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Corrosion of carbon steel under CO₂ conditions: effect of CaCO₃ precipitation on the stability of the FeCO₃ protective layer

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Abstract

This study investigates the effect of CaCO₃ precipitation on the corrosion of 1Cr carbon steel covered by protective FeCO₃ layer. Tests were conducted at atmospheric pressure in 1 wt.% NaCl solution saturated with CO₂ at 80 °C. Three different concentrations of Ca²⁺ (100, 1,000 and 10,000 ppm by mass) were studied. Linear polarization resistance (LPR), electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization were used to investigate the electrochemical behavior. Scanning electron microscopy (SEM) and X-ray powder diffraction (XRD) were used to analyze the corrosion products. Results suggested the precipitation of CaCO₃ led to an undersaturated solution with respect to FeCO₃ followed by dissolution of the protective layer.

Keywords: Carbon steel A; Polarization B; EIS B; Oxidation C; Interfaces C.

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22 Introduction

23 Despite its susceptibility to CO_2 corrosion, carbon steel is the most commonly used material for
24 pipeline in the Oil & Gas production. This is due to its relatively low price, its availability in the volume
25 required and the possibility of easily satisfying mechanical and fabrication requirements [1]. When
26 CO_2 dissolves in water and hydrates to carbonic acid (H_2CO_3), it promotes an electrochemical reaction
27 between the steel and the aqueous phase, leading to iron dissolution [2][3][4][5][6][7]. This process
28 has been under investigation for more than four decades, but the corrosion mechanism occurring at
29 the metal-electrolyte interface is still a subject of research [8][9]. In addition, precipitation processes
30 of corrosion products or mineral scales can occur, which has a significant influence on the corrosion
31 mechanism.

32 Siderite (FeCO_3) is the most commonly observed corrosion product in aqueous medium with sodium
33 chloride (NaCl) saturated with CO_2 [1] [10]. The influence of this layer on the corrosion rate of carbon
34 steel has been researched and documented in literature [11][12][13][14][15]. Under certain
35 conditions, it has been shown that FeCO_3 precipitation on the steel surface blocks the active sites of
36 dissolution and creates a barrier to the diffusion of the electrochemical active species, resulting in a
37 significant reduction in the corrosion rate. The protectiveness of the iron carbonate layer is strongly
38 dependent on several parameters such as CO_2 partial pressure [11][12][13][14] concentration of ionic
39 species [15][16][17], pH and temperature[18][19][20][21].

40 However, the potential effect of divalent ions such as Ca^{2+} is still poorly understood. Amongst other
41 ions, Ca^{2+} is present in the fluids of geological formations and can react with CO_2 , resulting in calcium
42 carbonate (CaCO_3) precipitation when solubility limit of CaCO_3 is exceeded [22][23]. This precipitation
43 has been reported to significantly influence the corrosion rate [24][25][26][27][28][29]. Calcite
44 (CaCO_3) and siderite share the same crystal structure and several authors state that Ca^{2+} ions can
45 substitute Fe^{2+} in the FeCO_3 structure. This substitution is reported to alter the morphology and
46 protectiveness of the FeCO_3 layer [28][29][32] [33].

How this process influences the corrosion product formation on the carbon steel material, particularly after a protective iron carbonate layer has formed, is still not well understood. Most of the studies [24][25][26][27][28][29] focus on the effect of simultaneous precipitation of both mineral scaling and corrosion products, even though these processes may occur at different moment in the lifetime of an oil & gas well due to ingress of formation water rich in Ca^{2+} and water injection for enhanced oil recovery[30][31].

Also investigations with Ca^{2+} ions have been reported to elucidate the effect of divalent ions on the corrosion of carbon steel in CO_2 saturated solution. However, the results from these experiments are rather limited and not fully coherent. Esmaeely et al. [28][29] have performed electrochemical tests on AISI 1018 at low and high concentration of Ca^{2+} at 80 °C in 1 bara CO_2 at pH 6.6. Results shows that at low Ca^{2+} concentration up to 100ppm, a protective layer was still able to form, reducing the corrosion rate. At higher concentrations (1,000 and 10,000 ppm), the layers were not protective and the corrosion rate did not decrease during the experiments. Severe pitting corrosion at 10,000 ppm was recorded and attributed to Ca^{2+} , as the Cl^- ion content in each experiment were kept constant . The authors suggested that this effect could also be caused by the rapid acidification of the solution when CaCO_3 precipitates in the solution at higher Ca^{2+} concentrations. $\text{Fe}_x\text{Ca}_{1-x}\text{CO}_3$ precipitation was recorded and the mole fraction of Ca^{2+} calculated. According to the authors when the mole fraction approached 1, the protectiveness of the scale was reduced.

Tavares et al. [34] have studied the effect of solid CaCO_3 on the corrosion rate of carbon steel. They performed autoclave tests for 28 days at 80 °C and 15 MPa pCO_2 in absence and presence of CaCO_3 . The authors reported the beneficial effect of CaCO_3 , which reduced the corrosion rate determined by weight loss. This reduction in corrosion rate could have been attributed to the increased pH of the solution from 2.71 to 4.7 in CaCO_3 containing solution, although authors haven't concluded this. The XRD patterns showed a different corrosion product consisting of $\text{Fe}_x\text{Ca}_{1-x}\text{CO}_3$ in solution containing CaCO_3 , while only FeCO_3 was measured in the absence of CaCO_3 . The authors have additionally

reported that the Ca^{2+} -containing layer was more porous and therefore more sensitive to Cl^- permeation and as a consequence, pitting.

