An electrochemical and X-ray computed tomography investigation of the effect of temperature on CO₂ corrosion of 1Cr carbon steel

Rizzo, Riccardo; Baier, Sina; Rogowska, Magdalena; Ambat, Rajan

Published in:
Corrosion Science

Link to article, DOI:
[10.1016/j.corsci.2020.108471](https://doi.org/10.1016/j.corsci.2020.108471)

Publication date:
2020

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Rizzo, R., Baier, S., Rogowska, M., & Ambat, R. (2020). An electrochemical and X-ray computed tomography investigation of the effect of temperature on CO₂ corrosion of 1Cr carbon steel. *Corrosion Science*, 166, [108471]. <https://doi.org/10.1016/j.corsci.2020.108471>

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Journal Pre-proof

An Electrochemical and X-ray Computed Tomography Investigation of The Effect of Temperature on CO₂ Corrosion of 1Cr Carbon Steel

Riccardo Rizzo, Sina Baier, Magdalena Rogowska, Rajan Ambat

PII: S0010-938X(19)32257-7
DOI: <https://doi.org/10.1016/j.corsci.2020.108471>
Reference: CS 108471

To appear in: *Corrosion Science*

Received Date: 25 October 2019

Revised Date: 10 January 2020

Accepted Date: 11 January 2020

Please cite this article as: Rizzo R, Baier S, Rogowska M, Ambat R, An Electrochemical and X-ray Computed Tomography Investigation of The Effect of Temperature on CO₂ Corrosion of 1Cr Carbon Steel, *Corrosion Science* (2020), doi: <https://doi.org/10.1016/j.corsci.2020.108471>

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2020 Published by Elsevier.

An Electrochemical and X-ray Computed Tomography Investigation of The Effect of Temperature on CO₂ Corrosion of 1Cr Carbon Steel

Riccardo Rizzo^{1,*}, Sina Baier², Magdalena Rogowska¹, Rajan Ambat¹

¹ Section of Materials and Surface Engineering, Department of Mechanical Engineering, Technical University of Denmark, Produktionstorvet, Kongens Lyngby, 2800 Denmark

² Department of Physics, Technical University of Denmark, Fysikvej, 2800, Kgs. Lyngby, Denmark

*Corresponding author: ririz@mek.dtu.dk

Highlights

- The effect of temperature on the corrosion behavior of 1Cr carbon steel in CO₂ saturated solution at 40 °C and 80 °C was investigated.
- X-ray CT was used to investigate the corrosion scale ex-situ.
- Temperature influenced the corrosion kinetics the precipitation of FeCO₃ and the corrosion mechanism.

Abstract

This paper presents the investigation on the effect of temperature on the corrosion behavior of 1Cr carbon steel at 40 °C and 80 °C in 1 wt. % NaCl aqueous solution saturated with CO₂. The evolution of the corrosion process was followed with Linear Polarization Resistance (LPR) and Electrochemical Impedance Spectroscopy (EIS). X-ray Computed Tomography was used for 3D structure of the scale *ex-situ* to correlate with electrochemical investigation. Additionally, the surface morphology of the corrosion products was analyzed with Scanning Electron Microscopy (SEM) and structural information using X-ray powder diffraction (XRD). Tomography results showed protective FeCO₃ formation with three different layers at 80 °C, where corrosion underneath the scale was uniform. The 3D image of the corrosion products formed at 40 °C showed loose and porous, and consequently did not reduce the corrosion rate unlike for 80°C. Low temperature test also showed signs of localized corrosion beneath the corrosion products.

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

Declaration of interest: none.

Funding: the project is funded by Danish Hydrocarbon Research and Technology Centre and Innovation Fund Denmark via grant 5152-00005B

Introduction

Corrosion of mild carbon steel due to the presence CO₂ is a common problem in the oil and gas industry. The CO₂ gas dissolves in the water phase and hydrates to carbonic acid, promoting electrochemical reaction at the metal-water interface leading to iron dissolution [1][2][3][4][5]. Despite the extensive literature published on the topic, CO₂ corrosion mechanisms and processes occurring at the metal-electrolyte interface are yet to be fully understood [6][7][8][9][10].

Siderite (FeCO_3) precipitation occurs as a result of the corrosion mechanism with significant influence on the kinetics of CO_2 corrosion processes. When protective FeCO_3 precipitates on the steel surface, it blocks the active sites of dissolution, which significantly reduces the corrosion rate of steels. The precipitation of protective FeCO_3 depends on several parameters of which pH, temperature [11][12][13][14], CO_2 partial pressure [15][16][14], and concentration of ionic species are the most important [17][18][19][20].

Temperature is one of the most important parameters that influences the corrosion of mild carbon steel in CO_2 environment. At low pH values (when solubility of FeCO_3 is high), an increase in temperature accelerates both the mass transport in the bulk solutions as well as the kinetics of chemical and electrochemical reactions at the metal-electrolyte interface. This leads to an increase in the corrosion rate [21]. At higher pH values, the solubility of FeCO_3 is exceeded and an increase in temperature accelerates the precipitation of protective FeCO_3 , decreasing the corrosion rate [22][21]. The peak in the corrosion rate that has been reported in literature to be between 60 °C and 80 °C [18][19][20]. Below 60 °C, no protective layer is formed and the corrosion products are porous and not well adherent to the steel surface. Above 60°C, the FeCO_3 layer becomes more dense and adherent to the surface, creating a solid barrier between the metal and the electrolyte, which reduces the corrosion rate of the steel [23][24][25][26][27].

In order to sustain oil and gas production, Enhanced Oil Recovery (EOR) techniques are employed. Seawater injection, amongst the other, is one of the most common EOR techniques for offshore oil fields [28][29]. With time, the water fraction in the produced fluid can reach levels of 95% or higher, increasing the contact between tube materials and electrolyte [30]. Additionally, the lower temperature of the injected seawater reduces the temperature of the overall produced fluid. As the temperature decreases, more CO_2 dissolves in the water, increasing its acidity [31]. These effects, combined with the higher solubility of protective scales described before, contribute to an increased

risk of the corrosion of the steel materials used in production tubing, therefore increasing the mitigation costs as the field ages [30].

X-Ray computed tomography (CT) is a powerful 3D characterization technique that enables non-destructive imaging of various samples, ranging e.g. from applications in medical and biological sciences[32], to material science[33]. This technique has found increased interest in the field of *in situ* and *ex situ* studies of localized, intergranular and pitting corrosion on aluminum and steel [34][35][36][37][38][39][40][41]. Stannard *et al.* [40] have performed *in situ* corrosion fatigue experiments in 3.5 wt.% NaCl solution on pre-corroded 7075 aluminum alloys using synchrotron X-ray tomography. This techniques allowed the authors to identify pre-existing cracks as preferential corrosion fatigue initiation sites. The technique was also implemented in the studies on the crack growth from pitting corrosion. The *in situ* and *ex situ* X-ray tomography have linked the shape of the pits to the location of the stress corrosion crack [34][42][43]. Gahari et al. [38] have investigated pitting corrosion of stainless steel under different applied currents and potentials. By using X-ray microtomography, the authors have monitored pit evolution at the tip of stainless steel pins and analyzed how MnS inclusions have modified the shape of the pits.

