characteristic of the deposit obtained in the presence of the solution (S_1) in free Mg^{2+} . This parameter increases when the concentration of these cations becomes larger. This change is likely due to the formation of different crystallographic nature of deposits according to the content of Mg^{2+} ions. To discuss this we used the scanning electron microscopy to characterize the deposits formed by chronoamperometry.

3.2. Scanning electron microscopy

This technique has been applied to determine the morphology of the deposits formed on the surface of the working electrode. The micrographs of Figure 2 relate to deposits formed on the steel surface immersed in the solution (S_1) in free Mg^{2+} ions. These images were taken at two different immersion time. Faces of the formed deposit indicate that it is calcite with conventional rhombohedrons crystallization with sharp edges, which is particularly evident in the micrograph in Figure 2a. These images show the progressive recovery as a function of immersion time of the active surface of the electrode by the crystals of calcium carbonate. This overlap is not reflecting the current decay observed on the chronoamperometric measurements (Figure 2b). In the presence of the solution (S_2), the micrographs show large structural deformations compared to basic rhombohedrons of the calcite which characterize the magnesium calcite (figure 3). The first variety is usually observed in the presence of sulphate ions [11, 12], so that the appearance of aragonite is related to the incorporation of the magnesium ions on the surfaces of crystalline calcite. These results are in agreement with what is generally cited in the literature [13, 14]. According to these references, in the presence of solution S_3 , the fixed operating conditions, including the polarization potential and the speed of rotation of the working electrode, should promote the formation of aragonite. After the deposition of the three varieties crystallographic, cathodic polarization stopped to follow the variation of the free potential as a function of immersion time.

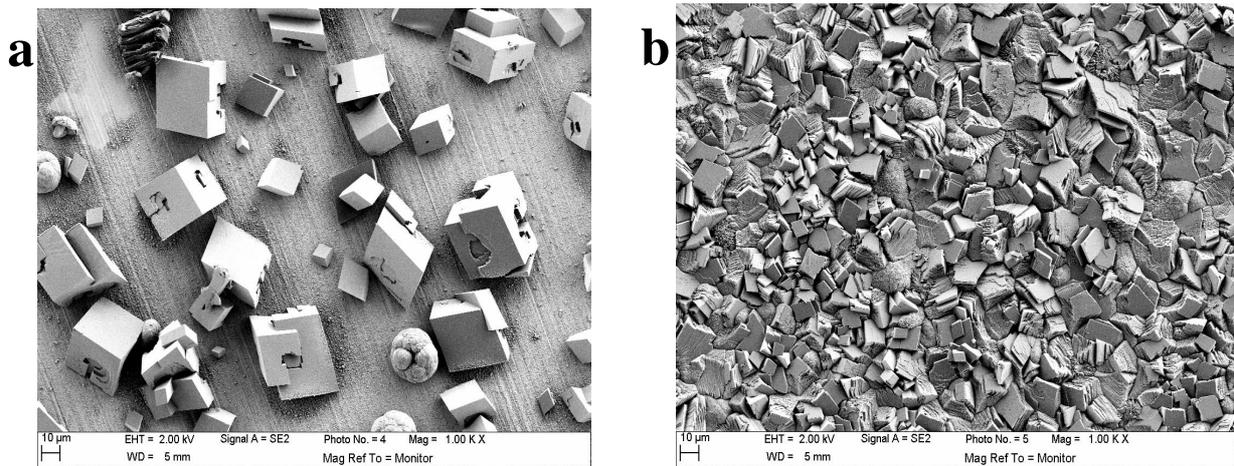


Figure 2: Characterization by scanning electron microscopy of the formed deposit at $-1 V_{ECS}$ in the presence of the solution (S1): (a) after 30 min, (b) after 180 min immersion.

