# A study by electrochemical impedance spectroscopy and surface analysis of corrosion product layers formed during CO<sub>2</sub> corrosion of low alloy steel

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## Abstract

In the following research, electrochemical and surface analysis techniques are used to define the main contributing factor to the protectiveness offered by a scale formed at high temperature and pH under  $CO_2$  saturated conditions. At 80°C and pH 6.6, trace amounts of a magnetite (Fe<sub>3</sub>O<sub>4</sub>) phase was identified at certain locations beneath a more dominant iron carbonate (FeCO<sub>3</sub>) film. Furthermore, over time, the evolution of the corrosion product layer towards a very low porosity results in a "diffusion barrier" that is indicated by a positive shift in the open circuit potential and is considered key to corrosion protection.

**Keywords:** carbon steel; electrochemical impedance spectroscopy analysis; CO<sub>2</sub> corrosion; iron carbonate; magnetite; pseudo-passivation.

## List of abbreviations acronyms and symbols:

Abbreviation	Meaning
<i>p</i> <sub>CO2</sub>	Carbon dioxide partial pressure
R <sub>ct</sub>	Charge transfer resistance
СРЕ	Constant phase element
α	CPE double layer capacity distribution
	parameter
Q <sub>dl</sub>	CPE double layer capacity parameter
Q <sub>film</sub>	CPE film parameter
Di	Diffusion coefficient of specie i
Z <sub>d</sub>	Diffusion impedance
Ki	Diffusion impedance dimensionless frequency
R <sub>d</sub>	Diffusion impedance scale factor
$\delta_{f}$	Diffusion layer thickness
C <sub>dl</sub>	Double layer capacity
EEC	Electrical equivalent circuit
EIS	Electrochemical impedance spectroscopy
S <sub>a</sub>	Electrochemically active surface area
R <sub>e</sub>	Electrolyte resistance
EDX	Energy dispersive X-Ray fluorescence
C <sub>film</sub>	Film capacity
A	Film covered area
d	Film thickness
GIXRD	Grazing incidence X-Ray Diffraction
HF	High Frequency
i	Imaginary unit
LPR	Linear polarization resistance
LF	Low Frequency
MF	Medium Frequency
ОСР	Open circuit potential
1	Pore length
R <sub>pore</sub>	Pore resistance
ξ	Porosity
ε	Relative permittivity of corrosion product film material.
VRMS	Root mean square voltage
SEM	Scanning electrochemical microscopy
STEM	Scanning transmission electron microscopy
R <sub>solution</sub>	Solution resistance
t	Time
$\varepsilon_0$	Vacuum permittivity
W <sub>d</sub>	Warburg semi-infinite element

#### 1. Introduction

Carbon dioxide (CO<sub>2</sub>) corrosion is encountered in a large sector of industries. Dissolved in water, it may cause significant corrosive degradation to carbon steel; however, under certain conditions, a "protective" scale by-product may form on the surface. This corrosion scale has been shown to reduce the initial CO<sub>2</sub> corrosion rates by as much as three orders of magnitude [1–4]. The importance of corrosion scale to CO<sub>2</sub> corrosion science and prevention is well recognised and has led to intensive investigation over the last decades in a both quantitative and qualitative capacity [5–10]. However, the complexity of the nucleation and growth process in iron carbonate (FeCO<sub>3</sub>) film formation results in a remaining uncertainty in the relationship between the growth of CO<sub>2</sub> corrosion product films and the protective ability of the corrosion scale i.e. the state of the developed film in which it may be deemed "protective".

Corroborating research has shown that "protective" corrosion product films can only be formed rapidly when the temperature is above 70°C and pH 6 [7,11]. The effect of pH and temperature on  $CO_2$  corrosion has been studied extensively in literature [12–14] and are considered prime factors in corrosion product film performance. However, despite continuous research showing how environmental factors affect the protective ability of the corrosion scale, as noted in a study by Kinsella et al. [1], the protectiveness of the developing scale is also a function of exposure time and is an important aspect of note in the evaluation of the "protective" ability of the film.

A series of long duration tests in a  $CO_2$  saturated environment at high temperature and pH have been carried out in literature [11,14–17] with experimental results showing a sudden increase in open circuit potential (OCP) accompanied with a significantly reduced mild steel corrosion rate at a noted point in time. This phenomenon has in some instances been termed "pseudo-passivation". Combined surface analysis techniques have shown that FeCO<sub>3</sub>, also known as siderite, is the dominant phase within these conditions however, in some cases, trace amounts of another compound is also observed to be present. In a study by Han et al. [16], experiments were carried out at a pH of 8 (at 80°C, 0.53 bar  $CO_2$ ) to investigate the morphology and chemical composition of the surface film that is projected to form under these conditions. The study showed that after approximately 60h of immersion, a rapid increase in the OCP was noticed. A combined grazing incidence X-Ray diffraction (GIXRD) and scanning transmission electron (STEM)/ energy dispersive X-ray fluorescence (EDX) profiles identified that a trace amount of magnetite (Fe<sub>3</sub>O<sub>4</sub>) was shown to be present after

"pseudo-passivation" and primarily located at the boundaries of FeCO<sub>3</sub> crystals. In another study by Li et al. [11], experiments were carried out at pH 5.6 to 7.8 at 80°C, 0.53 bar CO<sub>2</sub>. The results showed that "pseudo-passivation" occurred more rapidly at a higher pH and was only observed above a threshold pH of 6.0. However, unlike the study by Han et al. [16], the surface analysis techniques employed showed no direct indication of any phases other than Fe and FeCO<sub>3</sub> existing on the surface. The study concluded that a thin (~1 µm) adherent inner FeCO<sub>3</sub> layer is responsible for "pseudo-passivation" and given the rise in open circuit potential, it was deduced that the protection comes from the retardation of the anodic reaction more than the cathodic reaction. Other similar studies have proposed other carbonates containing compounds such as Fe(OH)<sub>2</sub>CO<sub>3</sub> [18] and Fe(OH)<sub>2</sub> [19] to be present amongst the FeCO<sub>3</sub> layer and is suspected responsible for "pseudo-passivation".

Electrochemical impedance spectroscopy (EIS) analysis has been frequently carried out to understand the corrosion mechanism of steel in a  $CO_2$  environment at ambient temperature and acidic pH [20–23]. Under these conditions, typical impedance diagrams contain a high frequency (HF) capacitive loop associated with the charge transfer resistance in parallel with the double layer capacitance. An additional contribution, either inductive or capacitive has also been observed at lower frequencies, in the mHz domain. Equivalent electrical circuit (EEC) modelling is used to provide an analysis of the experimental data and the evolution of the fitting parameters (double layer capacitance, charge transfer resistance, etc.) provide a real physical measuring of such parameters in the given conditions. There is a relative consensus on the impedance models used within this environment. However, only a few studies [1,7,14] are found that use EIS analysis in conditions that favour the formation of carbon dioxide corrosion scales.