Despite its advantages such as non-destructive imaging, the possibility to obtain a full 3D volume and to therefore obtain statistically relevant information due to virtually cross sectioning of the sample using the 3D image, the technique has not been used to investigate CO₂ corrosion on mild carbon steel. The high atomic number of ferrous materials goes along with a high photoelectric absorption and therefore with limited X-ray transmission [44]. High energies are therefore necessary to image ferrous materials, leading to resolution degradation and lower quality image [45]. However today powerful X-ray systems can effectively image relatively big steel specimens to understand the corrosion mechanisms and scale growth.

In the present work, *ex situ* X-ray CT was used to non-destructively analyze the FeCO₃ scale formed on 1Cr steel samples exposed to de-aerated saturated CO₂ aqueous solutions at 80°C and 40 °C. The

results from X-ray CT were compared with images obtained using Scanning Electron Microscopy (SEM). The corrosion and scale formation process was correlated with electrochemical behavior of the material using Linear Polarization Resistance (LPR) and Electrochemical Impedance Spectroscopy (EIS). X-ray powder diffraction (XRD) was used to confirm the presence of FeCO_3 precipitated on the steel surface.

Materials and methods

Material and sample preparation

The specimens were made from 1Cr carbon steel with a tempered martensitic microstructure as described in our previous work [46]. The chemical composition of the material is shown in Table 1. The material was machined in cylindrical samples with a diameter of 5 mm and height of 20 mm, giving a total surface area of 3.34 cm². The inside thread of the sample was machined down to 3 mm to the top surface. This was done in order to reduce the thickness of the sample, and therefore to increase the X-ray transmission for X-ray CT computed tomography. Before the experiments, samples were polished with SiC grade P220, P320, P500 and P1000 using de-ionized water as the lubricant. This was followed by degreasing in acetone, rinsing with isopropyl alcohol, and air-drying. After testing, the samples were retrieved, rinsed with isopropyl alcohol, and placed in a desiccator. No additional preparation procedure was used for samples analysed using XRD or X-ray tomography. However, the samples for the cross-section analysis were molded in cold epoxy, cut along the cross section, and polished using water-free method using ethanol with SiC grade P220, P320, P500, P1000 and P4000, followed by 3 and 1 μm abrasive particles.

Electrochemical tests

All corrosion experiments were performed at least twice. The average value was used in the Results section, where the error bars represent the maximum and minimum value observed in repeated experiments. A conventional three electrode electrochemical cell was used for the experiments.

Volume of the glass cell was 1.5 L, the electrolyte used for the experiment was 1 wt. % NaCl prepared using de-ionized water. The solution was left to de-aerate overnight by purging the solution with nitrogen gas. The CO₂ gas was then purged for 4 hours to allow the solution to saturate, while the temperature was raised to either 40 °C or 80 °C. The resulting partial pressure of CO₂ (p_{CO_2}) was 0.93 bar and 0.53 bar at 40 °C or 80 °C, respectively. The sample was then inserted into the solution and bubbling of CO₂ was kept throughout the testing in order to minimize oxygen entrance. The experimental conditions for corrosion studies are summarized in Table 2.

The Ag/AgCl reference electrode was placed in contact with the solution through a glass lugging capillary and a concentric platinum wire ring was used as counter electrode. The corrosion potential (E_{corr}) was monitored and the corrosion rate was measured using linear polarization resistance (LPR) at every six hours. During LPR measurements, the potential was scanned in a potential range of ± 10 mV vs. open-circuit potential (OCP) at a scan rate of 0.165 mV/s. The corrosion current density and corrosion rate were calculated from the polarization resistance (R_p) by 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 constants, respectively, EW is the equivalent weight in grams, and 3272 is mm/yr conversion constant. The β value were obtained from the Tafel interpolation of potentiodynamic curves performed on samples polarized from -250 mV to +250 mV vs OCP after one hour immersion in 1 wt.% NaCl solution saturated with CO₂ at 40 °C and 80 °C. The final β values used in Eq. 1 were found to be equal to 20 mV/decade and 26 mV/decade at 40 °C and 80 °C, respectively.

The EIS measurements also performed on the sample every six hours with an AC signal amplitude of 10 mV vs. OCP in a frequency range from 10 kHz to 10 mHz. All corrosion experiments were performed

at least twice. The average value was used in the Results section, where the error bars represent the maximum and minimum value observed in repeated experiments.

Water chemistry and chemical equilibria determination

The pH was left free to settle and monitored *in situ*, and the solution was sampled every 48 hours to measure the concentration of Fe^{2+} by UV-Vis spectrophotometry using phenantroline as reagent [47]. The pHSim software from Scale Consult AS [48] was used to predict saturation ratio (SR) and precipitation of FeCO_3 .

X-Ray tomography

X-ray tomograms of the samples were obtained using a "ZEISS XRadia 410 Versa" device. The instrument was operated at 150 kV and 10 W using the high energy filter HE3. For overview measurements, image acquisition was performed using the LFOV objective and 1601 projections with 3 s exposure time per projection. A pixel size of 9.9 μm was obtained after a 2x2 binning. For scans with a higher spatial resolution, a 4X objective was used resulting in a pixel size of 2.0 μm . Also here, a 2x2 binning was used and tomograms were recorded with 3201 projections using an exposure time of 21 s per projection. Image reconstruction was performed using the inbuilt acquisition and reconstruction software package provided by ZEISS, which is based on a Feldkamp, Davis and Kress algorithm using filtered back-projection [49]. For further analysis and visualization, the software "Avizo Lite 2019.1" (Thermo Fisher Scientific) was used.

Surface and phase analysis

The morphology of the corrosion product and the cross section of the samples were investigated using a ThermoScientific™ Quanta™ FEG 200 high-resolution scanning electron microscope (SEM) fitted with energy dispersive X-ray (EDS) analysis.

The 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 Cr-K α radiation ($\lambda = 0.22909$ nm), and the 2θ ranged from 30° to 70° , with a 0.02° step, and a 4 s count time at each step.

Results

The E_{corr} and LPR measurements

Results from the LPR measurements (corrosion potential and corrosion rate) on 1Cr steel at the temperature of 80°C and 40°C are shown in Figure 1 a and b. Results show that the evolution of the corrosion potential dependent on the exposure temperature. For sample exposed to 80°C , the corrosion potential was dynamically increasing with time (Figure 1 a). Over the first two days of exposure, E_{corr} increased from approximately -640 mV to approximately -620 mV, which remained without significant change until six days of exposure. A steep increase in corrosion potential up to -530 mV was observed after this within the course of two days, and then remained without significant change. However, the sample tested at 40°C showed a different behavior without significant variation of corrosion potential over the period of the experiment. Only a slow increase of potential from -660 mV to $\approx$ -640 mV was measured initially until 18 days, which followed a plateau until the end of the experiment.

Corrosion rate in Figure 1b followed a similar trend of higher variation for 80°C , while the lower variation for 40°C . At 80°C , an initial rapid increase of corrosion rate is seen from ≈ 7 mm/year to ≈ 8 mm/year over the first two days. However, the corrosion rate showed a significant decrease after this reaching a value of approximately 1.8 mm/year after 10 days of exposure followed by slow decrease below 1 mm/year. On the other hand, the sample exposed at 40°C showed little variation in corrosion rate, which remained between 2.5 mm/yr and 2.6 mm/yr over the whole length of the experiment.