In a more recent work, Hua et al. [27] have investigated the individual effect of Cl^- , Mg^{2+} and Ca^{2+} ions on the corrosion behavior of carbon steel in simulated CO_2 storage environments at 60 °C and 100 bar CO_2 for 96 h. In order to separate the effects of these aforementioned ions, separate solutions containing only Ca^{2+} or Mg^{2+} at 1,000 and 10,000 ppm were produced. The Cl^- was kept constant at 35,249 ppm by adding NaCl. Therefore, two additional solutions containing only Cl^- at 4,200 and 35,249 ppm were tested to explore the effect of Cl^- ions on corrosion behavior, scale formation and pitting. Reported results shows that after 6 hours, when the protective corrosion products had not precipitated from the solution, an increase in Cl^- and Mg^{2+} resulted in an increase in general corrosion rate, while an opposite effect was found in presence of Ca^{2+} . The XRD patterns showed different crystalline products with FeCO_3 as the main carbonate in pure NaCl solution. The presence of Ca^{2+} and Mg^{2+} resulted in the formation of iron- calcium/magnesium carbonate ($\text{Fe}_x\text{Ca}/\text{Mg}_{1-x}\text{CO}_3$) respectively. More severe pitting propagation has been reported in presence of Ca^{2+} compared to Mg^{2+} containing solutions

Research related to Ca^{2+} in CO_2 corrosion of carbon steel has shown an influence of this cation on both the general and pitting corrosion with the precipitation of a mixed iron-calcium carbonate layer ($\text{Fe}_x\text{Ca}_y\text{CO}_3$ where $x + y = 1$)[25][28][29][32][34]. According to Mansoori et al. [34], one of the most important parameters that has often been omitted in literature is the saturation degrees of carbonates in the solution as it influences the precipitation kinetics of carbonate [36][37]. Most of the research focused on the effect of Ca^{2+} on the precipitation and the protectiveness of the carbonate layer on bare carbon steel.

None of these investigations have clearly focused on the effect of Ca^{2+} on the stability and protectiveness of an already precipitated FeCO_3 scale, which is a situation that can be experienced

during the lifetime of a well in connection with enhanced oil recovery and water injection. Therefore, the present study focus on determining the effect of Ca^{2+} on the corrosion behavior of carbon steel with an already formed FeCO_3 layer developed at 80 °C at pH 6.5 in an aqueous solution saturated with CO_2 (partial pressure $p_{\text{CO}_2} = 0.5$ bar). The influence of this cation is investigated in terms of structure, thickness, morphology and composition of the corrosion scale after injection of Ca^{2+} at different concentrations. The corrosion rates were determined by Linear Polarization Resistance (LPR), while the properties of the precipitated layers were investigated using Potentiodynamic Sweep (PS) and Electrochemical Impedance Spectroscopy (EIS). Morphology of the scale, of the cross section and of the corrosive attack on the steel surface were investigated using scanning electron microscopy, energy dispersive X-ray analysis, and X-ray diffraction.

Material and methods

Materials and specimen preparation

The specimens were made of 1Cr steel with a chemical composition shown in Table 1. The material presented a tempered martensitic microstructure visible in Figure 1. The specimens were machined into cylindrical shape with an exposed surface area of 3.95 cm². The surface of the samples was polished mechanically with SiC grade P220, P320, P500 and P1000, while being cooled down with de-ionized water. Immediately after polishing, the samples were degreased with acetone, flushed with isopropyl alcohol and air-dried. The dried sample were then mounted on the sample holder and immersed into the solution. Two additional samples were placed in the solution for surface characterization of the morphology and composition of the corrosion products. At the end of the test the samples were retrieved, rinsed with isopropyl alcohol, dried in air and stored in a desiccator.

Electrolyte preparation

All the tests were conducted in a 1 wt.% NaCl solution at 80 °C and atmospheric pressure. The Ca^{2+} ions were added from a stock solution of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$. Before the sample was inserted in the solution,

the electrolyte was purged overnight with nitrogen to deoxygenate. The gas was then switched to CO₂ and purged for 4 hours in order to saturate the solution with test gas. The pH was adjusted to 6.5 by adding NaHCO₃ in order to facilitate FeCO₃ precipitation. After pH adjustment the solution was left to de-aerate for at least one hour with test gas to remove possible oxygen that may have entered during this operation. During testing, the electrolyte was continuously purged with CO₂ to maintain the solution saturated and avoid oxygen entrance.

Experimental conditions and procedure

All the experiments were performed at least twice to ensure reproducibility. The average value was used in the Results section, where the error bars represent the maximum and minimum values observed in repeated experiments. All the tests were performed in a standard three-electrode corrosion cell, described in the Electrochemical measurements Section. Test conditions are summarized in Table 2 and the experimental procedure is shown in Figure 2. This procedure was designed to investigate the effect of Ca²⁺ on the corrosion of carbon steel in CO₂ environment in the presence of a pre-deposited FeCO₃ layer. Four different Ca²⁺ concentrations were tested, namely: 0, 100, 1,000 and 10,000 ppm. During the initial stage (Step 1), the sample was left to corrode in the solution until Fe²⁺ ions were sufficient to super-saturate the solution and precipitated as FeCO₃. This event, described in the literature as Pseudo-Passivation [38][39], was detected by a steep rise in the corrosion potential and a decrease in corrosion rate below 0.1 mm/yr. This layer was left to stabilize for approximately 15 hours (Stage 2), after which a de-aerated stock solutions of CaCl₂·2H₂O was diluted in the electrolyte by means of a syringe to achieve the desired concentration of Ca²⁺ ions (Stage 3). The stock solution was de-aerated for at least 4 hours with test gas, before being added to the test solution. The test continued until a stable value of corrosion potential and corrosion rate was reached. The changes in corrosion rate were measured throughout the test by Linear Polarization Resistance (LPR) and the related corrosion potential was recorded. Water samples were taken at the end of each stage to evaluate variation in water chemistry and link them to the corrosion behaviour. Electrochemical Impedance Spectroscopy (EIS) were performed at the end of Stage 3 in order to study