In a study by Gao et al. [7], experiments were performed in order to investigate the growth mechanism of CO<sub>2</sub> corrosion product films in a high pressure and temperature environment. Tests were performed in conditions of 75 and 90°C, 10 bar pCO<sub>2</sub> and pH 6.6. EIS analysis results showed a single capacitive loop at all-time instances with the amplitude of the loop increasing with respect to corrosion time indicating that the charge transfer process slows down. A further analysis through linear polarisation resistance (LPR) measurements and scanning electron microscopy (SEM) observations showed that a corrosion product film layer initially developed on the carbon steel surface causing the decline in corrosion rate. After a noted "critical point", the values of LPR remained approximately stable at a high value and this behaviour was addressed to correspond with the appearance of an outer layer above the

carbon steel original surface. Therefore, two different equivalent electrical circuits, shown in Figure 1, were used to fit the impedance data at the different time instances and to quantify the differences in  $CO_2$  corrosion product film structures near the "critical point". The equivalent circuit shown in Figure 1(a) was used to simulate an electrode surface with a low conducting surface film present [24] and features one layer of  $R_1$  and  $C_1$  in addition to the existing structure that consists of an electric double layer capacitance  $C_{dl}$  and charge transfer resistance,  $R_t$ . After the "critical point", a second layer was observed corresponding to  $R_2$  in parallel with  $C_2$  as shown in figure 1. The evolution of the fitting parameters showed that the transfer resistance  $R_t$  was observed to increase with time indicating that the corrosion product films became denser. Furthermore, the values of  $R_2$  and  $C_2$  were calculated to be both lower than  $R_1$  and  $C_1$  indicating that this second layer was thinner than the first layer as observed in the SEM images. Within this study, EIS results showed no evidence of a clear change due to the formation of a second film.

#### [Figure 1]

In contrast, in another study by Tanupabrungsun et al. [14], EIS results showed characteristic changes in the impedance behaviour of mild steel exposed to a  $CO_2$  corrosive environment at conditions of high temperature (80-200°C) and pH values of 4.0 and 6.0. The changes in the impedance behaviour was attributed to the formation of FeCO<sub>3</sub> scales. In the tests carried out at pH 4.0 and 80°C, where SEM observations showed no corrosion product, the Nyquist plot represented corrosion behaviour indicative of the charge transfer process (single capacitive loop). At a higher pH of 6.0, the Nyquist plot similarly showed a single semi-circle which is characteristic of Faradaic impedance implying a charge transfer controlled corrosion phenomena at the early time periods. At later time periods, it changed to a double semi-circle which indicated mass transfer dependence which coincided with SEM images that showed that the steel surface was covered by a corrosion product layer. At higher conditions of temperature ( $> 120^{\circ}C$ ), where superior formations of FeCO<sub>3</sub> scales were observed, EIS analysis results showed that the Nyquist plot indicated diffusion control for both pH values at low frequency. In this study, semicircle fitting of Nyquist plots was not carried out to provide a quantitative understanding of impedance behaviour.

Within this work, EIS, in conjunction with surface characterisation techniques, was used to study the corrosion scales formed under two conditions of pH at atmospheric total pressure for a 12 days time-frame. Electrical equivalent circuit (EEC) modelling is used to interpret the electrochemical and interfacial processes on the electrode surface in the given conditions.

The aim of this paper is to track the development of the corrosion scale deposit and characterize the protective states of film development, to identify the composition of the "pseudo-passive film" and to use EIS analysis to further understand the "pseudo-passivation" behaviour observed in literature.

#### 2. Experimental

Hereafter a brief experimental procedure will be outlined, a more detailed version has been reported in a previous article [33].

#### 2.1 Sample Preparation

The material investigated is API 5L X65 carbon steel sample. The microstructure of the steel, as shown in Figure 2, consists of a ferro-pearlitic grain structure and its chemical composition is indicated in Table 1. A cylindrical rod (surface area =  $6.9 \text{ cm}^2$  for pH 6.6 test and  $4.6 \text{ cm}^2$  for pH 6) was the working electrode and rectangular corrosion coupons (surface area =  $4.0 \text{ cm}^2$ ) were added in order to perform ex-situ surface analysis. All the samples were polished up to 600 grit SiC paper.

#### [Figure 2]

#### [Table 1]

#### 2.2 Experimental Procedure

Temperature was kept constant at  $80 \pm 2$  °C for every test. An electrolyte concentration of 0.2 wt% NaCl was added. All the experiments were performed in stagnant conditions at atmospheric pressure, moreover the solution was kept saturated with CO<sub>2</sub> by continuously bubbling the gas into the cell. At the above-mentioned conditions carbon dioxide partial pressure is 0.54 bar. Two tests were performed at pH 6 and 6.6 correcting the pH with sodium bicarbonate. The procedure for solution preparation is detailed in a previous article [33].

This test procedure ensures that the residual dissolved oxygen content in maintained below 50 mass. ppb.

A Biologic SP200 potentiostat monitored the corrosion rate using electrochemical impedance spectroscopy (EIS) measurements. EIS measurements were carried out with the cylindrical carbon steel sample as the working electrode, a KCl saturated Ag/AgCl reference electrode and platinum wire as the counter electrode. A perturbation of  $\pm$  10 mV sinus amplitude (V<sub>RMS</sub>  $\approx$  7.1 mV) around the corrosion potential was applied with a range of frequency of 30 kHz to 0.1 Hz for pH 6.6 and to 0.01 Hz to pH 6. Ten impedance values were registered for each

frequency decade. Each EIS measurement was preceded by an open circuit potential (OCP) measurement of about 15 min. OCP and EIS measurements were repeated over a time period of 10 to 12 days.

Sample coupons were removed from the cell rinsed with acetone and distilled water, dried and subsequently stored under vacuum for preventing corrosion to continue. The samples were both extracted during the test and at its completion. The samples were then retained under vacuum before scanning electron microscopy (SEM), X-Ray diffraction (XRD) and electron backscatter diffraction (EBSD) analysis. SEM imaging was carried out on a FEI Nova NanoSEM 450 microscope, XRD analysis of the samples was carried out using a PANalytical X'Pert Pro Diffractometer, using Cu-K $\alpha$  radiation and EBSD analysis was performed using a ZEISS Supra 55 VP microscope. The samples were observed on direct preparations, polished sections and after ionic polishing (Gatan llion + at 5kV for four hours).

## 3. Results and discussion

## 3.1 Impact of pH on impedance behaviour of mild steel in a CO<sub>2</sub> environment

To study the electrochemical behaviour of X65 carbon steel during the corrosion process, EIS measurements were carried out and recorded over time. Figures 3 and 4 show the EIS spectra corrected by the ohmic drop for a carbon steel surface exposed to a  $CO_2$  saturated solution at conditions of  $80\pm2^{\circ}C$ , pCO<sub>2</sub> 0.54 bar and solution pH of 6 and 6.6, respectively. Figure 3 shows the EIS spectra observed at both conditions of pH until 4 days of testing whereas Figure 4 shows the EIS spectra obtained after 5 days of testing and onwards. The results are organised as such in order to clearly identify the observed changes in the impedance behaviour over time.

## [Figures 3 and 4]

Three different characteristic changes were observed in the shape of the Nyquist plots similar to that observed in the study by Tanupabrungsun et al.[14]. Under both conditions of pH, the Nyquist curve features initially a single time constant which is characterized by a semi-circle with the diameter increasing with immersion time. At later time periods (Figure 4), a second time constant appears in the low frequency domain (LF). The first and the second semicircle are both observed to increase in diameter with exposure time. However, At pH 6.6, a linear

tail gradually appears at the low frequency region and is clearly observed after 8 days of immersion.

The corrected Bode plot shown in figure 3 highlights a CPE behaviour, the dispersion of the phase did not allow a precise derivation of the  $\alpha$  parameter. However the fitted values of the model were in the range of the extimated phase reported in figures 3 and 4.

In addition to these three characteristic changes, at both pH conditions, a high frequency (HF) capacitive loop is also identified (figure 5), from day 5 at pH 6 and at pH 6.6. This feature is observed to grow with exposure time merging successively with the intermediate frequency time constant. This process is observed to be faster at the higher pH.