Water chemistry equilibria

The evolutions of pH, Fe^{2+} concentration, and saturation ratio for FeCO_3 (S_{FeCO_3}), for samples exposed to 80°C and 40°C, are shown in Figure 2 a and b, respectively. The pH, Fe^{2+} concentration, and SR for the sample exposed to 80°C (Figure 2a) showed an increase with time over nine days of exposure followed by a declining trend. The pH value increased from 4.2 up to 6 (after nine days) finally reaching an equilibrium value of 5.7 at the end of the experiment. A similar behavior was observed for the changes in Fe^{2+} concentration, where the maximum content of 120 ppm was seen on after eight days of exposure, followed by a decrease approximately to 70 ppm at the end of the experiment. Calculated saturation ratios showed that the solution reached values above the saturation of FeCO_3 within the first two days of exposure, and increasing beyond the equilibrium with a maximum value of approximately 25 after eight days of exposure. This was followed by a rapid decline of the saturation degree down to approximately 4 at the end of the test.

A different trend for the parameters were observed for the experiments at 40 °C as shown in Figure 2b. The pH of the solution continuously increased over time from 3.9 to approximately 5.4 at the end of the test. Similarly, the Fe^{2+} concentration increased with time, reaching a maximum level of approximately 120 ppm after 12 days of exposure, where it stabilized. The solution remained undersaturated with respect to FeCO_3 until day 12, where it remained slightly above equilibrium level until the end of the test.

Electrical Impedance Spectroscopy investigation

Figure 3 a-f presents results from the EIS measurements shown as Nyquist and Bode representations. The Nyquist plot, for the sample exposed at 80 °C (see Figure 3 a) shows two depressed semicircles with different amplitudes, one at high-medium (HF -MF) frequencies and one at low frequencies (LF). The amplitude of the second semicircle increased with time (Figure 3 a). Similar changes in response can be seen in the Bode plots in Figure 3 b and c. Two slopes, one at MF and one at LF, are clearly visible in the $\log|Z|$ vs. frequency diagram (Figure 3 b) during the first 8 days, confirming that more

than one time constant is involved in the process. As the experiment proceeded, these slopes seem to merge at LF with an increase in $\log|Z|$ value, with almost overlapping values after day 15 until the end of the test. The phase angle vs. frequency graph (Figure 3 c) further confirms the hypothesis of two time constants, where two maxima were recorded, namely one at MF and one at LF. The maximum at MF increased towards higher degree angles, while at the same time moving towards lower frequency values as the experiment proceeded. Similarly, the maximum at LF seems to be smoothened out by the end of the experiment.

The Nyquist plot for the sample exposed to the solution at 40 °C (Figure 3 d) similarly presents two depressed semicircles at HF-MF frequencies and LF frequencies. The second semicircle is more visible during the initial days of the experiment, but seems to be smoothened out after day 8. The amplitude of the semicircles grew with the experimental time. However the growth was considerably lower compared to the sample exposed to 80 °C (Figure 3 a). The $\log|Z|$ vs. Frequency plot (Figure 3 e) has a two-slope response which slightly increased at LF (from $\approx 50 \Omega \cdot \text{cm}^2$ $\approx 80 \Omega \cdot \text{cm}^2$ at 10mHz) with the exposure time. Two maxima were also detected in the Phase angle vs. Frequency response (see Figure 3 f), confirming the presence of two time constants. The first peak at MF increased from -35° to -45° by the end of the test, while the maximum at LF was smoothened with exposure time.

The EIS results of the experiments at 80 °C and 40 °C was further analyzed using the numerical fitting with equivalent circuit shown in Figure 5. The modelled equivalent circuit is adapted from the commonly used circuit with surface of an electrode covered with a low conducting layer on the top [43][44]. The R_s represents the solution resistance of the electrolyte, R_{po} is the pore resistance of the scale layer, C_{sc} is the the capacitance of the precipitated layer, R_{ct} is the charge-transfer resistance, and C_{dl} is the double layer capacitance.

The impedance parameters obtained by fitting the circuit to the EIS results are shown in Table 3 and Table 4, respectively.

X-diffraction analysis of scale

Figure 5 shows the XRD analysis of the scale formed on the specimen during the electrochemical experiments in 1 wt. % NaCl solution at $T=80^{\circ}\text{C}$ and $T=40^{\circ}\text{C}$. Siderite (FeCO_3) was detected on both samples as indicated in the figure. The high intensity peak for siderite corresponded to the (104) plane and was recorded at $2\theta=48.403^{\circ}$ at both temperatures. The intensity for this peak was lower for the sample tested at 40°C . Cementite (Fe_3C) was also detected on both samples with comparable peak intensities at 40°C and 80°C .

X-Ray tomography analysis

Results of the ex-situ X-ray tomography analysis of the specimen exposed at 80°C is shown in Figure 6. Figure 6 a shows a volumetric representation of the analyzed area showing differential contrast based on the density of the material and scale. The strongly absorbing 1 Cr base material on the bottom is followed by three different layers of decreased absorption levels suggesting the presence of less dense corrosion products. Close to the steel surface shows a densely packed initial layer, which is uniformly distributed. A second layer on the top of the first layer shows coarser crystals of the scales with voids. A third thinner layer compared to layers forms the outer shell appearing loosely attached. The image in inset (Figure 6b) shows the volumetric reconstruction of the image Figure 6a without scale. Image shows that the steel surface is corroded uniformly with no signs of localized attacks, which is also clear from the virtual cross sections along the XY and XZ direction shown in Figure 6c and 7d. The cross sections in Figure 6c and 7d also shows that the first layer of the scale is uniformly distributed across the surface, whilst the second layer contained porosities, which are covered by the third layer (outer shell).

The volumetric representation of the investigated area of the sample tested at 40°C (Figure 7 a) using tomography shows a porous scale precipitated on the top of the steel surface, while the inset image Figure 7b showing steel surface after reconstruction removing scale shows signs of localized corrosion. The porous scale extends to the a thin outer layer with as tree like structures as visible in Figure 7a,

which is also evident in the virtual cross section images in Figure 7c and 8d. The images in Figure 7c and 8d also shows that the scale is more porous compared to scale observed at 80°C.

Scanning electron microscopy and X-ray mapping

Figure 8 shows the SEM pictures of the sample exposed to 80 °C. The top view image in Figure 8a shows the scale covered surface with prism shape crystals, which is similar to the previously reported literature for iron carbonate [24][50], and confirmed to be FeCO_3 based on the XRD results. The FeCO_3 crystals with average sizes of approximately 20 μm are coarse and cover the whole surface of the sample uniformly. The cross section of the sample (Figure 8 b) shows a similar results as in tomography with a thick and dense FeCO_3 layer on top of which additional crystals of FeCO_3 are precipitated. This second layer is less dense, as noticeable by the presence of voids and porosities filled with embedding epoxy. These voids are confirmed by the high content of elemental carbon from the epoxy that penetrated in these areas, detected by the X-ray mapping (Figure 8 c). The outer shell detected during CT scanning (Figure 6 a-d) is also visible in the SEM cross section (Figure 8 b).