the evolution of the electrical charge transfer characteristics of the system. These measurements were followed by Potentiodynamic Sweeps (PS) to evaluate the changes in electrochemical behaviour of the pseudo-passivated sample after Ca^{2+} addition.

Two additional tests were performed. One without Ca^{2+} injection and one where the pH of the solution was reduced during Stage 3. The former one was carried out in order to have a reference test for comparing the results. The latter test was performed in order to relate the effect of Ca^{2+} addition to pH changes. In this experiment the pH of the test solution without calcium was reduced from 6.5 down to 5.4 by adding HCl during Stage 3. The final pH value of 5.4 represented the equilibrium pH for the 10,000 ppm Ca^{2+} experiment recorded during this test. This equilibrium value was confirmed to be accurate by calculating the equilibrium pH of a 1 wt.% NaCl solution saturated with CO_2 at 80 °C containing 10,000 ppm Ca^{2+} . The equilibria calculations have been performed with pHSim software from Scale Consult AS [39].

Additional samples were placed in the solution for surface characterization of the morphology, and composition of corrosion products were evaluated using Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray Spectroscopy (EDS) and X-Ray Diffraction (XRD). These samples were quickly removed from the cell and their inlet immediately plugged just before the potentiodynamic sweep in Step 3 in order to avoid the influence of possible changes in the solution occurring during anodic and cathodic polarization. Oxygen contamination during this operation was avoided by continuously purging the solution with test gas and the samples were removed quickly and their inlet immediately plugged.

Electrochemical measurements

The corrosion tests were carried out in a 1.5 L glass cell arranged as a standard three-electrode cell. A schematic of the test cell is shown in Figure 3. An Ag/AgCl reference electrode was placed in contact with the solution through a glass luggin capillary and a concentric platinum wire ring was used as the counter electrode. The instantaneous corrosion rates were monitored with linear polarization resistance (LPR) measurements every two hours. Using the obtained polarization resistance (R_p) and

Tafel slopes, the corrosion current density and corrosion rate were calculated using equation (1) and (2):

$$i_{corr} = \frac{\beta}{R_p} = \frac{\beta_a \beta_c}{2.303 \cdot R_p \cdot (\beta_a + \beta_c)} \quad (1)$$

$$C_{rate} = \frac{i_{corr} \cdot 3272 \cdot EW}{\rho} \quad (2)$$

where β_a and β_c are the anodic and cathodic Tafel constant respectively, EW is the equivalent weight in grams and 3272 is a constant factor used to convert values in mm/yr. The β value was obtained by Tafel interpolation of the potentiodynamic curves obtained on samples polarized from -250 mV to +250mV vs OCP after one hour immersion in 1wt.% NaCl solution saturated with CO₂ at 80 °C and pH= 6.5. The β value was equal to 26 mV and was kept constant throughout the experiments. During LPR measurements the potential was scanned in a range of ± 10 mV vs. open-circuit potential (OCP) at a scan rate of 0.165 mV/s.

The EIS measurements were performed by applying an AC signal amplitude of 10 mV vs resting potential in a frequency range from 10 kHz to 10 mHz. The potentiodynamic scans were carried out from the OCP down to -900 mV vs Ag/AgCl reference electrode with a scan rate of 10 mV/min. The OCP was then left to stabilize back to its original value (approximately 30 minutes duration). The anodic scan was then performed from OCP to -400 mV vs Ag/AgCl under the same scan rate.

Water chemistry and chemical equilibria determination

The pH was monitored in situ and the solution was sampled at the end of each stage to measure the concentration of Fe²⁺ and Ca²⁺. 10 mL of solution were retrieved for Fe²⁺ analysis and transferred to a 50 mL volumetric flask containing 4 mL of 10% hydroxylamine hydrochloride solution and 4 mL 0.3% o-phenanthroline solution. De-ionized water was added to the 50 mL mark and the sample was analyzed by UV-Vis spectrophotometry against pre-recorded standard curves. A UV-2600 UV-Vis

spectrophotometer from Shimadzu was used for the analysis. 10 additional mL of test solution were retrieved for Ca^{2+} analysis by inductive coupled plasma (ICP) spectroscopy with a Thermo Scientific ICAP 7200 ICP-OES Analyzer.

The Fe^{2+} and Ca^{2+} values recorded were then inserted in pHSim software to predict saturation degree of FeCO_3 (S_{FeCO_3}) and CaCO_3 (S_{CaCO_3}).

Surface characterization and phase analysis

The morphology and elemental analysis of the corrosion product were investigated using a ThermoScientific™ Quanta™ FEG 200 high-resolution scanning electron microscope (SEM) assisted with energy dispersive X-ray (EDS) analysis equipment. The cross-section was analysed with SEM by moulding the sample in cold epoxy resin in order to avoid damage of the corrosion products. The sample was then sliced along the cross-section and polished with ethanol with SiC grade P220, P320, P500, P1000 and P4000, followed by 3 and 1 μm abrasive particles. The morphology of the steel surface after corrosion products removal was investigated with SEM to evaluate possible changes in the corrosion mechanism. The corrosion products were removed by wiping the surface of the samples with a cotton pad and immersing it in Clarke's solution as per ASTM Standard G1-03[40].