## [Figure 5]

Electrochemical equivalent circuit (EEC) was used to help interpret the EIS data obtained and understand the characteristic changes in impedance behaviour observed in Figures 3 and 4.

Figure 6 shows the two different equivalent circuit models that are used to fit the impedance curves observed at different time periods. Figure 6(a) shows the EEC model used to fit the impedance behaviour observed in Figure 3, whereas the EEC model in Figure 6(b) was used to fit the impedance behaviour observed in Figure 4. The full lines plotted in Figures 3 and 4 represent the EEC model fit.

## [Figure 6]

The proposed circuits are based on literature observations of similar phenomenon, and will be discussed later in the article.

Stages 1 and 2 below intend to justify/explain the development of the two EEC models used in Figure 6 (a) and (b) respectively and to extract physico-chemical parameters related to the developing film over time.

## Stage 1. Formation of a single capacitive loop

This region is modelled using a simple Randles electrical equivalent circuit model as shown in Figure 6 a. This model is commonly used in literature [22,23] to characterise a corroding metal interface and provides a quantitative evaluation of the increasing charge transfer resistance. Figure 3 shows the relevant Nyquist plots for this stage of the corrosion process and related fittings for the different selected time periods at pH 6 and pH 6.6, respectively.

Table 2 shows the values of the fitted electrochemical parameters of Randles circuit over time along with other derived parameters.

#### [Table 2]

In Table 2, the double layer capacitance,  $C_{dl}$  ( $\mu$ F/cm<sup>2</sup>), is determined according to Brugg's Equation (1) [25]

$$\begin{bmatrix} Q & (- & --)^{(\alpha \ 1)} \end{bmatrix}^{(-)} \tag{1}$$

where  $R_e$  represents the solution resistance,  $R_{ct}$  represents the charge transfer resistance and  $Q_{dl}$  along with  $\alpha$  are a constant phase element (CPE) parameters. A constant phase element is used instead of a pure capacitance so as to account the distribution of properties at the electrode surface due to non uniform current-potential lines.

At both conditions of pH,  $R_{ct}$  is observed to increase with exposure time of the electrode in the corrosive environment. Charge transfer resistance, measured with EIS, is attributed to the kinetics of the iron anodic dissolution reaction. The observed changes can be attributed to the formation of the porous protective scale which covers the surface leading to a reduction of the active surface area (S<sub>a</sub>).

In support to this argument, the product of  $R_{ct}$  and  $C_{dl}$  is considered. Charge transfer resistance is considered to be inversely proportional to the active surface, whereas the double layer capacity is directly proportional to  $S_{a}$ . As the iron carbonate scale develops over time, the extension of the active surface decreases leading to a similar increase of  $R_{ct}$  and decrease of  $C_{dl}$ . Therefore a constant product between  $R_{ct}$  and  $C_{dl}$  is expected whenever the two parameters change because of  $S_a$  reduction [26]. This feature is indeed observed as Table 2 reports. Furthermore, the relationship between double layer capacity and  $S_a$  is useful in calculating the fraction of active surface at a given time during the test. In fact, assuming constant physico-chemical conditions such as temperature and ionic strength on the bare metal surface, the fraction of active surface area can be calculated with the ratio between initial double layer capacity ( $C_{dl}(0)$ )and capacity at time *t* ( $C_{dl}(t)$ ) (eq. 2).  $C_{dl}(0)$  is calculated as a mean of the double layer capacities in the first day of exposure. The values and development of this parameter over time is also shown in Table 2, showing that 60 % of the surface is active after 4.5 days at pH 6, and 18 % after 5.5 days at pH 6.6.

$$\%(t) \quad \frac{dl(t)}{dl(0)} \tag{2}$$

In order to verify that the result obtained at the OCP is due to the anodic contribution of the electrochemical process, successive impedance measurements were performed in a pH 6.8 CO<sub>2</sub> saturated water solution after 24 h of immersion at the OCP, and with an overvoltage of 40 mV, 80 mV and 120 mV in anodic and cathodic direction (for the both cases, different sample were used). Before measuring the impedance of the system, a potentiostatic polarization was carried out for 15 min in order to reach a stationary current. The impedance results are reported in figure 7.[Figure 7]

The Nyquist plot shows that the diameter of the capacitive loop is smaller with respect to the diagram obtained at the OCP for the anodic polarization, whereas it is higher for the cathodic one. Therefore, the charge transfer resistance of the anodic reaction is smaller than the cathodic one. For this reason the impedance measurements at OCP are representative of the iron dissolution reaction.

Finally figure 7 shows that the LF resistance measured at OCP has a factor two difference for the two experiments, this lack of reproducibility may be due to different stabilization conditions for the two experiments.

#### Stage 2. Changes induced by the development of corrosion scales

Over a longer duration of testing, the appearance of a second low frequency time constant is evident. Figure 4 shows the Nyquist plot for these time instances at pH 6 and pH 6.6. The appearance of this second time constant is believed to be due to the onset of mass transfer limitations through the scale. However, a linear tail in the low frequency range is only

observed at the higher pH. In literature, authors [26,27] have indicated that when such a linear tail at low frequency presents itself, it signifies the onset of diffusion impedance suggesting that the diffusion of corrosive species to the scale/substrate interface becomes constrained. Moreover, the transformation of the low frequency time constant into a linear tail is concomitant with the characteristic "pseudo-passive" rise at the OCP.

Furthermore, a closer look identified that a high frequency third time constant also becomes evident and was shown in Figure 5. This time constant subsequently merges with the medium frequency (MF) semicircle at pH 6.6 whereas at pH 6, it can be still distinguished until the end of the experiment. We believe that this high frequency (HF) semicircle is associated with the corrosion product film, leading to a pore resistance ( $R_{pore}$ ) and a film capacitance ( $C_{film}$ ). Its contribution to the EIS spectra only becomes evident after 3 days at both pH.

Overall, amongst the remaining characteristics of the impedance curve observed at this stage, the MF time constant is associated to the contribution of the double layer capacity and charge transfer reaction impedance to the comprehensive system impedance. Whereas the film contributes at the same time to the high frequency part of EIS through  $R_{pore} / C_{film}$ , and to the LF part, as a result of diffusion limitation through the pores. A similar model was already propoed by Jaouhari et al. in a study of calcium carbonate scaling onto the surface of a stainless steel electrode [28]. The complete EEC is presented in Figure 6(b). It incorporates  $R_{pore}$  and  $C_{film}$  which represent the impedance of the corrosion product layer (HF impedance).  $R_{ct}$  and  $Q_{dl}$  characterise the corrosion reactions (at MF).  $R_{ct}$  is in series with a Warburg semi-infinite element (W<sub>d</sub>) representing that corrosion reactions are limited by mass transfer (LF part of the impedance diagram).

The equation and physical parameters of Warburg finite length diffusion element are:

$$\frac{\tanh(\sqrt{i})}{\sqrt{i\omega}} \tag{3}$$

Where  $\omega$  is the frequency,  $R_d$  is the scale factor of the diffusion impedance and  $K_i$  is the dimensionless frequency, i.e. the ratio of the square of diffusion length on the diffusion coefficient of the species *i* (D<sub>i</sub>) undergoing diffusion limitation.

Table 3 shows the results of the fitting of the experimental data with the developed EEC model.