Figure 9 shows the SEM observations for the sample exposed to 40 °C. The surface morphology of the scale (Figure 9 a) was similar to the observation at 80°C and the scale is made up of FeCO_3 crystals. However, the crystals were smaller (approximately 5-10 μm) compared to the scale formation observed at 80°C. At some locations, crystals seemed to grow in a tree-like structure making the topography of the scale surface very uneven (see inset picture in Figure 9 a). Below this layer, coarser FeCO_3 crystals have precipitated, forming a porous and less dense structure than the one observed at 80 °C. Porosities across the FeCO_3 layer were visible in the cross section (Figure 9 c) and confirmed by the high content of elemental carbon from the epoxy, as shown in the X-ray mapping (Figure 9 c). Signs of localized corrosion were detected at the interface between steel and the precipitated layer, as shown in Figure 9 b.

Discussion

The changes to lower temperature of the produced fluid, due to seawater injection to enhance oil recovery, can significantly affect the corrosion resistance of the carbon steel used in production tubing. The results presented in this paper confirm the importance of the temperature as one of the most important factors influencing the corrosion behavior of 1Cr carbon steel in CO₂ corrosion as it affects the nature and morphology of the corrosion product layer. This study shows how the FeCO₃ corrosion film formed at different temperatures influences the CO₂ corrosion process and the corrosion resistance of 1Cr steel. This effect was linked to the characteristics of the FeCO₃ layer developed at different temperatures and how they affected the protectiveness of this film.

FeCO₃ is formed via a one-stage reaction process with carbonates (Eq. 3)[50] and temperature plays a role in accelerating the kinetics of FeCO₃ precipitation and lowering the solubility of FeCO₃ [25] [51].

The driving force responsible for FeCO₃ precipitation is the saturation ratio of the bulk solution with respect to FeCO₃ (S_{FeCO_3}) [52], defined as:

$$S_{FeCO_3} = \frac{c_{Fe^{2+}} \cdot c_{CO_3^{2-}}}{K_{sp}} \quad 4)$$

where $c_{Fe^{2+}}$ and $c_{CO_3^{2-}}$ are the ferrous and carbonate ions concentrations (in mol/L), respectively, and K_{sp} is the solubility product of FeCO₃. Solid FeCO₃ precipitation in aqueous solution occurs when the concentration of Fe²⁺ and CO₃²⁻ ions exceed the solubility limit K_{sp} which depends on temperature and ionic strength as shown in Eq. 5) and Eq. 6) [17]:

$$\log(K_{sp}) = -59.3498 - 0.041377(T_K) - \frac{2.1963}{T_K} + 24.5724\log(T_K) + 2.518(I^{0.5}) - 0.657(I) \quad 5)$$

$$I = \frac{1}{2} \sum_i c_i z_i^2 \quad 6)$$

Where c_i is the concentration of the species in the solution and z_i is the charge of the species.

The effect of temperature on the solubility limit of FeCO_3 was confirmed during this study. At 80 °C the S_{FeCO_3} of the bulk solution followed rapidly the increase in Fe^{2+} ions, maintaining the solution above equilibrium (Figure 2 a). The pH increased as well due to reduction of carbonic acid to bicarbonate during the cathodic corrosion process, as previously reported by Dugstad [50]. FeCO_3 precipitation occurred at this temperature after approximately 8 days, as shown by the decline in both Fe^{2+} and S_{FeCO_3} as a consequence. X-ray results confirmed the precipitation of siderite as corrosion product (Figure 5). The bulk solution of the experiments performed at 40 °C remained mostly under saturated for most of the time despite the increase in pH and the high Fe^{2+} concentration (Figure 2 b). During current study, crystalline FeCO_3 was detected on the steel surface after 18 days of exposure time (Figure 5), despite the bulk solution being only slightly oversaturated with respect to FeCO_3 after day 10. Literature reports that a certain degree of super-saturation with respect to FeCO_3 is required in order to facilitate FeCO_3 precipitation [53]. It is believed that the local increase of pH value close to the steel surface may be the cause for the local higher S_{FeCO_3} , and consequently higher driving force for FeCO_3 precipitation.

Dense crystalline films are formed at high temperature (> 60 °C), where the precipitation rate is fast and the super-saturation is low [50]. These film are able to provide good protection to the underlying steel. At lower temperature, non-protective corrosion products are expected [24]. The results from SEM cross section presented in this study are consistent with these expectations. The film formed at 80 °C (Figure 8b) were denser and more adherent than those formed at 40 °C (Figure 9 b) and therefore more protective. These differences in nature and morphologies of the precipitated FeCO_3 corroborate the changes in the corrosion rate at the two temperatures and the differences in the evolution of the EIS results.

The corrosion process for both temperatures followed therefore a mechanism of dissolution of iron and precipitation of iron carbonate. However, differences in the FeCO_3 precipitation kinetics and

morphology of the corrosion products at 40 °C and 80 °C, influenced the corrosion behavior of the 1Cr steel. At 80 °C, the corrosion behavior of the 1Cr steel was characterized by three stages described by Farel et al. in their series of flow loop experiments at 80 °C and pH= 6.0, namely: active corrosion, nucleation and growth of FeCO_3 and pseudo-passivation [54]. The increase in Fe^{2+} concentration presented in Figure 2 a and b confirmed the dissolution of the steel substrate and the release of iron ions in to the solution (active stage). The higher corrosion rate at 80 °C compared to 40 °C, during the first eight days of exposure, can be explained by the increased electrode kinetics as a function of temperature [55][56][57]. Active corrosion stage was followed by nucleation and growth of a protective corrosion scale, which resulted in an increase in E_{corr} and decrease of corrosion rate at 80 °C (see Figure 1 a and b, respectively). However, the presence of FeCO_3 in a Fe_3C matrix (Figure 8 b) suggests that active dissolution sites were being closed by FeCO_3 precipitation, confirmed by continuous increase in E_{corr} . Similar conclusions have been reported by Pessu et al. in their investigation of pitting corrosion on X65 carbon steel in a CO_2 saturated environment at 80 °C [58]. Authors correlated the increase in OCP with faster cathodic reaction as a consequence of more Fe_3C sites being exposed. In the current results, rapid FeCO_3 precipitation occurred between day 8 and 10 due to the high S_{FeCO_3} value of the bulk solution. This was reflected by a steep increase in E_{corr} (Figure 1 a), rapid decrease of the corrosion rate (Figure 1 b) and Fe^{2+} concentration in the solution from ≈ 120 ppm to ≈ 90 ppm (Figure 2 a). From day 10 until the end of the test, a continuous reduction in uniform corrosion rate was observed, while the potential remained comparatively stable (pseudo-passivation stage). [54]. Similar conclusions on the evolution of FeCO_3 corrosion products were observed by Ingham et al. [59] and Guo et al.[60]. Both reported the presence of an amorphous ferrous carbonate phase as precursor for siderite, but it was not found in the present in the investigation. The sample exposed to the solution saturated with CO_2 at 40 °C showed only small changes in corrosion rate throughout the test, confirming that the FeCO_3 precipitate was not able to protect the underlying steel.

The evolution of the FeCO_3 layer was followed by the EIS (Figure 3 a-f). For the sample exposed to 80 °C, the C_{sc} values increased until day 10 (see results in Table 3). This indicates the growth of the FeCO_3 layer as reported by Farelàs et al. in their dissolution study [61]. After day 10 the C_{sc} drop to almost half of the value. This change to lower C_{sc} has been linked to the layer becoming more dense and less porous [62], as confirmed by the increasing values of R_{po} . Similar behavior was recorded for C_{dl} and R_{ct} indicating the formation of protective layer, covering the underlying steel and consequently reducing its corrosion rate [61][63]. The R_{ct} and C_{dl} magnitude follow the evolution of the corrosion rate obtained by LPR, and the increased $|Z|$ module with time (Figure 3 b) support this mechanism. In addition, the increase of peak height with exposure time (Figure 3 c) indicates that the response became more capacitive; indeed as immersion time increased, the pores are closed by rapid FeCO_3 precipitation reducing the current flow through the defects.