X-Ray diffraction (XRD) was used to determine the phase composition of the formed layer using Bruker D8 Advance. The instrument was operated at 40 kV and 40 mA with $\text{Cr-K}\alpha$ radiation ($\lambda = 0.22909 \text{ nm}$), resulting in a penetration depth of up to 17 μm

Results

The pH monitoring

The changes in pH during the three stages (see Figure 2) are shown in Figure 4. At 100ppm Ca^{2+} concentration, the pH values remained stable during the whole test interval, while the addition of 1,000 and 10,000 ppm Ca^{2+} during Stage 3 resulted in a marked drop in pH, which decreased from ≈ 6.5 down to 6.0 and 5.4 respectively.

220 The OCP and LPR measurements

221 The results of OCP and corrosion rate measurements during the three experimental stages are
222 summarized in Figure 5 a & b, where the error bars represent the maximum and minimum values
223 observed in repeated experiments. Stage 1 was characterized by a continuous increase of both
224 potential and corrosion rate. This behavior was followed by a sharp increase in the corrosion potential
225 from ≈ -650 mV to ≈ -500 mV and by a rapid decrease of the corrosion rate from ≈ 2.5 mm/yr down to
226 values lower than 0.1 mm/yr due to FeCO_3 precipitation. Stage 2 was characterized by a stable value
227 of both potential and corrosion rate without significant variation with time. The addition of 100 ppm
228 of Ca^{2+} at the end of Stage 2 did not influence the corrosion behavior of the steel as the corrosion rate
229 essentially remained similar to that prior to addition of calcium. This is indicated by the stable value
230 of the OCP and corrosion rate until the end of Stage 3, which is comparable to the experiment with no
231 Ca^{2+} . With the injection of 1,000 ppm Ca^{2+} ions, the OCP rapidly decreased, which stabilized at ≈ 150
232 mV below the stable potential observed under Stage 2. When the concentration of Ca^{2+} was increased
233 to 10,000 ppm, the value of the OCP instantaneously decreased by approximately 200 mV, which was
234 followed by a slow increase of about 20 mV. This behavior was reflected on the corrosion rate, which
235 jumped from the steady value of 0.1 mm/yr at the end of Stage 2 to 1.5 mm/yr, which remained almost
236 stable until the end of the test. Similarly, the lowering of the pH at the end of Stage 2 from 6.5 to 5.4
237 (marked as "pH Drop" in Figure 5 a, b) led to a sharp decrease of the OCP and increase of corrosion
238 rate. The introduced pH change at the end of stage 2 has resulted in a steady increase of the corrosion
239 rate unlike the case for calcium ion addition experiments.

240 Just to confirm Cl^- ions are not influencing the corrosion process after the FeCO_3 has been formed, an
241 additional experiment was performed. In this experiment 17,692 ppm Cl^- were injected during Stage
242 3 corresponding to the Cl^- concentration of the 10,000 ppm Ca^{2+} experiment. The Cl^- ions were injected
243 as NaCl. This experiment is marked as "NaCl" in Figure 5 b. For clarity purpose only the corrosion rate
244 is reported. As noticeable, after the injection of 17,692 ppm Cl^- the corrosion rate remained

unchanged until the end of the test. Therefore, further analysis on the sample exposed to high chloride environment have been omitted.

The Fe^{2+} and Ca^{2+} ion concentration monitoring

The concentration of Fe^{2+} and Ca^{2+} ion was monitored during the three different stages of the experiments and analyzed together with the pH results in order to evaluate the chemical equilibria and possible precipitations in the solution. The high initial Fe^{2+} concentration during Stage 1, decreased to a value less than 1 ppm during Stage 2 when the protective layer of FeCO_3 precipitated on top of the sample (Figure 6 a). At the end of Stage 3, the amount of Fe^{2+} in the solution increased with increased amount of injected Ca^{2+} (Figure 6 a). The highest Fe^{2+} concentration recorded for the corresponding pH drop reflects the higher corrosion rate experienced by the sample during the Stage 3 of this test. The solution with the addition 100 ppm of Ca^{2+} during Stage 3 did not show an increase of Fe^{2+} by the end of the experiment.

The variation of FeCO_3 saturation degree (S_{FeCO_3}) with time is shown in Figure 6 b. It can be seen that after Stage 2, all the solutions remained under-saturated with respect to FeCO_3 until the end of the test. The saturation ratio for CaCO_3 was based on pH and Ca^{2+} concentrations injected at the start of Stage 3 and measured at the end of Stage 3 (Figure 7). Precipitation was visually recorded in the solution at 1,000 and 10,000 ppm, which turned “cloudy”. At 100 ppm Ca^{2+} the solution remained clear. The final measured concentrations were 52, 511 and 5,526 ppm for the 100, 1,000 and 10,000 ppm Ca^{2+} respectively, confirming that precipitation occurred in Stage 3 until the equilibrium was reached. The unexpected undersaturation recorded at the end of Stage 3 for the 10,000 ppm Ca^{2+} (Figure 7) could be due the error related to the calcium ion measurement values from the ICP.