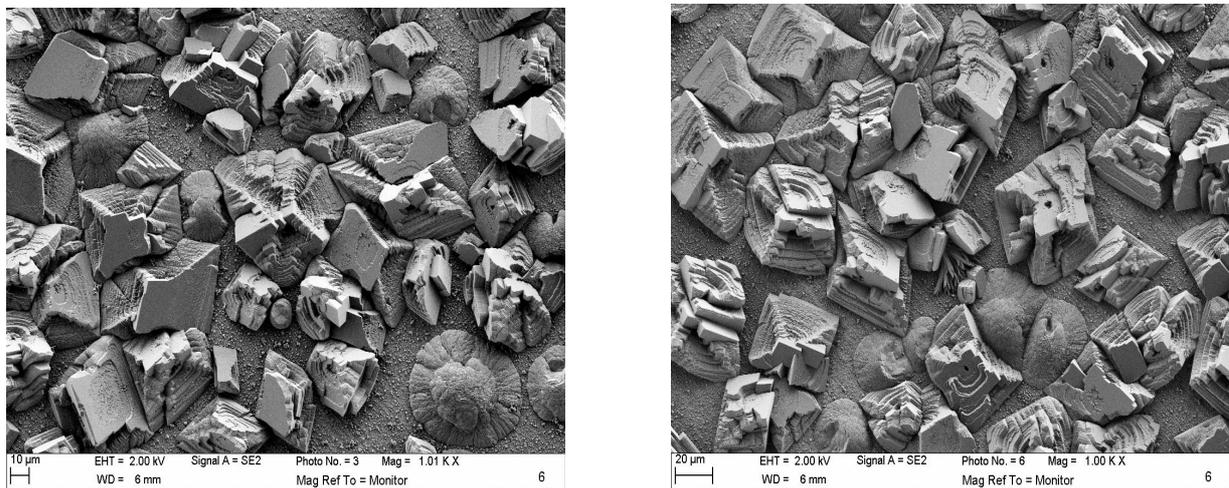


Figure 3: Characterization by scanning electron microscopy of the formed deposit at $-1 V_{ECS}$ in the presence of the solution (S₂): $[Mg^{2+}] = 3 \cdot 10^{-3} \text{ mol L}^{-1}$. Images of two different areas on the electrode surface.

This monitoring is performed at the same speed of rotation of the working electrode. After two hours of stabilization, electrochemical impedance measurements are performed in order to characterize the three interfaces to the same potential. The results for this part of the work will be presented in the following paragraph.

3.3. Electrochemical impedance spectroscopy

Electrochemical impedance measurements (EIS) were performed at a free potential the electrode of carbon steel covered with scale deposit after two hours of stabilization. The speed of rotation is once again fixed at 1200 rpm. Figure 4 shows the patterns obtained in the three studied solutions. These graphs are made up of two capacitive loops. The first high frequency (HF) over 10 Hz and the second, larger in size, is located at lower frequency (LF). The shape of the latter involves a limited diffusion process. This same functionality was already assigned [6]. Careful observation of the high frequency loop also shows a form similar to that of a limited diffusion impedance, but at frequencies much higher than those characteristic of that process. This shift is related to a current distribution inside the interstices between the crystals of calcium carbonate and the metal surface [15]. Indeed this will be discussed when we propose the equivalent model to the interface that will be adopted to reproduce the electrochemical impedance measurements.

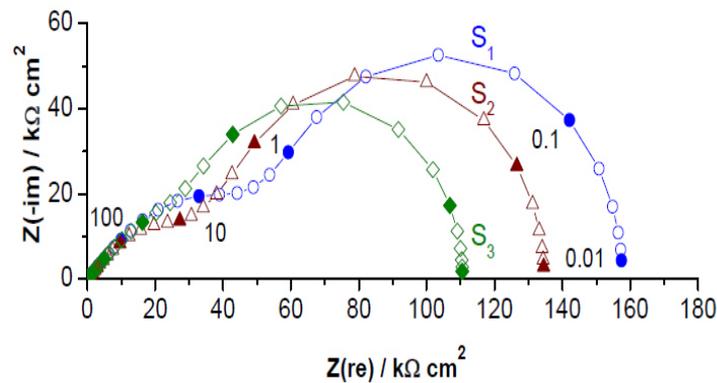


Figure 4: Electrochemical impedance spectrum at open circuit potential of the electrode coated with a scale deposition in three solutions: (S₁) Mg²⁺ free, (S₂) [Mg²⁺] = 3 × 10⁻³, (S₃) [Mg²⁺] = 6 × 10⁻³ mol L⁻¹.