At low temperature several authors suggest that the amorphous FeCO_3 can precipitate on the surface, favored by the low pH of the solution [60][64]. The formation of this layer could be identified by the increase in C_{sc} for the sample exposed to 40 °C as reported in Table 4. This layer was, however, not compact and contained some porosities as shown in Figure 7 and 10 b. It is likely that solution could have penetrated the porosities (as evidenced by the approximatively constant low value of R_{po}) and continued the dissolution of the underlying steel layer reflected by the decrease in C_{dl} . The slight increase of R_{ct} suggests that the precipitated FeCO_3 may have still given some degree of protection. However, these values are too low for claiming the protectiveness of this layer, and the results confirm the LPR corrosion rate observed in Figure 1 b, that was almost constant during the same time.

Several authors report the risk of more localized attack on carbon steel in CO_2 saturated solution at temperature lower than 60 °C [58][60][64]. They identify the galvanic effect between Fe_3C rich regions and exposed areas of steel within the pores, as a potential cause for more localized corrosion at low temperature. The results obtained with X-Ray CT support this findings and have been further

confirmed by the SEM cross section. By changing the threshold used for visualization, it was possible to only show the under laying steel surface, i.e. to “digitally remove the corrosion scale” (Figure 6 b and Figure 7 b). The steel surface was uniformly corroded and no sign of localized corrosion were detected on the sample exposed to the solution at 80 °C. The ortho slice in XY direction (Figure 6 d) and the equivalent SEM cross section (Figure 8 b) showed comparable results confirming a uniform corrosion mechanism. This is in agreement with a theory regarding reduction of pitting corrosion at 80 °C, as also previously reported by Pessu et al. [58]. The authors proposed a self-healing mechanism at high temperature based on the ability of FeCO_3 to precipitate under the Fe_3C network reducing pit propagation. Signs of more localized corrosion were detected on the sample exposed to the solution saturated with CO_2 at 40 °C as visible in the X-ray CT results and SEM cross section.

During this study, X-ray CT was used to investigate the corrosion scale formed in CO_2 saturated solutions at 40 °C and 80 °C *ex-situ*. The technique provided access to the different morphologies of the corrosion products formed at these two temperatures and has proven to be a complementary technique to SEM. This was done without any type of sample preparation (molding, polishing or corrosion products removal) conserving all the details that may get lost during conventional sample preparation. *Ex-situ* results obtained in this study were comparable to the results obtained with SEM and complementary information were obtained. X-ray CT has been successfully employed as a complementary non-destructive technique (NDT) in the investigation of corrosion products from shipwrecks [65] and stress corrosion cracks from failed pearlitic steel wires [66]. Both studies highlight the ability to obtain images from within the samples without the need for destructive sectioning. Similarly, in the current research the volumetric representation of the samples obtained from X-ray CT showed that a denser and more compact FeCO_3 had precipitated at 80 °C, while a looser and more porous structure was recorded at 40 °C. Similar information were recorded with SEM analysis. However, the surface morphology of the FeCO_3 layer formed at 40 °C obtained with SEM (Figure 9 a) seems to suggest that the FeCO_3 was densely packed on top of the steel surface. Only the cross section of the sample revealed underlying corrosion features, which in this investigation was possible with X-

ray CT analysis without mechanically cross-sectioning the specimen with fragile scale. By using X-ray CT Ramandi et al. [66] were able to detect internal branching of the crack in the bulk specimen, even though it was not present in the surface. Whilst the technique allows to gain data from larger regions and detailed 3D analysis of the features of interest, the quality to resolve this feature of interest can be compromised [67][68]. Recent work from Perini et al. [69] has attempted to improve the resolution to the deca-nanometer scale by developing an SEM-based X-ray tomography system. Whilst the resolution achieved during this research was still in the order of the micron scale, results show that a combination of various characterization techniques may be highly advantageous to study feature of interest. This could be beneficial, for example, for study of pitting corrosion and propagation, where this phenomena can occur randomly on the sample surface. Potentially, the technique can be used to perform an overall scan *ex-situ* of the sample and select specific area for FIB and TEM analysis as performed by Burnett et al. [41]. In their study they combined X-ray computed tomography with FIB-SEM tomography EDS and TEM, allowing them to observe competing mechanism between pitting and intergranular corrosion on a 316H austenitic stainless steel. However, large data volumes can requires considerable computational time for analysis and visualization [66].

One of the disadvantages of using X-ray CT is the risk of encountering artifacts in which the edges of the sample appear brighter than the center. This is known as beam hardening [70]. During this study beam hardening was limited by using appropriate software techniques [71] to correct for it (see Figure 6 a and Figure 7 b).

Several authors have demonstrated the advantages of X-ray CT to investigate corrosion in-situ of aluminium [72], iron based alloys[73][74] and magnesium alloys [75]. Amongst those, is the possibility of accessing features of localized corrosion and gaining a more comprehensive analysis of the corrosion process. The electrochemical measurement performed in this research gave information on the corrosion kinetics and the stability and protectiveness of the FeCO_3 layer. However these information were not compared with the visual evolution of the corrosion process and scale precipitation.

In-situ studies using X-ray CT or Synchrotron tomography in combination with electrochemical measurements can provide further insight into the precipitation, stability and protectiveness of FeCO_3 layer and competition between various corrosion mechanisms, which is presently being investigated.

Conclusions

- Temperature influences both the corrosion kinetics and FeCO_3 precipitation. However, despite the higher corrosion kinetics at 80 °C, the precipitation of crystalline FeCO_3 resulted in a reduction of the uniform corrosion rate as a function of exposure time. The FeCO_3 precipitated at 40 °C was not protective due to the loose and porous structure that was formed under these conditions.
- The denser FeCO_3 layer at 80 °C resulted in lower corrosion rate, which is ten times lower than the corrosion rate at 40 °C.
- The high S_{FeCO_3} at 80 °C was responsible for the faster precipitation kinetics of FeCO_3 and its protectiveness.
- EIS results revealed a mechanism of iron dissolution and FeCO_3 precipitation. The porosity in the layer influenced the corrosion rate and its mechanism.
- X-ray tomography enabled non-destructive visualization of the corrosion scale. Result shows that due to the difference in the stability of FeCO_3 layer at different temperatures, signs of localized corrosion were detected on the sample exposed to the solution at 40 °C unlike for 80 °C.

Data Availability

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

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Author Statement

Riccardo Rizzo: Conceptualization, Methodology, Formal analysis, Investigation, Writing - Original Draft, Writing - Review & Editing, Visualization

Sina Baier: Formal analysis, Investigation, Writing - Original Draft, Writing - Review & Editing, Visualization

Magdalena Rogowska: Writing - Review & Editing, Supervision.

Rajan Ambat: Conceptualization, Supervision, Writing - Review & Editing, Project administration

Acknowledgments

The authors would like to thank the Danish Hydrocarbon Research and Technology Centre (DHRTC) for the financial and technical support provided during this work.