Electrochemical Impedance Spectroscopy investigation

Figure 8 shows the results of impedance measurements under stage 3 of the experiments as in Figure 1. A Nyquist diagram was used to investigate the effect of the different Ca^{2+} concentrations at the end of Stage 3 on the stability and protectiveness of the FeCO_3 layer (Figure 8 a). The 0 ppm test showed

two loops with different amplitudes. At High Frequency (HF), a small semicircle was present and at Medium-Low Frequency (MF-LF) a second loop with higher amplitude was seen. The presence of two responses was further confirmed by a Bode Plot (Figure 8 b, c). Two slopes which are typical of a system with more than one time constant were recorded in the $|Z|$ vs frequency graph. Similarly in Figure 6 c the presence of two maximum points at MF and HF indicates that more than one time constant resulted in the process [41]. The addition of 100ppm Ca^{2+} did not lead to significant changes in the shape of the Nyquist and Bode Plot from the pseudo-passivated sample. The diameter of the Nyquist plot decreased, however, only with the addition of 1,000 and 10,000 ppm Ca^{2+} , which suggested a re-initiation of the corrosion process for both cases. This was further confirmed by the value $|Z|$ for 1,000 and 10,000 ppm Ca^{2+} (Figure 8 b) which decreased during the whole frequency range compared to the previous values at 0 and 100 ppm Ca^{2+} . The sample exposed to 1,000 ppm Ca^{2+} recorded a higher $|Z|$ at the LF range than for 10,000 ppm. The $|Z|$ values converged to similar values at High Frequencies. A more capacitive behavior at HF was recorded in the phase diagram plot for 1,000 and 10,000 ppm with values of the phase angle closer to -90° (Figure 8 c). A second maximum with a decrease in phase angle values was recorded in the LF range, confirming the presence of more than one time constant. The sample that underwent a pH drop from 6.5 to 5.4, behaved very similarly to the one exposed to 10,000 ppm Ca^{2+} during Stage 3. For both conditions, two suppressed loops were also recorded which showed a further decrease in diameter (Figure 8 a) and lower $|Z|$ at LF (Figure 8 b)

The evolution of various interfaces on the sample surface after Ca^{2+} addition can be characterized by an equivalent circuit (Figure d), which is commonly used to simulate the surface of an electrode with a low conducting layer present on the top [42][43]. The R_s represents the solution resistance of the electrolyte, R_{po} and C_{sc} are the pore resistance and capacitance of the scale, R_{ct} is the charge-transfer resistance and C_{dl} the capacitance of the double-layer. The impedance parameters obtained by circuit fitting are listed in Table 3. The polarization resistance values obtained with EIS showed similar trend with the one measured with LPR with increase calcium addition.

Potentiodynamic polarization results

The potentiodynamic polarization curves obtained at the end of Stage 3 is shown in Figure 9. The anodic polarization for the 0 and 100 ppm Ca^{2+} showed a slow increase in current density with increase in over potential, while the difference between the two concentrations is minimal. The addition of 1,000 and 10,000 ppm Ca^{2+} enhanced the anodic reaction compared to the 0 and 100 ppm Ca^{2+} cases. A passive area was recorded for the addition of 1,000 ppm Ca^{2+} between -550 and -450 mV, above which it sharply increased. This passive area disappeared with the addition of 10,000 ppm Ca^{2+} and with the drop in pH and was substituted by a rapidly increasing anodic current as soon as the over potential turned positive. Similarly, an enhanced cathodic reaction was recorded for each increase in Ca^{2+} concentration above 100 ppm Ca^{2+} ions and for the drop in pH.

The XRD analysis of the scale

Results from X-Ray diffraction analysis of the scale formed under different conditions are shown in Figure 10. The XRD patterns showed that FeCO_3 was the predominant corrosion product on the surface of all samples. A CaCO_3 layer was detected only on the sample exposed to 10,000 ppm Ca^{2+} ions during Stage 3, suggesting that CaCO_3 precipitated on an already formed layer of FeCO_3 . The presence of an Iron peak was detected at 1,000 and 10,000 ppm Ca^{2+} ions suggesting dissolution of the carbonate layer so that X-ray beam could penetrate to the steel. Similar results were obtained for the case where the pH was lowered from 6.5 to 5.4.

Surface Morphology of scale using SEM

The surface morphology of the scale and the cross section analysis is shown in Figure 11. The SEM images are presented in top view and cross section of the samples at the end of Stage 3. Typical prism-shaped crystals covering the whole surface were detected at 0 and 100ppm, which formed a dense and compact layer (noticeable in the cross section images), which is confirmed as FeCO_3 from the previous XRD results. The thickness around the cross section for the samples exposed to 0 and 100 ppm averaged to approximately 19 μm . The presence of an initial porous cementite layer (Fe_3C) with

FeCO₃ precipitated within the Fe₃C network can also be seen in the cross section. A top film consisting only of FeCO₃ precipitated on top of this initial layer. Similar structure was recorded on the surface of the sample exposed to the solution where 1,000 ppm Ca²⁺ was injected. However, the cross section analysis revealed a partially dissolved and more porous inner film just underneath the top layer. At 10,000 ppm, the surface deposit showed a platelet-like morphology, which produced a less densely packed structure. The cross section area exhibited significant FeCO₃ inner film dissolution and on the top of which a loose CaCO₃ layer had formed (see layered image determined by EDS in Figure 11). Similarly, the cross section for the pH Drop experiment showed a dissolving FeCO₃ layer with a loose and porous structure above the steel surface.