3.4. Choosing an equivalent model

If recovery of the metal surface by the scale deposit is partial, diagrams obtained are generally attributed to the diffusion of dissolved oxygen with a partially blocked area [14]. Otherwise, the electrode surface becomes strongly blocked against the oxygen diffusion. Under these conditions, the limit of the high frequency loop reflects a slope close to unity. This is linked to the behavior of a porous electrode. In this model the oxygen diffuses through the pores and cavities which are formed between the crystals of calcium carbonate and the surface of the electrode [15]. Taking into account the morphology of the deposit and the appearance of the electrochemical impedance spectra of the studied interface can be represented by the diagram of Figure 5. In this figure, the CaCO₃ crystals are shown by blocks, in agreement with the SEM images of Figures 2 and 3.

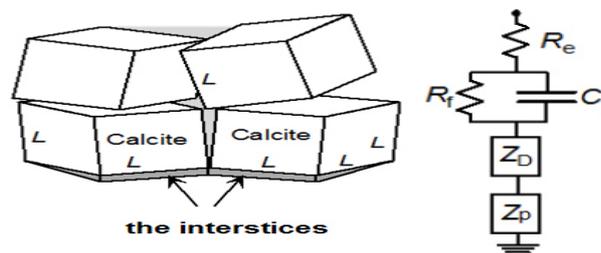


Figure 5: Physical model of the carbon steel/synthetic water interface and the equivalent model.

In this model the electrolyte penetrates between the cubic calcium carbonate and comes into contact with the metal. These gaps are shaped V. They are shown in light gray in the figure. From these geometrical considerations, an equivalent electric circuit is then provided as illustrated in figure 7. In this circuit R_e is the resistance of the electrolyte, R_f, C_f and Z_f represent the resistance of the solution through the film and the capability of the dielectric nature of the layer of calcium carbonate and the impedance of the film. To evaluate the charge transfer process, we have reproduced in Table 2 the values of R_t and C_d. The ability inversely proportional to R_t, is the active surface in the crystals of calcium carbonate.

Table 2: Charge transfer parameters

[Mg ²⁺]/mol L ⁻¹	0×10 ⁻³	3×10 ⁻³	6 ×10 ⁻³
Formed deposit	Calcite	Deformed calcite	Argonite
R _t (Ω.cm ²)	310	120	35
C _d (μF.cm ⁻²)	45	68	75

The corresponding values are in agreement with the model proposed by the porous electrode Gabrielli et al. [15]. They are of the order of magnitude of a double layer capacitance (a few μF.cm⁻²) and show that the surface is accessible to diffusion of dissolved oxygen. Examination of these values also shows that the presence of

aragonite (solution S₃), the surface of the steel is much more accessible than that covered by the magnesium calcite (solution S₂) and calcite (in the case of solution S₃). The transfer resistance is inversely proportional to the corrosion rate [16]. For the different media studied, the R_t values are relatively low, they vary in the range of 35-310 Ω cm². In addition, more the concentration of magnesium ion is more important the resistance of charge transfer is low. This seems to disagree with the retarder effect of the corrosion kinetics observed in the presence of these cations [13]. This contradiction is explained by the blocking effect of the three crystallographic varieties formed on the carbon steel surface. Indeed, the protection against corrosion provided by calcite appears to be more effective than that of magnesium calcite and aragonite including that or the transfer resistance is 10 times lower compared to its value obtained in the presence of free areas Mg²⁺ ion.

Conclusion

The objectives of this work were aimed at to provide a better understanding of the influence of magnesium ions on the calcareous deposits formed on steel under cathodic protection in artificial underground Tunisian waters and to propose a physical model which explains the interfacial behavior. The chronoamperometric measurements were performed at a potential of -1V_{ECS}. The curves obtained show that increasing the Mg²⁺ ion content retards limestone deposition and causes the formation of a scale deposit covering less. Observations by scanning electron microscopy show the presence of three crystallographic varieties of calcium carbonate. Calcite is formed in the presence of magnesium ion-free solution. In the presence of these cations, calcite becomes magnesium calcite and aragonite for the most responsible solution Mg²⁺. These crystallographic varieties were subsequently characterized by electrochemical impedance spectroscopy at open circuit potential to evaluate their effectiveness in protecting steel against corrosion. The values of charge transfer resistance and the double layer capacitance extracted from these measurements show that whatever the variety formed on the metal surface, it is accessible to the diffusion of the dissolved oxygen. However, it seems that the calcite provides more protection than the magnesium calcite and aragonite.

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