#### [Table 3]

In Table 3, C<sub>film</sub> is also calculated with Hsu and Mansfeld Equation (4) [29]:

$$\left(Q \qquad {}^{(\alpha)}\right)^{-} \qquad (4)$$

The values of  $C_{film}$  become constant after six days at both pH, and their values are in the order of unities of  $\mu$ F/cm<sup>2</sup> at pH 6 and tenth of  $\mu$ F/cm<sup>2</sup> at pH 6.6 (Table 3). Values of film capacitance of 0.1  $\mu$ F.cm<sup>-2</sup> were obtained by Jaouhari et al. for calcium carbonate films formed onto a 316L electrode under cathodic polarization in salted water [28].

As will be shown later in this paper, the thickness of the siderite layer formed on the metal surface is in the range of 20 to 60  $\mu$ m. The theoretical capacitance of a 20  $\mu$ m siderite film can be calculated according to Equation 5.

(5)

Where  $\varepsilon_0 = 8.85 \cdot 10^{-12}$  F/m, the vacuum permittivity,  $\varepsilon$  is the relative permittivity of siderite (9.3 according to Olhoeft [30]), and *A* and *d* represent the electrode area and the film thickness, respectively.

The theoretical value of  $C_{film}$  for a 20 µm thick siderite layer is thus in the range of 0.4 nF/cm<sup>2</sup>, which is two-three order of magnitudes lower than measured values. Therefore, it may be argued that the HF semicircle does not represent the siderite film grown on the metal surface, and another hypothesis to explain this capacitance has to be proposed.

According to several authors, protective iron carbonate films are often associated with a thin underlying layer of another type of mineral. Some authors mention the formation of chukanovite alongside with iron carbonate [31]. However, they consider that chukanovite is only a metastable product formed at low immersion times, which rapidly transforms into the more stable siderite. Han et al. report the formation of magnetite with a thickness of 12 to 140 nm, below the FeCO<sub>3</sub> scale in a CO<sub>2</sub> saturated solution at alkaline pH and 80 °C [32]. The theoretical capacitance of a nanometric magnetite film was thus calculated. Considering  $\varepsilon = 80.5$  for magnetite [33] and a 100 nm thick film, a capacity of 0.7  $\mu$ F/cm<sup>2</sup> is estimated and is in the same of order of magnitude of C<sub>film</sub> determined for the tests at pH 6.6. Same

assumptions can be made with a 10 nm magnetite film yielding 7  $\mu$ F/cm<sup>2</sup> value which is similar to the results at pH 6. The formation of magnetite could be subsequent to pH rise at the bottom of the pores through the thick FeCO<sub>3</sub> layer.

The HF loop is also characterized by the pore resistance  $R_{pore}$ . As shown on Table 3, fitted values of  $R_{pore}$  vary between 10 and 100  $\Omega$ .cm<sup>2</sup> at pH 6, and between 40 and 10<sup>3</sup>  $\Omega$ .cm<sup>2</sup> at pH 6.6. However, in the latter case, the highest values of R<sub>t</sub> obtained at long exposure times were obtained with a poor accuracy due to the merging of the HF anf MF semi-circles. These values compare well with previous results by Jaouhari et al. for calcium carbonate scales formed onto a stainless steel electrode [28]. The increase of R<sub>pore</sub> with time is related to the rise in pore length and/or to the decrease in pore diameter. Since the film thickness was lower at pH 6.6 compared to pH 6, the higher values of R<sub>pore</sub> at pH 6.6 must indicate less pores of smaller diameter for this condition.

In a sudy referring to calcium carbonate scales formed onto transparent and conductive electrodes, Devos et al. proposed to use  $R_{pore}$  values in order to determine the film thickness [26]. They made the assumption that the pores geometry could be approximated by a cylinder whose diameter corresponds to the diameter of the active surface  $S_a$ , with a length ( $l_{pore}$ ) equal to the thickness of the film. This assumption was only valid at ratios of surface coverage below 90 %, i.e. active surface above 10 % of the initial surface. The same methodology was applied to our experimental results. The theoretical length of the pores was calculated with the following equation:

The resistivity of the test solution was measured with a conductivity probe in the same test solution at 80 °C. Its value was  $102 \pm 6 \ \Omega \cdot \text{cm}$ .  $R_{pore}$  values corresponding to an active surface of 10 % of the initial surface was selected. These surface coverages were obtained after 11 days at pH 6, with  $R_{pore} = 96 \ \Omega \cdot \text{cm}^2$ , and after 6.5 days at pH 6.6 with  $R_{pore} = 43 \ \Omega \cdot \text{cm}^2$ . The calculated pore lengths were 940 µm at pH 6 and 420 µm at pH 6.6, i.e. much above the effective film thicknesses observed at the end of the tests, as will be shown later. Thus, it appears that the assumption that the pore section could be approximated by the active surface area is not valid. As already proposed by Jaouhari et al. [28], it is likely that large cavities are

formed at the metal surface beneath the carbonate cristals, leading to pore sizes of much smaller diameter than the active surface (Figure 8).

#### [Figure 8]

Figures 9 to 12 aim to show an analysis of the other parameters derived from the above impedance analysis. Figure 9 shows the variation of charge transfer resistance with time for pH 6 and 6.6.

## [Figure 9]

As previously mentioned, the observed increase in  $R_{ct}$  is mainly due to the reduction of the active surface area with the growth of the corrosion product layer. In fact, the double layer capacity declines monotonically because of the scale blocking effect.

Moreover, the product of  $C_{dl}$  and  $R_{ct}$ , which is independent of active surface, remains constant as Figure 10 shows at pH 6 and up to 5 days at pH 6.6. Therefore, the protective mechanism of the corrosion product can be explained simply by a coverage effect of steel active sites. At pH 6.6, deviation from the constant value shows that the protection offered by the corrosion products is not totally ascribed to a physical blocking but it may be related to a change of electrochemical reactions at the metal surface, maybe associated with a modification of local chemistry of the solution.

## [Figure 10]

Interestingly, no change of corrosion potential is seen for the test at pH 6, while a significant rise of potential appears after 8 days at pH 6.6 (Figure 11). This increase of the corrosion potential can also be ascribed to a change of electrochemical kinetics at the metal surface.

#### [Figure 11]

Figure 12 illustrates the percentage of active surface area, calculated according to Equation 2, as a function of time. At the beginning of the experiment, the observed increase in active surface at pH 6 may be explained due to roughening effect of corrosion. Subsequently, as observed at both conditions of pH, the active surface decreases progressively due to the precipitation of a protective film. The faster decrease in surface active area at higher pH is

due to a smaller porosity that can be explained by a better packing of iron carbonate scales. In fact faster scales nucleation leads to the appearance of smaller crystals that produce a compact layer.

## [Figure 12]

A similar pattern is displayed by metal corrosion rates as shown in Figure 11. Through the Stern-Geary equation, the corrosion rate can be calculated from the values of charge transfer resistance. A Stearn-Geary coefficient of 17 mV/dec ( $\beta_a=60 \text{ mV/dec } \beta_c=120 \text{ mV/ dec}$ ) is used.

As previously discussed, in long duration tests conducted at high pH and temperature in a  $CO_2$  corrosive environment, a sudden increase in open circuit potential (OCP) that occurs concurrently with a significantly reduced corrosion rate is considered a distinctive indication of "pseudo-passivation" [11]. Consequently, Figure 11 plots the corrosion rate (in mm/yr), derived from the  $R_{ct}$  values shown in Figure 10, and the varying OCP measured over the duration of the experiment.