The morphology of the surface after the removal of the corrosion products is shown Figure 12. Uniform corrosion was clearly detected on the sample exposed to 100 ppm and 1,000 ppm Ca²⁺ during Stage 3 as noticeable by the evenly corroded surface (Figure 12 a and b). At higher concentrations and for the pH Drop case (Figure 12 c and d), the attack started to be more localized showing areas of larger dissolution. These areas increased with increased Ca²⁺ content during the third stage of the experiment. Even though pits were not found at these high concentrations, the sites of more confined corrosion could represent initiation areas of localized attack, which could have further develop into pits had the experiment run for longer time.

Discussion

Calcium and iron carbonates are commonly observed scales in the oilfield industry [31]. Calcium is present in the formation brine or the injected seawater, whilst iron can be released from the production string due to the corrosion process [44]. Ca²⁺ ions can precipitate as CaCO₃ in the production string on top of a pre-existing iron carbonate layer [22][27][29] [32][35].

This study has identified that the introduction of Ca²⁺ ions can change the stability of the protective FeCO₃ layer formed on top of a 1Cr steel and therefore its electrochemical behavior. When Ca²⁺ ions

precipitate in the form of CaCO_3 , they can lead to acidification of the solution according to Equation 3).

Precipitation of iron carbonate and calcium carbonate is highly dependent on their saturation degree with respect of the bulk solution [35][36]. Precipitation occurs when the saturation degree is greater than one. The saturation degree with respect of FeCO_3 and CaCO_3 depends on ion concentration, pH and temperature as shown in Equation 4) and Equation 5) for FeCO_3 [45] and Equation 6) and Equation 7) for CaCO_3 [46], where K_{SPFeCO_3} and $K_{\text{SP,CaCO}_3}$ are the solubility products of FeCO_3 and CaCO_3 , respectively, and I the ionic strength (Equation 8) [35]:

$$S_{\text{FeCO}_3} = \frac{[\text{Fe}^{2+}][\text{CO}_3^{2-}]}{K_{\text{SPFeCO}_3}} \quad 4)$$

$$\text{Log}K_{\text{SPFeCO}_3} = -59.3498 - 0.041377 \cdot T - \frac{2.1963}{T} + 24.5724 \cdot \text{Log}T + 2.518 \cdot I^{0.5} - 0.657 \cdot I \quad 5)$$

$$S_{\text{CaCO}_3} = \frac{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}{K_{\text{SPCaCO}_3}} \quad 6)$$

$$\text{Log}K_{\text{SPCaCO}_3} = -1228.732 - 0.299444 \cdot T + \frac{35512.75}{T} + 485.818 \cdot \text{Log}T \quad 7)$$

$$I = \frac{1}{2} \sum_i c_i z_i^2 \quad 8)$$

where T is temperature in Kelvin.

When the concentration of Ca^{2+} was slightly above the saturation level with respect to CaCO_3 , as for the case where 100 ppm Ca^{2+} were added to the solution, the protectiveness of the FeCO_3 layer was not affected. This can be seen in a stable corrosion rate and potential during Stage 3 which remained around comparable values of the pseudo-passivated sample in Stage 2 (Figure 5 a & b). The potentiodynamic curves for those cases were almost overlapping indicating a comparable electrochemical behavior of the reference experiment and the addition of 100 ppm Ca^{2+} (Figure 9).

The slow increase of the anodic current density for the reference and the 100 ppm Ca^{2+} test suggests the presence of a protective layer, which limited the dissolution of iron. The presence of a thick layer able to create a diffusion barrier which prevented further metal dissolution was also confirmed by the high impedance at LF (Figure 8 a) and R_{po} and R_{ct} values recorded (Table 3). The SEM images support these results showing a solid, dense, and intact layer of FeCO_3 on top of a mixture of FeCO_3 - Fe_3C layer, still able to ensure corrosion protection to the underlying steel (Figure 11). The presence of this Fe_3C layer has been reported in literature and estimated to be beneficial, since it can act as an anchoring point for iron carbonate precipitation [47]. Similar morphologies have been described by Esmaeely et al. with the presence of 100ppm Ca^{2+} at the start of the experiment. Authors reported that Ca^{2+} in low concentration does not affect the formation of the FeCO_3 layer and the corrosion rate [29].

The higher the saturation degree at a specific temperature and pH with respect to CaCO_3 , given by the higher concentration of Ca^{2+} ions added to the solution, the stronger the pH drop to reach equilibrium (Figure 4). The drop in pH below the saturation degree with respect to FeCO_3 is able to chemically remove the protective layer to an extent that is dependent on the level of under saturation in the solution [20]. This effect was recorded by an increase in corrosion rate and fall in OCP for both high S_{CaCO_3} and forced pH Drop (Figure 5 a & b). The increase in corrosion rate was followed by an increase in Fe^{2+} counts during the third Stage as shown in Figure 6 a. Similar observation was made by Ruzic et al. [20] in their series of dissolution experiments after FeCO_3 was formed. The authors showed strong dependence of FeCO_3 removal kinetics on the level of saturation in the solution, determined by the pH level.