The 3D Imaging Centre at The Technical University of Denmark is gratefully acknowledged.

Sina Baier is grateful for financial support from Innovation Fund Denmark via grant 5152-00005B.

References

- [1] R.H. Hausler, H.P. Gaddart, *Advances in CO₂ Corrosion*, Volume 1, NACE International, Houston TX, 1985.
- [2] R.H. Hausler, H.P. Gaddart, *Advances in CO₂ corrosion*, Volume 2, NACE International, Houston TX, 1986.
- [3] S. Nešić, Key issues related to modelling of internal corrosion of oil and gas pipelines - A review, *Corros. Sci.* 49 (2007) 4308–4338. doi:10.1016/j.corsci.2007.06.006.
- [4] M. Rogowska, J. Gudme, A. Rubin, K. Pantleon, R. Ambat, Effect of Fe ion concentration on fatigue life of carbon steel in aqueous CO₂ environment, *Corros. Eng. Sci. Technol.* 51 (2015) 90–103. doi:10.1179/1743278215y.0000000035.
- [5] M. Rogowska, J. Gudme, A. Rubin, K. Pantleon, R. Ambat, Effect of Fe ion concentration on fatigue life of carbon steel in aqueous CO₂ environment, *Corros. Eng. Sci. Technol.* 51 (2015) 90–103. doi:10.1179/1743278215y.0000000035.
- [6] C. De Waard, D.E. Milliams, CARBONIC ACID CORROSION OF STEEL., *Corrosion*. 31 (1975) 177–181. doi:10.5006/0010-9312-31.5.177.
- [7] A. Kahyarian, S. Nesic, A New Narrative for CO₂ Corrosion of Mild Steel, *J. Electrochem. Soc.* 166 (2019) C3048–C3063. doi:10.1149/2.0071911jes.
- [8] T. das Chagas Almeida, M.C.E. Bandeira, R.M. Moreira, O.R. Mattos, New insights on the role of CO₂ in the mechanism of carbon steel corrosion, *Corros. Sci.* 120 (2017) 239–250. doi:10.1016/j.corsci.2017.02.016.

- [9] E. Remita, B. Tribollet, E. Sutter, V. Vivier, F. Ropital, J. Kittel, Hydrogen evolution in aqueous solutions containing dissolved CO₂: Quantitative contribution of the buffering effect, *Corros. Sci.* 50 (2008) 1433–1440. doi:10.1016/j.corsci.2007.12.007.
- [10] A. Kahyarian, M. Achour, S. Nesic, Mathematical modeling of uniform CO₂ corrosion, in: *Trends Oil Gas Corros. Res. Technol.*, Woodhead Publishing, 2017: pp. 805–849. doi:10.1016/b978-0-08-101105-8.00034-6.
- [11] M. Nordsveen, S. Nešić, R. Nyborg, A. Stangeland, A mechanistic model for carbon dioxide corrosion of mild steel in the presence of protective iron carbonate films - Part 1: Theory and verification, *Corrosion*. 59 (2003) 443–456. doi:10.5006/1.3277576.
- [12] S. Nešić, M. Nordsveen, R. Nyborg, A. Stangeland, A mechanistic model for carbon dioxide corrosion of mild steel in the presence of protective iron carbonate films - Part 2: A numerical experiment, *Corrosion*. 59 (2003) 489–497. doi:10.5006/1.3277579.
- [13] D.A. López, W.H. Schreiner, S.R. De Sánchez, S.N. Simison, The influence of carbon steel microstructure on corrosion layers: An XPS and SEM characterization, *Appl. Surf. Sci.* 207 (2003) 69–85. doi:10.1016/S0169-4332(02)01218-7.
- [14] Z.D. Cui, S.L. Wu, C.F. Li, S.L. Zhu, X.J. Yang, Corrosion behavior of oil tube steels under conditions of multiphase flow saturated with super-critical carbon dioxide, *Mater. Lett.* 58 (2004) 1035–1040. doi:10.1016/j.matlet.2003.08.013.
- [15] M.B. Valcarce, M. Vázquez, Carbon steel passivity examined in alkaline solutions: The effect of chloride and nitrite ions, *Electrochim. Acta.* 53 (2008) 5007–5015. doi:10.1016/j.electacta.2008.01.091.
- [16] J.B. Sun, G.A. Zhang, W. Liu, M.X. Lu, The formation mechanism of corrosion scale and electrochemical characteristic of low alloy steel in carbon dioxide-saturated solution, *Corros. Sci.* 57 (2012) 131–138. doi:10.1016/j.corsci.2011.12.025.

- [17] W. Sun, S. Nešić, Kinetics of corrosion layer formation: Part 1 - Iron carbonate layers in carbon dioxide corrosion, *Corrosion*. 64 (2008) 334–346. doi:10.5006/1.3278477.
- [18] V. Ruzic, M. Veidt, S. Nešić, Protective iron carbonate films - Part 1: Mechanical removal in single-phase aqueous flow, *Corrosion*. 62 (2006) 419–432. doi:10.5006/1.3278279.
- [19] V. Ruzic, M. Veidt, S. Nešić, Protective Iron Carbonate Films—Part 2: Chemical Removal by Dissolution in Single-Phase Aqueous Flow, *Corrosion*. 62 (2006) 598–611. doi:10.5006/1.3280674.
- [20] V. Ruzic, M. Veidt, S. Nešić, Protective iron carbonate films - Part 3: Simultaneous chemo-mechanical removal in single-phase aqueous flow, *Corrosion*. 63 (2007) 758–769. doi:10.5006/1.3278425.
- [21] S. Wang, K. George, S. Nesic, HIGH PRESSURE CO₂ CORROSION ELECTROCHEMISTRY AND THE EFFECT OF ACETIC ACID, Paper No. 04375, in: *Corrosion*, NACE International, 2004: pp. 1–17.
- [22] K. (Ohio U. George, S. (Ohio U. Nesic, C. (CorCon) de Waard, Electrochemical investigation and modeling of carbon dioxide corrosion of carbon steel in the presence of acetic acid, in: *NACE Conf.*, NACE International, 2004: p. 25.
- [23] Z.F. Yin, Y.R. Feng, W.Z. Zhao, Z.Q. Bai, G.F. Lin, Effect of temperature on CO₂ corrosion of carbon steel, *Surf. Interface Anal.* 41 (2009) 517–523. doi:10.1002/sia.3057.
- [24] A. Dugstad, Mechanism of protective film formation during CO₂ corrosion of carbon steel, in: *NACE Conf.*, NACE International, 1998: pp. 1–11.
- [25] M.B. Tomson, M.L. Johnson, How Ferrous Carbonate Kinetics Impacts Oilfield Corrosion, in: *SPE Int. Symp. Oilf. Chem.*, Society of Petroleum Engineers, 1991. doi:10.2118/21025-ms.
- [26] F.D. de Moraes, J.R. Shadley, J. Chen, E.F. Rybicki, Characterization of CO₂ Corrosion Product Scales Related to Environmental Conditions, in: *Corros. 2000*, NACE International, 2000: p. Paper No.00031.