Figure 11 (b) is annotated indicating the characteristic changes in the development of the impedance behaviour. The results show that, as observed in literature [11,16], a sudden increase in the OCP is observed to take place at 8 days at pH 6.6. The low values of corrosion rate deduced after this time instant indicates superior protectiveness of the developed film which coincides with the formation of the linear tail in the Nyquist plot that was characterised as diffusion impedance. This phenomenon was not observed at pH 6 with the OCP remaining relatively stable and the corrosion rate gradually dropping over the 11 day period.

The precipitation of iron carbonate scales on the metal surface produced significant changes in the impedance spectra that reflect the evolution of scale protectiveness and their impact on the electrochemical reactions that take place at the surface. In fact, for short immersion time, EIS spectra suggest that the overall corrosion process rate is under kinetic controlled. At longer immersion time at pH 6.6, electrochemical reactions are under mixed control, i.e. mass transfer control of electrochemical reactions.

In order to further add value to the above electrochemical analysis, in the following study, carbon steel coupons were extracted for surface analysis after exposure times of 5 days and at the end of test. The results are discussed in the following sections.

#### 3.2 Investigation of the corrosion product film morphology and composition

The corrosion product film formed on the mild steel surface was studied under an electron microscope in order to identify the difference in microstructure at two varying conditions of solution pH, i.e. at pH 6 and 6.6, at day 5 and at the end of test. Multiple images were taken at varying locations and magnifications to provide a complete understanding of the complex formation of crystals. XRD analysis was further carried out to identify the composition of the developed film responsible for the surface protection under the conditions studied. The results within this section are divided into four subsections to provide a clear systematic presentation of the parameters studied and experimental techniques used.

#### Heterogeneous properties of the developed film - SEM surface analysis

Figures 13 and 14 show the characteristic differences observed at different regions of the surface for the experiment carried out at pH 6 and a second experiment at pH 6.6 respectively at the end of test.

## [Figure 13]

#### [Figure 14]

Under both conditions of pH, the distribution of crystals was observed to be not exactly alike throughout the surface area. The crystals were observed to be either in the form of small interlinked crystals, large isolated crystals or plate-like formations. Figures 13 (a) and 14 (a) show an image taken at ×100 magnification identifying a region of the surface with all mentioned formations. The figures are annotated identifying regions of the surface that are magnified in Figures 13 (b-c) and 14 (b-c) to provide a more detailed observation of the varying morphology of the developed film. Figures 13 (b) and 14 (b) show a compact, dense formation of interlinked crystals. Within this region, the growth of the crystals seems limited due to a lack of freedom and are observed to be, on average, the smallest variety of crystals formed. In contrast, Figures 13 (c) and 14 (c) show larger, more isolated crystals and plate-like formations in between formed crystals. The plate-like formations may be considered to be chukanovite crystals (FeCO<sub>3</sub>(OH)<sub>2</sub>) [17].

Comparing Figure 13 with Figure 14, it is observed that the film is more dense and compact at pH 6.6. At pH 6, the crystals size is considerably larger in both distinct regions of

formation identifying that the growth process is more dominant at a lower pH. Similarly, the evidently larger quantity of crystals and smaller size distribution observed at pH 6.6 (Figure 14) may imply that the crystal nucleation rate is higher for a higher pH.

The images showing a more compact film for the pH 6.6 conditions are in agreement with the impedance results where corrosion rate is lower for a higher pH, suggesting a link between compactness and protectiveness of the corrosion scales. Moreover, an enhanced film compactness can explain the linear tail observed at pH 6.6 highlighting enhanced diffusion limitations of reactive species.

## Film propagation and development - SEM surface analysis

Figure 15 shows a comparative analysis of the size distribution across the mild steel surface at the two pH studied after 5 days and at the end of test. The figure takes into account the formation of both small and large crystal formations that were addressed in Figures 13 and 14. The histogram also indicates the respective instantaneous corrosion rate calculated through the electrochemical analysis to highlight the comparative protectiveness/effectiveness of the surface coverage of the film formed at each of the conditions studied. The crystal sizes were determined using an image analysis software (ImageJ) to measure the size of each individual crystal and an average of the varying crystal sizes across the captured images was deduced.

## [Figure 15]

At pH 6, there is a significant difference in the average crystal size of larger crystals between 5 days and the end of test. However, the smaller crystals were observed to not significantly change in size due to the space restrictions as observed in Figure 13 (b). At pH 6.6, there is a less significant increase of both the larger and smaller crystals between 5 days and the end of test. An overall view of the surface after both periods of exposure also shows a more uniform film formation at pH 6.6. To provide visual evidence to the histogram analysis in Figure 15, Figure 16 shows selected surface SEM images at the end of 5 days and end of test for both conditions of pH 6 and 6.6. The images in figure 16 c and d are also part of a previous study [33]. The images show regions of the surface that have been characterised as "large crystal formation" where the development of the crystals from one time instance to the next was observed to be more significant. The figures provided are representative images of approximately  $508 \times 508 \ \mu\text{m}^2$  area of the sample surface.

#### [Figure 16]

Comparing the images with the same magnification a significant difference crystals size and distribution is noticed, as discussed previously. Figures 16 (b) and (d) show that the crystals continue to grow under both conditions of pH for a longer duration of exposure upon comparison with Figure 16 (a) and (c).

It must be emphasized that the top-view SEM observations may be somewhat misleading regarding the evaluation of the efficiency of a porous protective surface layer but may give significant clue on the controlling parameters of its formation and growth.

The first point appears clearly by comparing the top-views of surface layers developed after 12 days at pH 6 (figure 16 (b)) and after 5 days at pH 6.6 (figure 16 (c)): the later looks more compact and dense than the former, but figure 12 and table 2 show that, despite its poorer aspect, the layer developed during 13 days at pH 6 is more protective (lower corrosion rate and smaller active surface, 10 % versus 22 %) than that developed for 5 days at pH 6.6.

The second point has already been pointed out by Gao et al. [7] who attributed the difference in crystal size to differences in the nucleation conditions of the siderite crystals. Large crystals are produced when nucleation is not so easy and produce layers with large pores, progressively shrunk by crystal growth; small crystals are produced when their nucleation is easier and lead to smaller pores and lower porosity: this is consistent with the observation that at pH 6 siderite layers must be thicker than at pH 6.6 to afford the same level of protection. Moreover considering a reduction of 50% of active surface the ratio of corrosion rates between pH 6 and pH 6.6 is 1.3 which produces a greater quantity of dissolved iron. As a result more iron is available for scales precipitation therefore corrosion product layer is thicker at more acidic pH.

#### Film propagation and development – SEM cross-sectional analysis

Film thickness at the end of test can be identified with the cross-section analysis in Figure 17 reporting the two pH conditions investigated. Figures 17 (b) and (d) show a higher magnification of the Figures 17 (a) and (c). At both conditions of pH, a thin dark line is observed somewhat separating the layer in two parts.

[Figure 17]

In literature, there are two identified instances where a similar observation was noted where the corrosion product film is assumed to be formed by two layers, an inner and an outer layer. Palacios et Shadley consider that an outer layer of low pororsity is deposited on top of ther inner layer and provides additional protection [34]. Gao et al. [7] carried out experiments in a high pressure (10 bar) environment and the study concluded that an inner layer initially develops protecting the surface from further corrosion. The outer layer is considered to appear after a specific instant in time and indicates adequate protection of the entire corrosion film. In a separate study by Li et al. [11], the authors suggest that an outer, more porous FeCO<sub>3</sub> layer forms first and retards the diffusion of corrosive species to the surface but also the diffusion of ferrous ions away from it creating conditions for the formation of a more protective inner layer.