The low pH kept the solution under saturated with respect to FeCO_3 until the end of the test (Figure 6 b) preventing possible precipitation during the last stage. The re-initiation of the corrosion processes for these cases was supported by the smaller diameter of the Nyquist plot and the lower $|Z|$ module at LF (Figure 8 a & b). The smaller diameter of the second semicircles was related in this experiment to the FeCO_3 selectively being dissolved from the top of the bare steel. The R_{ct} represents polarization

resistance of the steel substrate [48][49]. Therefore, the lower values detected with increasing S_{CaCO_3} and pH Drop further confirmed the re-initiation of the corrosion process during Stage 3. As shown in Table 3, the value of C_{sc} increased with increasing Ca^{2+} concentration and decreasing pH, followed by a decrease of the pore resistance R_{po} . These changes have in previous studies been linked to an increase in the porosity of the layer as the exposed area increases as more pores are revealed [50][51]. Similarly, the changes in C_{sc} and R_{p} obtained at higher Saturation Ratio of CaCO_3 and lower pH, suggested the partial dissolution of the protective FeCO_3 layer, re-exposing the underlying steel to the corrosive environment. The presence of a thick FeCO_3 layer which was dissolved by adding Ca^{2+} ions was further confirmed by the absence of the iron peak at 0 and 100ppm Ca^{2+} . The thickness of the FeCO_3 layer under these conditions ($\approx 19 \mu\text{m}$) was higher than the penetration depth for the Cu radiation (up to $17 \mu\text{m}$), which did not reach the steel substrate. Similar observations were made by Esmaeely et al. [29] where they confirmed the presence of a thick FeCO_3 layer by the absence of the main peak of $\alpha\text{-Fe}$ linked to diffraction from steel substrate. The dissolving protective layer partially exposed the underlying steel as suggested by the Iron peaks detected in the XRD patterns for 1,000, 10,000 ppm Ca^{2+} ions, and pH Drop (Figure 10). The thickness of the FeCO_3 layer was reduced to $\approx 8 \mu\text{m}$ for the 1,000 ppm case. For the 10,000 ppm and the pH Drop, full FeCO_3 dissolution was recorded on several areas along the cross section. The cross section images showed for these cases a loose and porous FeCO_3 layer in which the solution could penetrate and re-initiate the corrosion process, and in agreement with the results from electrochemical testing. This porous structure could behave like initiation sites of localized corrosion and pitting as detected by SEM images of the samples at 1,000 and 10,000 ppm Ca^{2+} after the removal of corrosion products (Figure 12). Comparable morphology was found on the sample that underwent a pH drop during the third stage. The dissolution of the FeCO_3 protective layer could also be seen in the Potentiodynamic curves for 1,000 and 10,000 ppm Ca^{2+} and forced pH Drop (Figure 9), where both the anodic and cathodic current densities are enhanced by the dissolution of this film. The passive area recorded on the potentiodynamic curves from

417 ≈ -550 mV to ≈ -450 mV for the sample at 1,000 ppm Ca^{2+} confirm the presence of a thinner FeCO_3 layer
418 compared to the 0 and 100 ppm cases. This layer was broken down at higher anodic potential.

419 By evaluating the shift in peak position for FeCO_3 and CaCO_3 , several authors report the formation of
420 a mixed iron-calcium carbonate layer when Ca^{2+} ions are present in the solution[25][27][28][29]. This
421 compound results from the isostructurality of FeCO_3 and CaCO_3 , where Ca can replace Fe in the
422 structure of siderite and form a substitutional solution with larger d-spacing [52]. The mixed iron-
423 calcium carbonate was not found during this study. The XRD peak for both siderite and calcite (Figure
424 10) did not shift with increasing Ca^{2+} concentrations. The high intensity peak for siderite (104) was
425 recorded at $2\theta=48.403^\circ$ under all concentrations, suggesting that none of the atoms were substituted.
426 The Ca^{2+} was injected after the FeCO_3 layer had stabilized. After it precipitated as CaCO_3 it left the
427 solution under-saturated with respect to FeCO_3 . This salt could therefore not precipitate again within
428 the experimental time, removing the possibility of a mixed iron-calcium carbonate deposition as
429 detected by other researchers.

430 Results reinforced previous conclusions, where the bulk saturation degree with respect to the
431 associated carbonate is more relevant than the individual ions concentration when investigating their
432 influence in CO_2 corrosion of mild steel [34]. Results confirmed that the bulk saturation degree, which
433 depends not only on ion concentration but also on temperature and pH, was the main driving force of
434 carbonate precipitation and subsequent pH drop, leading to the dissolution of the FeCO_3 protective
435 layer. This dependence can be made clearer by plotting the corrosion rate measured at the end of
436 Stage 3 against the S_{CaCO_3} corresponding to 100, 1,000 and 10,000 ppm Ca^{2+} in the solution at 80°C
437 and $\text{pH}=6.5$ (Figure 13). A high S_{CaCO_3} leads to higher corrosion rate, due to the drop in pH below the
438 solubility limit of FeCO_3 and subsequent dissolution of the protective layer. Had the solution been
439 under-saturated with respect to CaCO_3 at the same Ca^{2+} concentrations tested in this paper (because
440 of low temperature and/or pH), there would not have been a fall in pH and subsequent FeCO_3
441 dissolution and increase in corrosion rate.

The results obtained in this paper could suggest that a similar effect could be recorded with other ions that consume carbonates from the solution reducing the pH. Amongst those, Mg^{2+} is frequently present in oil and gas production and is able to precipitate as $MgCO_3$, despite this event being less common than $CaCO_3$ precipitation [25][27][54]. This precipitation may occur during production and it may lower the pH of the fluid, dissolving the protective $FeCO_3$ layer depending on its saturation degree.