- [27] L.G. Llongueras, J. Hernandez, A. Munoz, J.M.- Flores, Mechanism of FeCO₃ Formation on API X70 Pipeline Steel in Brine Solutions Containing CO₂, NACE - Int. Corros. Conf. Ser. (2005) 1–13.
- [28] M. Mahmoud, S. Elkatatny, K.Z. Abdelgawad, Using high- and low-salinity seawater injection to maintain the oil reservoir pressure without damage, J. Pet. Explor. Prod. Technol. 7 (2017) 589–596. doi:10.1007/s13202-016-0279-x.
- [29] T. Puntervold, S. Strand, T. Austad, Coinjection of seawater and produced water to improve oil recovery from fractured north sea chalk oil reservoirs, Energy and Fuels. 23 (2009) 2527–2536. doi:10.1021/ef801023u.
- [30] T.E. Perez, Corrosion in the oil and gas industry: An increasing challenge for materials, J. Miner. Met. Mater. Soc. 65 (2013) 1033–1042. doi:10.1007/s11837-013-0675-3.
- [31] W. Gerrard, Effect of Temperature on Gas Solubility, in: Gas Solubilities, Pergamon, 2013: pp. 13–66. doi:10.1016/b978-0-08-025248-3.50007-x.
- [32] F. Léonard, X-ray Computed Tomography - 3.Phase contrast and Case studies, Phys. Med. Biol. 51 (2006) R29–R43. doi:10.1088/0031-9155/51/13/R03.
- [33] C. Denison, W.D. Carlson, R.A. Ketcham, Three-dimensional quantitative textural analysis of metamorphic rocks using high-resolution computed X-ray tomography: Part I. Methods and techniques, J. Metamorph. Geol. 15 (1997) 29–44. doi:10.1111/j.1525-1314.1997.00006.x.
- [34] B.J. Connolly, D.A. Horner, S.J. Fox, A.J. Davenport, C. Padovani, S. Zhou, A. Turnbull, M. Preuss, N.P. Stevens, T.J. Marrow, J.-Y. Buffiere, E. Boller, A. Groso, M. Stampanoni, X-ray microtomography studies of localised corrosion and transitions to stress corrosion cracking, Mater. Sci. Technol. 22 (2006) 1076–1085. doi:10.1179/174328406X114199.
- [35] L. Babout, T.J. Marrow, D. Engelberg, P.J. Withers, X-ray microtomographic observation of intergranular stress corrosion cracking in sensitised austenitic stainless steel, Mater. Sci. Technol. 22 (2006) 1068–1075. doi:10.1179/174328406x114090.

- [36] S.P. Knight, M. Salazaras, A.R. Trueman, The study of intergranular corrosion in aircraft aluminium alloys using X-ray tomography, *Corros. Sci.* 53 (2011) 727–734. doi:10.1016/j.corsci.2010.11.005.
- [37] G.E. Thompson, T. Hashimoto, X.L. Zhong, M. Curioni, X. Zhou, P. Skeldon, P.J. Withers, J.A. Carr, A.G. Monteith, Revealing the three dimensional internal structure of aluminium alloys, in: *Surf. Interface Anal.*, John Wiley & Sons, Ltd, 2013: pp. 1536–1542. doi:10.1002/sia.5221.
- [38] S.M. Ghahari, A.J. Davenport, T. Rayment, T. Suter, J.P. Tinnes, C. Padovani, J.A. Hammons, M. Stampanoni, F. Marone, R. Mokso, In situ synchrotron X-ray micro-tomography study of pitting corrosion in stainless steel, *Corros. Sci.* 53 (2011) 2684–2687. doi:10.1016/j.corsci.2011.05.040.
- [39] S.P. Knight, M. Salazaras, A.M. Wythe, F. De Carlo, A.J. Davenport, A.R. Trueman, In situ X-ray tomography of intergranular corrosion of 2024 and 7050 aluminium alloys, *Corros. Sci.* 52 (2010) 3855–3860. doi:10.1016/j.corsci.2010.08.026.
- [40] T.J. Stannard, J.J. Williams, S.S. Singh, A.S. Sundaram Singaravelu, X. Xiao, N. Chawla, 3D time-resolved observations of corrosion and corrosion-fatigue crack initiation and growth in peak-aged Al 7075 using synchrotron X-ray tomography, *Corros. Sci.* 138 (2018) 340–352. doi:10.1016/j.corsci.2018.04.029.
- [41] T.L. Burnett, S.A. McDonald, A. Gholinia, R. Geurts, M. Janus, T. Slater, S.J. Haigh, C. Ornek, F. Almuaili, D.L. Engelberg, G.E. Thompson, P.J. Withers, Correlative tomography, *Sci. Rep.* 4 (2014) 4711. doi:10.1038/srep04711.
- [42] D.A. Horner, B.J. Connolly, S. Zhou, L. Crocker, A. Turnbull, Novel images of the evolution of stress corrosion cracks from corrosion pits, *Corros. Sci.* 53 (2011) 3466–3485. doi:10.1016/j.corsci.2011.05.050.
- [43] A. Turnbull, Corrosion pitting and environmentally assisted small crack growth, *Proc. R. Soc. A Math. Phys. Eng. Sci.* 470 (2014) 20140254–20140254. doi:10.1098/rspa.2014.0254.

- [44] H. Toda, F. Tomizato, F. Zeismann, Y. Motoyashiki-Besel, K. Uesugi, A. Takeuchi, Y. Suzuki, M. Kobayashi, A. Brueckner-Foit, High-resolution Observation of Steel Using X-ray Tomography Technique, *ISIJ Int.* 52 (2012) 516–521. doi:10.2355/isijinternational.52.516.
- [45] D. Seo, F. Tomizato, H. Toda, K. Uesugi, A. Takeuchi, Y. Suzuki, M. Kobayashi, Spatial resolution of synchrotron x-ray microtomography in high energy range: Effect of x-ray energy and sample-to-detector distance, *Appl. Phys. Lett.* 101 (2012) 261901. doi:10.1063/1.4773239.
- [46] R. Rizzo, S. Gupta, M. Rogowska, R. Ambat, Corrosion of carbon steel under CO₂ conditions: effect of CaCO₃ precipitation on the stability of the FeCO₃ protective layer, *Corros. Sci.* (2019) 108214. doi:10.1016/j.corsci.2019.108214.
- [47] W.B. Fortune, M.G. Mellon, Determination of Iron with o-Phenanthroline: A Spectrophotometric Study, *Ind. Eng. Chem. - Anal. Ed.* 10 (1938) 60–64. doi:10.1021/ac50118a004.
- [48] B. Kaasa, Prediction of pH, mineral precipitation and multiphase equilibria during oil recovery, Norwegian University of Science and Technology (NTNU), 1998.
- [49] L.A. Feldkamp, L.C. Davis, J.W. Kress, Practical cone-beam algorithm, *J. Opt. Soc. Am. A.* 1 (1984) 612. doi:10.1364/josaa.1.000612.
- [50] A. Dugstad, Fundamental Aspects of CO₂ Metal Loss Corrosion Part I: Mechanism, in: NACE Conf., NACE International, 2006: pp. 1–18.
- [51] S. Yean, H. Al Saiari, A.T. Kan, M.B. Tomson, Ferrous carbonate nucleation and inhibition, in: Soc. Pet. Eng. - 9th Int. Conf. Oilf. Scale 2008 - “Managing Scale Through F. Lifetime,” Society of Petroleum Engineers, 2008: pp. 531–549. doi:10.2118/114124-MS.
- [52] J. Garside, ADVANCES IN THE CHARACTERISATION OF CRYSTAL GROWTH, in: AIChE Symp. Ser., American Institute of Chemical Engineers, 1984: p. 126.