In this study, this combined outer and inner layer is observed for all experiments, both conditions of pH and duration. Figures 17 (b) and (d) are annotated showing that film thickness (inner and outer) is larger at pH 6 matching the greater average crystals size observed from the surface analysis (Figure 15). If it is assumed that this thin line represents the initial surface level prior to corrosion, it is further observed that a larger material loss is evident at pH 6. The results may suggest that the film development is similar to that suggested in the research articles by Palacios et al. [34] and Gao et al. [7]. It is believed that protective crystals nucleate and grow on the corroding surface as a result of the surface conditions forming an inner layer. Subsequently porosities between inner layer crystals are filled in by further precipitation, leading to the formation of an outer porous layer that afford corrosion protection in cooperation with the inner one. A greater porosity of the outer layer is to be expected because of its distance from the metal which implies less iron carbonate supersaturation than the near-surface area.

Over time, the filling of the corrosion product layer porosity might be linked with the appearance of the LF time constant in EIS spectra and associated with the occurrence of diffusion limitation of reactive species. This clear separation is not evident throughout the surface however, certain regions are observed to exhibit a compact deposit formation with limited visible porosity as shown in Figure 18 for both conditions of pH 6 and pH 6.6. This cross-sectional region is believed to correlate with the surface regions of small interlinked crystals shown in Figure 13 (b) and 15 (b). This assumed connection is because the compact structure of crystals may suggest limited porosities at the crystal boundary layer that may be considered responsible for the propagation of the dual layer structure observed in Figure 17.

#### [Figure 18]

Furthermore, in Figure 18, certain regions (circled in figure) show indications of the formation of a lighter grey shade below the compact crystal layer at both pH 6 and pH 6.6. The different shades of grey observed in SEM images are indicative of compositional variation in the corrosion product layer. As will be shown later, these light grey areas located between the siderite outer layer and the metal correspond to magnetite.

### 3.3 Investigation of the composition of the protective film

XRD was already carried out in a previous study on the same samples, the results are reported there and briefly summarized hereafter [33].

The XRD pattern shows that iron and iron carbonate are the main component of the film. At pH 6,  $FeCO_3(OH)_2$  phase, known as chuckanovite, can be detected. Nonetheless in this case  $FeCO_3$  represents the main component of the iron carbonate film.

To effectively identify the composition of the lighter grey formation identified in Figure 18 (zones marked by dotted circles), an electron backscatter diffraction (EBSD) analysis was carried out. Figure 19 (a) shows a SEM analysis of the cross-section identifying the region of interest below the FeCO<sub>3</sub> corrosion product layer. The sample specimen was prepared through ion polishing, a method where ions are fired at the surface from an angle. Figure 19 (b) shows the results of the EBSD analysis that effectively indicates that the under-deposit layer is magnetite (Fe<sub>3</sub>O<sub>4</sub>).

## [Figure 19]

This observed formation is in concurrence with the work done by Han et al. [16] where magnetite was similarly formed at the boundaries of  $FeCO_3$  crystals. However, in the following study, the lighter grey formation was found below the  $FeCO_3$  film at both pH (Figure 18) and therefore the formation of magnetite cannot be linked to "pseudo-passivation" as in the study by Han et al. [16].

Furthermore, the lack of evidence of a continuous film of magnetite that was hypothesized to be responsible for the HF capacity measured through EIS can only mean that  $C_{film}$  is attributed to the scattered deposits upon the surface. Nonetheless, this hypothesis is hard to prove since the magnetite layer thickness, if a continuous layer exists at all, is not constant and experimental identification of the actual complete magnetite surface coverage is difficult.

#### 3.4 Result-based analysis of the development of a "protective film" in a CO<sub>2</sub> environment

In the following section, from previous [7,14,15,15,16] and current research results, a mechanism for the development of a protective film over time in a CO<sub>2</sub> environment is proposed. When a carbon steel sample is immersed in CO<sub>2</sub> aqueous electrolyte at a high enough pH and temperature, iron carbonate forms blocking the steel surface from continuing to corrode. Nature, crystal morphology and protectiveness offered by the FeCO<sub>3</sub> film depends on the environmental conditions primarily due to the surface FeCO<sub>3</sub> supersaturation achieved. As shown in Figure 14, the morphology of the film varies significantly at both pH studied. This is believed to be due to the competition between the simultaneous nucleation and growth processes with a higher surface supersaturation favouring a higher nucleation of crystals and limited growth. Furthermore, the visible heterogeneity of the crystals formed on the surface (Figures 13 and 14) implies that variations in microstructure and imperfections such as surface roughness also play an important role in formation characteristics of the developing film.

Over time, the iron carbonate scale was observed to become more compact at both conditions of pH with increasing resistance of the developing film as shown by the EIS results. After an exposure time of 5 days (Figure 16), the physical structure of the scale already showed a relatively high surface coverage that suggested that the scale is likely highly impermeable to solution/ ion movement. With decreasing permeability, there would come a point when the diffusion of  $CO_{2(aq)}$  towards the metal surface and the diffusion of  $Fe^{2+}$  away from the interface are both restricted enough to control (or at least to participate to the control of) the overall corrosion kinetics. This phenomenon is the origin of the LF time constant which gradually evolves at pH 6.6 into a linear tail at the same time of the increase in OCP as shown in figures 4 and 11. It may be perceived that at this point in time, the tortuosity of the diffusion path becomes so high that the diffusion processes becomes very slow and takes control of the corrosion rate. The observed increase in potential (OCP) is considered to be due to the decrease of the anodic reaction more than the cathodic reaction suggesting that the controlling diffusion process is the diffusion of carbon dioxide participating in the iron dissolution reaction or a restriction of Fe<sup>2+</sup> diffusion away from he surface.

In the research study by Han et al. [16], the appearance of magnetite islands is linked to the observation of a rise in the OCP and identified as a "passive film". In the following study, the inconsistent formation of the magnetite phase along with its identification at both pH 6.6 and pH 6 (where no rise in OCP is noted) indicates that the magnetite formation is a result of

local under-deposit conditions. As such, it is not responsible for the rise in OCP and cannot be considered as a passivating species. The formation of magnetite is an indication of a high local pH at the bottom of the pores formed by iron carbonate, which is a close neighbour of magnetite in the stability diagram shown on Figure 20 [16].

#### [Figure 20]

Overall, it is not the formation of the magnetite phase but the direct blocking of corroding surface by the general corrosion product layer that is responsible for the protectiveness of the film. At higher solution pH conditions, the combined EIS and surface analysis indicated a less porous corrosion product layer. This implies that consequently the active corrosive sites were blocked at a faster rate than at pH 6 and the barrier effect of the deposits increased more rapidly, resulting in the sudden increase in OCP and the development of a more protective film establishing a diffusion-controlled corrosion process towards the end of test.