Despite the similarities, the corrosion behavior for the sample that underwent a pH drop during the last stage differed from the 10,000 ppm Ca^{2+} Stage. The former showed a continuous increase of the corrosion rate, whilst the latter stabilized shortly after the addition. This difference could be due to the $CaCO_3$ which precipitated on top of the dissolving $FeCO_3$ layer (see cross section at 10,000 ppm and pH Drop in Figure 11). This layer could create, depending on the conditions, an additional barrier that could limit the rate of iron dissolution. Based on these results, the authors speculate that the $CaCO_3$ generated in aqueous CO_2 environment may lead to some level of protection against further corrosion, although inferior to $FeCO_3$. However more detailed investigation is required to validate this hypothesis.

The $CaCO_3$ precipitation is a common event within Oil & Gas production [22][23][44]. The result presented in this paper shows that $CaCO_3$ precipitation may be able to dissolve a previously formed $FeCO_3$ protective layer. This effect was determined not only by the individual concentrations of Ca^{2+} in the solution, but by the bulk saturation degree with respect to calcium carbonate, which is influenced also by pH and temperature [31][46]. Further studies aiming at investigate the effect of calcium in CO_2 saturated solutions, should therefore focus on the bulk saturation degree of $CaCO_3$ and should define and document the water chemistry of the system throughout the testing. The present study is conducted in stagnant condition with the purpose to investigate the effect of $CaCO_3$ precipitation on the stability of a previously formed $FeCO_3$ protective layer. Emphasis was given to changes in saturation degree of the bulk solution with respect to $CaCO_3$ and $FeCO_3$ and their effect on the

corrosion rate. Corrosion processes and scale precipitation are, however, significantly affected by concentration gradients and therefore by mass transfer between the bulk solution and the metal surface [53]. Changes in these parameters may affect results and are beyond the scope of this research. Dedicated studies, aiming at elucidating the influence of mass transfer on the stability of a previously formed FeCO_3 layer under CaCO_3 precipitation, should be performed

Conclusions

The effect of Ca^{2+} on the protective FeCO_3 layer formed on top of 1Cr steel and its influence on the corrosion behavior was investigated in CO_2 -saturated aqueous NaCl solution in the presence of 100, 1,000 and 10,000 ppm Ca^{2+} at atmospheric pressure and 80 °C. Focus was given to understanding the influence of CaCO_3 precipitation during oil and gas production on the morphology and structure of the protective FeCO_3 layer, as well as the consequences for general and localized corrosion. The following conclusions can be drawn from this study:

- The effect of Ca^{2+} addition is linked to the saturation ratio of CaCO_3 as main driving force for CaCO_3 precipitation and the subsequent pH drop of the solution to equilibrium levels.
- The larger the S_{CaCO_3} the larger the drop in pH from saturated to equilibrium conditions.
- Equilibrium pH values that made the solution conditions drop below the saturation degree of FeCO_3 were identified as the cause for FeCO_3 dissolution and an increased corrosion rate.
- Electrochemical studies supported a mechanism of protective layer dissolution and increased porosity which allowed the solution to enter the voids and re-initiate the corrosion process.
- SEM images confirmed that selective dissolution of FeCO_3 occurred which exposed the underlying steel to the aggressive environment. These exposed areas could become potential sites of localized corrosion.

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Data Availability

The raw/processed data generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

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Figure Captions

Figure 1 Microstructure of the 1Cr steel after etching with Nital. Magnification 50 x 10.

Figure 2 Experimental procedure for corrosion study at different Ca^{2+} concentrations.

Figure 3 Schematic of experimental cell.

Figure 4 pH change vs. time during the three different stages of corrosion in 1% wt. NaCl solution with calcium ions, $T=80^\circ\text{C}$, initial pH=6.5.

Figure 5 Variation of: OCP (a) and corrosion rate (b) of 1Cr steel at different Ca^{2+} concentration injected during Stage 3 in 1% wt. NaCl solution, $T=80^\circ\text{C}$, initial pH=6.5. The error bars represent the maximum and minimum values observed in repeated experiments

Figure 6 Variation of Fe^{2+} concentration (a) and saturation ratio of FeCO_3 (b) exposed to different Ca^{2+} ppm at different stages of corrosion in 1% wt. NaCl solution, $T=80^\circ\text{C}$, initial pH=6.5.

Figure 7 Saturation Ratio of CaCO_3 at different Ca^{2+} concentrations during Stage 3 of corrosion experiment in solution with 1 wt. % of NaCl, $T=80^\circ\text{C}$, initial pH=6.5.

Figure 8 Impedance results obtained for a 1Cr Steel after the addition of Ca^{2+} ions: Nyquist plots (a), Bode plots (b), Phase angle (c) and equivalent circuit (d).

Figure 9 Potentiodynamic curves performed at the end of Stage 3 for different Ca^{2+} concentrations.

Figure 10 Results of XRD analysis of scale formed on 1Cr steel exposed to different Ca^{2+} concentration and lower pH during Stage 3.

650 Figure 11 Surface morphology and cross section of the samples at 0, 100, 1,000, 10,000 ppm Ca^{2+} and
651 pH Drop.

652 Figure 12 Surface of the sample after scale removal with Clarke Solution: (a) 100 ppm; (b) 1,000 ppm;
653 (c) 10,000 ppm Ca^{2+} , (d) pH Drop.

654 Figure 13 Corrosion rate taken at the end of Stage 3 vs. S_{CaCO_3} . The error bars represent the maximum
655 and minimum values observed in repeated experiments

656 Table Captions

657 Table 1 Chemical composition in wt.% of the L80-1Cr material

658 Table 2 Test conditions and electrolyte composition

659 Table 3 Electrochemical impedance parameters fitted from the measured EIS data