#### 4. Conclusion

This study performed a combined EIS and surface analysis to study the pH effect on protective corrosion product layer formation in mild steel  $CO_2$  corrosion. Tests were conducted at 80°C, 0.54 bar pCO<sub>2</sub> and a solution pH of 6 and 6.6 over a duration of 10 or 11 days. Hereafter the conclusions from the results and discussions of this study:

- The electrochemical impedance behavior is observed to adapt over time at varying pH. The two initial steps of impedance evolution are due, at both pH values, to the formation of a porous protective layer whose effect on the corrosion rate is mainly due to a coverage effect on the metal surface limiting the active dissolution areas.
- The onset of diffusion impedance at pH 6.6 is believed to be the result of the evolution of the deposit layer towards a very low porosity and very high tortuosity which results in a diffusion barrier promoting corrosion control by diffusion of carbon dioxide to the metal surface participating in the iron dissolution reaction or of Fe<sup>2+</sup> getting away from the surface. This layer is clearly not a passive layer (through which cations are transported by solid transport processes) but could rather be qualified as "pseudo-passive". Moreover decrease of the anodic reaction because of mass transfer

limitation explain the rise in open circuit potential linked to "pseudo-passive" behavior.

- Analysis of the HF part of impedance spectra excluded that the measured capacity is the siderite layer. Moreover the values observed are consistent with a 10 – 100 nm magnetite film. Nonetheless, no continuous magnetite film was observed with SEM images, rather some areas underneath the siderite layer shows the presence of small magnetite deposits. Finally, the contribution of R<sub>pore</sub> was modelized as the resistance of the solution passing through iron carbonate permeable pathways. The results of the pore length calculated with equation 6 are in agreement with the scales thickness observed in the SEM images.
- At both pH conditions, a phase of different compositional variation was identified below the FeCO<sub>3</sub> film in some regions. EBSD analysis identified the foreign layer as magnetite (Fe<sub>3</sub>O<sub>4</sub>) and it is considered the result of high pH conditions below certain regions of the FeCO<sub>3</sub> product layer.

## **Competing interests**

The authors declare that they have no competing interests

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## Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical limitations.

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## **Figure Captions:**

- Figure 1. Equivalent electrical circuit (a) before and (b) after the "critical point" [7].
- **Figure 2.** Microstructure of API 5L X65 carbon steel material. Microstructure was obtained after etching in a 10% nital solution.
- **Figure 3.** Nyquist plots and related bode plots obtained at corrosion potential during time in the solution at: (a) pH 6 and (b) pH 6.6 (solid line: EEC model fit).
- **Figure 4.** Nyquist plots and related bode plots obtained at corrosion potential during time in the solution at: (a) pH 6 and (b) pH 6.6 (solid line: EEC model fit).
- **Figure 5.** Nyquist plots details of High frequency domain of EIS spectra for different selected time periods at (a) pH 6, (b) and (c) pH 6.6.
- **Figure 6.** Equivalent electrical circuit evolution with time: a) simple model of a corroding surface at the beginning of the test b) EEC after scale formation, appearance of second and third time constant. The circuit includes contributions from pore resistance and diffusion.
- Figure 7. Nyquist plots details of impedance spectra at different potentials, a) anodic and
  b) cathodic. The spectra were collected after a potentiostatic polarization in
  order to attain stationary conditions. The working electrode was exposed to a
  carbon dioxide saturated water solution with 2% dissolved NaCl at pH 6.8
- Figure 8. Scheme of the scaled electrode, adapted from ref. [28].
- Figure 9. Charge transfer resistance  $R_{ct}$  as a function of immersion time in the solution at differents pH.
- **Figure 10.** Charge transfer capacity resistance product  $(R_{ct} \cdot C_{dl})$  as a function of immersion time at pH 6 and pH 6.6.
- **Figure 11.** Open circuit potential and corrosion rate for corrosion test at a) pH 6 and b) pH 6.6.
- **Figure 12.** Calculated active surface area percentage in relation to initial geometrical surface as a function of immersion time.
- **Figure 13.** Surface morphology of corrosion product films formed at 80°C, 0.54 bar, pH 6 after 12 days: (a)  $\times 100$ , (b) location 1,  $\times 1000$ , (c) location 2,  $\times 1000$ .

- **Figure 14.** Surface morphology of corrosion product films formed at 80°C, 0.54 bar, pH 6.6 after 12 days: (a)  $\times 100$ , (b) location 1,  $\times 1000$ , (c) location 2,  $\times 1000$
- **Figure 15.** Comparative surface analysis of overall crystal size of small and large crystals and instantaneous corrosion rate observed at both pH 6 and pH 6.6 at the end of 5 and 12 days of exposure
- Figure 16. Surface morphologies of the scales at 80°C, 0.54 bar under varying conditions of pH and at different times: (a) pH 6, 5 days, (b) pH 6, 12 days, (c) pH 6.6, 5 days, (d) pH 6.6, 12 days.
- Figure 17. Cross-section morphologies of corrosion product films formed at 80°C, 0.54 bar under varying conditions of pH after 12 days: (a) pH 6, ×250, (b) pH 6, ×1000, (c) pH 6.6, ×250, (d) pH 6.6, ×1000 (thickness is given in μm).
- Figure 18. Cross-section morphologies of corrosion product films formed at 80°C, 0.54 bar under different pH after 12 days: (a) pH 6, (b) pH 6.6. Figure is annotated to indicate instances of compositional variation in the corrosion product layer (thickness is given in μm).
- Figure 19. (a) Cross-section analysis of corrosion product films formed at 80°C, 0.54 bar under conditions of pH 6.6 after 12 days sample prepared through ion polishing. (b) EBSD analysis of "oxide".
- **Figure 20.** Pourbaix diagram of Fe-C-H<sub>2</sub>O system at 80°C indicating the possibility of the formation of magnetite at high local pH conditions [16].

## **Table Captions:**

**Table 1.**API 5L X65 Carbon Steel Composition (weight %)

**Table 2.** EIS spectra fitting results before second time constant appearance. The standard errors reported in the table are calculated during the fitting of experimental data with the electrical circuit model by R nls function using the "port" algorithm. Other circuits may give different errors independently of their physical meaning. For the calculation of Sa  $C_{dl}(0) = 197 \ \mu\text{Fcm-2}$  and  $C_{dl}(0) = 321 \ \mu\text{Fcm-2}$  for pH 6 and pH 6.6 respectively

**Table 3.** EIS spectra fitting results after third time constant appearance. The standard errors reported in the table are calculated during the fitting of experimental data with the electrical circuit model by R nls function using the "port" algorithm. Other circuits may give different errors independently of their physical meaning. For the calculation of Sa  $C_{dl}(0) = 197 \ \mu$ Fcm-2 and  $C_{dl}(0) = 321 \ \mu$ Fcm-2 for pH 6 and pH 6.6 respectively



Figure 1. Equivalent electrical circuit (a) before and (b) after the "critical point" [7].



**Figure 2.** Microstructure of API 5L X65 carbon steel material. Microstructure was obtained after etching in a 10% nital solution.

 Table 1. API 5L X65 Carbon Steel Composition (weight %)

С	Si	Mn	Р	S	Cr	Мо	Ni	Cu	Nb	Ti	V
0.04	0.33	1.33	0.009	0.002	0.056	0.015	0.041	0.029	0.042	0.016	< 0.005



**Figure 3.** Nyquist plots and related bode plots (phases) obtained at corrosion potential during time in the solution at: (a) pH 6 and (b) pH 6.6 (solid line: EEC model fit).



**Figure 4.** Nyquist plots obtained at corrosion potential during time in the solution at: (a) pH 6 and (b) pH 6.6 (solid line: EEC model fit).



**Figure 5.** Nyquist plots details of High frequency domain of EIS spectra for different selected time periods at (a) pH 6, (b) and (c) pH 6.6.



**Figure 6. Electrical** equivalent circuit evolution with time: a) simple model of a corroding surface at the beginning of the test and b) EEC after scale formation, appearance of second

and third time constants. The circuit includes contributions from pore resistance and diffusion.



Figure 7. Nyquist plots obtained at different potentials in : a) anodic and b) cathodic domain. The spectra were collected after a potentiostatic polarization in order to attain stationary conditions. Before measurements, the working electrode was exposed during 24h to a carbon dioxide saturated water solution with 2% dissolved NaCl at pH 6.8

рΗ	Time (d)	R <sub>ct</sub> fitted	Err. R <sub>ct</sub>	Q <sub>dl</sub> fitted	Err. Q <sub>dl</sub>	α	C <sub>dl</sub>	$R_{ct} C_{dl}$	Sa
		(Ωcm²)	(Ωcm²)	(μFcm⁻²) <sup>α</sup>	(μFcm⁻²) <sup>α</sup>	fitted	calculate	calcul	(%)calculated
							d eq. 1	ated	eq. 2
							(µF.cm <sup>-2</sup> )	(s)	
6	1.0	219	2	327	6	0.90	205	0.045	103
	2.0	198	1	346	6	0.92	241	0.048	122
	3.0	262	1	292	3	0.89	175	0.046	89
	4.5	425	2	266	3	0.8	117	0.050	60
6.6	1.0	201	1	305	4	0.87	145	0.029	104
	2.0	302	2	222	3	0.88	115	0.035	82
	3.0	486	2	164	1	0.87	76	0.037	54
	4.0	767	2	118	1	0.86	48	0.037	34
	5.0	1101	3	89	1	0.84	31	0.034	22
	5.5	1307	5	76	1	0.84	25	0.033	18

**Table 2.** EIS spectra fitting results before second time constant appearance. The standard errors reported in the table are calculated during the fitting of experimental data with the electrical circuit model by R nls function using the "port" algorithm. Other circuits may give different errors independently of their physical meaning. For the calculation of Sa  $C_{dl}(0) = 197 \ \mu \text{Fcm}^{-2}$  and  $C_{dl}(0) = 140 \ \mu \text{Fcm}^{-2}$  for pH 6 and pH 6.6 respectively..

рН	Time (d)	R <sub>ct</sub> fitted (Ωcm²)	R <sub>pore</sub> fitted (Ωcm²)	C <sub>film</sub> calc. eq. 4 (μFcm <sup>-2</sup> )	C <sub>dl</sub> calc. eq. 1 (μFcm <sup>-2</sup> )	R <sub>d</sub> fitted (Ωcm²)	Ki fitted (s)	Sa (%) calc. eq. 2
6	5.0	463±2	10±1	10.3	91	49±4	20±3	46
	6.0	617±3	20±2	2.4	68	167±3	26.9±0.8	34
	7.0	828±4	39±3	1.2	55	314±4	30.3±0.6	28
	8.0	1086±7	55±2	0.77	42	478±7	36±1	21
	9.0	1318±9	$(8\pm1)\cdot10^{1}$	1.1	33	646±9	38.1±0.9	17
	10.0	$(1.60\pm0.01)\cdot10^3$	81±5	1.6	26	$(8.3\pm0.1)\cdot10^2$	41±1	13
	11.0	1840±8	96±7	1.9	22	(9.2±0.2)·10 <sup>2</sup>	42±1	11
6.6	6.5	1471±6	43±4	0.33	17	$636 \pm 9.10^{2}$	17.4±0.4	12.4
	7.0	1626±6	61±5	0.20	15	$(8.9\pm0.1)\cdot10^2$	18.1±0.3	10.4
	7.5	1863±7	87±8	0.28	12	$(1.21\pm0.02)\cdot10^{3}$	21.0±0.4	8.2
	8.0	1958±9	129±9	0.24	10	$(1.61\pm0.03)\cdot10^{3}$	23.2±0.6	6.9
	8.5	$(2.24\pm0.01)\cdot10^{3}$	(3.2±0.2)·10 <sup>2</sup>	0.063	7	$(2.62\pm0.04)\cdot10^{3}$	27.0±0.6	4.8
	9.0	$(2, 43+0, 02), 10^3$	(1.10±0.08)·1			$(4.07\pm0.2)\cdot10^3$	37±2	1.6
		(2.45±0.02)*10	0 <sup>3</sup>	0.026	2			
	9.2	$3.45\pm0.03\cdot10^{3}$	/	/	2	$(4.35\pm0.2)\cdot10^3$	40±2	1.2
	9.5	$(7.17\pm0.05)\cdot10^{3}$	/	/	1	$(7.79\pm0.2)\cdot10^{3}$	44±2	0.4

**Table 3.** EIS spectra fitting results after third time constant appearance. The standard errors reported in the table are calculated during the fitting of experimental data with the electrical circuit model by R nls function using the "port" algorithm. Other circuits may give different errors independently of their physical meaning. For the calculation of Sa  $C_{dl}(0) = 197 \ \mu \text{Fcm}^{-2}$  and  $C_{dl}(0) = 140 \ \mu \text{Fcm}^{-2}$  for pH 6 and pH 6.6 respectively.



Figure 8. Scheme of the scaled electrode, adapted from ref. [28].



Figure 9. Charge transfer resistance R<sub>ct</sub> as a function of immersion time in the solution at differents pH.



Figure 10. Charge transfer capacity resistance product  $(R_{ct} \cdot C_{dl})$  as a function of immersion time at pH 6 and pH 6.6.



**Figure 11.** Open circuit potential and corrosion rate for corrosion test at a) pH 6 and b) pH 6.6.



**Figure 12.** Calculated active surface area percentage in relation to initial geometrical surface as a function of immersion time. Error bars are calculated using algorithm errors related to the film capcity.



**Figure 13.** Surface morphology of corrosion product films formed at 80°C, 0.54 bar, pH 6 after 12 days: (a)  $\times 100$ , (b) location 1,  $\times 1000$ , (c) location 2,  $\times 1000$ .



**Figure 14.** Surface morphology of corrosion product films formed at 80°C, 0.54 bar, pH 6.6 after 12 days: (a)  $\times 100$ , (b) location 1,  $\times 1000$ , (c) location 2,  $\times 1000$ 



**Figure 15.** Comparative surface analysis of overall crystal size of small and large crystals and instantaneous corrosion rate observed at both pH 6 and pH 6.6 at the end of 5 and 12 days of exposure.



**Figure 16.** Surface morphologies of the scales at 80°C, 0.54 bar under varying conditions of pH and at different times: (a) pH 6, 5 days, (b) pH 6, 12 days, (c) pH 6.6, 5 days, (d) pH 6.6, 12 days. The images in figure 15 c and d are also part of a previous study [33].



**Figure 17.** Cross-section morphologies of corrosion product films formed at 80°C, 0.54 bar under varying conditions of pH after 12 days: (a) pH 6, ×250, (b) pH 6, ×1000, (c) pH 6.6, ×250, (d) pH 6.6, ×1000 (thickness is given in  $\mu$ m).



**Figure 18.** Cross-section morphologies of corrosion product films formed at 80°C, 0.54 bar under different pH after 12 days: (a) pH 6, (b) pH 6.6. Figure is annotated to indicate instances of compositional variation in the corrosion product layer (thickness is given in  $\mu$ m).



**Figure 19.** (a) Cross-section analysis of corrosion product films formed at 80°C, 0.54 bar under conditions of pH 6.6 after 12 days – sample prepared through ion polishing. (b) EBSD analysis of "oxide".



**Figure 20.** Pourbaix diagram of Fe-C-H<sub>2</sub>O system at 80°C indicating the possibility of the formation of magnetite at high local pH conditions [16].