- [53] K. Chokshi, W. Sun, S. Nesic, Iron carbonate scale growth and the effect of inhibition in CO₂ corrosion of mild steel, in: NACE - Int. Corros. Conf. Ser., NACE International, 2005.
- [54] F. Farelas, B. Brown, S. Nesic, Iron Carbide and its Influence on the Formation of Protective Iron Carbonate in CO₂ Corrosion of Mild Steel - Paper 2291, NACE - Int. Corros. Conf. Ser. (2013).
- [55] Z. Ahmad, CORROSION KINETICS, in: Princ. Corros. Eng. Corros. Control, Butterworth-Heinemann, 2007: pp. 57–119. doi:10.1016/b978-075065924-6/50004-0.
- [56] D. cheng KONG, C. fang DONG, K. XIAO, X. gang LI, Effect of temperature on copper corrosion in high-level nuclear waste environment, Trans. Nonferrous Met. Soc. China (English Ed. 27 (2017) 1431–1438. doi:10.1016/S1003-6326(17)60165-1.
- [57] N. Hackerman, Effect of Temperature on Corrosion of Metals by Water, Ind. Eng. Chem. 44 (1952) 1752–1755. doi:10.1021/ie50512a020.
- [58] F. Pessu, R. Barker, A. Neville, Understanding pitting corrosion behavior of X65 carbon steel in CO₂-saturated environments: The temperature effect, Corrosion. 72 (2016) 78–94. doi:10.5006/1338.
- [59] B. Ingham, M. Ko, N. Laycock, N.M. Kirby, D.E. Williams, First stages of siderite crystallisation during CO₂ corrosion of steel evaluated using in situ synchrotron small- and wide-angle X-ray scattering, Faraday Discuss. 180 (2015) 171–190. doi:10.1039/c4fd00218k.
- [60] S. Guo, L. Xu, L. Zhang, W. Chang, M. Lu, Corrosion of alloy steels containing 2% chromium in CO₂ environments, Corros. Sci. 63 (2012) 246–258. doi:10.1016/j.corsci.2012.06.006.
- [61] F. Farelas, M. Galicia, B. Brown, S. Nesic, H. Castaneda, Evolution of dissolution processes at the interface of carbon steel corroding in a CO₂ environment studied by EIS, Corros. Sci. 52 (2010) 509–517. doi:10.1016/j.corsci.2009.10.007.
- [62] C. Liu, Q. Bi, A. Leyland, A. Matthews, An electrochemical impedance spectroscopy study of the corrosion behaviour of PVD coated steels in 0.5 N NaCl aqueous solution: Part I. Establishment of

equivalent circuits for EIS data modelling, *Corros. Sci.* 45 (2003) 1243–1256. doi:10.1016/S0010-938X(02)00213-5.

[63] C. Liu, Q. Bi, A. Leyland, A. Matthews, An electrochemical impedance spectroscopy study of the corrosion behavior of PVD coated steels in 0.5 N NaCl aqueous solution: Part II. EIS interpretation of corrosion behaviour, *Corros. Sci.* 45 (2003) 1257–1273. doi:10.1016/S0010-938X(02)00214-7.

[64] M. Gao, X. Pang, K. Gao, The growth mechanism of CO₂ corrosion product films, *Corros. Sci.* 53 (2011) 557–568. doi:10.1016/j.corsci.2010.09.060.

[65] M. Albahri, A. Barifcani, D. Dwivedi, S. Iglauer, M. Lebedev, I.D. MacLeod, L.L. Machuca, X-ray micro-computed tomography analysis of accumulated corrosion products in deep-water shipwrecks, *Mater. Corros.* 70 (2019) 1977–1998. doi:10.1002/maco.201910842.

[66] H. Lamei Ramandi, H. Chen, A. Crosky, S. Saydam, Interactions of stress corrosion cracks in cold drawn pearlitic steel wires: An X-ray micro-computed tomography study, *Corros. Sci.* 145 (2018) 170–179. doi:10.1016/j.corsci.2018.09.009.

[67] Y. Jing, R.T. Armstrong, H.L. Ramandi, P. Mostaghimi, Coal cleat reconstruction using micro-computed tomography imaging, *Fuel*. 181 (2016) 286–299. doi:10.1016/j.fuel.2016.04.127.

[68] H.L. Ramandi, R.T. Armstrong, P. Mostaghimi, Micro-CT image calibration to improve fracture aperture measurement, *Case Stud. Nondestruct. Test. Eval.* 6 (2016) 4–13. doi:10.1016/j.csndt.2016.03.001.

[69] L.A. Gomes Perini, P. Bleuet, J. Filevich, W. Parker, B. Buijsse, L.F.T. Kwakman, Developments on a SEM-based X-ray tomography system: Stabilization scheme and performance evaluation, *Rev. Sci. Instrum.* 88 (2017). doi:10.1063/1.4989406.

[70] J. Hsieh, *Computed tomography: principles, design, artifacts, and recent advances*, SPIE Press Book, 2009.

- [71] G. Van Gompel, K. Van Slambrouck, M. Defrise, K.J. Batenburg, J. De Mey, J. Sijbers, J. Nuyts, Iterative correction of beam hardening artifacts in CT, in: *Med. Phys.*, John Wiley and Sons Ltd, 2011. doi:10.1118/1.3577758.
- [72] F. Eckermann, T. Suter, P.J. Uggowitzer, A. Afseth, A.J. Davenport, B.J. Connolly, M.H. Larsen, F. De Carlo, P. Schmutz, In situ monitoring of corrosion processes within the bulk of AlMgSi alloys using X-ray microtomography, *Corros. Sci.* 50 (2008) 3455–3466. doi:10.1016/j.corsci.2008.09.015.
- [73] S.M. Ghahari, A.J. Davenport, T. Rayment, T. Suter, J.P. Tinnes, C. Padovani, J.A. Hammons, M. Stampanoni, F. Marone, R. Mokso, In situ synchrotron X-ray micro-tomography study of pitting corrosion in stainless steel, *Corros. Sci.* 53 (2011) 2684–2687. doi:10.1016/j.corsci.2011.05.040.
- [74] P.A. Itty, M. Serdar, C. Meral, D. Parkinson, A.A. MacDowell, D. Bjegović, P.J.M. Monteiro, In situ 3D monitoring of corrosion on carbon steel and ferritic stainless steel embedded in cement paste, *Corros. Sci.* 83 (2014) 409–418. doi:10.1016/j.corsci.2014.03.010.
- [75] I. Ročňáková, E.B. Montufar, M. Horynová, T. Zikmund, K. Novotný, L. Klakurková, L. Čelko, G.L. Song, J. Kaiser, Assessment of localized corrosion under simulated physiological conditions of magnesium samples with heterogeneous microstructure: Value of X-ray computed micro-tomography platform, *Corros. Sci.* 104 (2016) 187–196. doi:10.1016/j.corsci.2015.12.009.

Figure captions

Figure 1: Variation of: (a) E_{corr} and (b) corrosion rate from LPR measurements for 1Cr steel at $T=80^{\circ}\text{C}$ and $T=40^{\circ}\text{C}$ in 1wt.% NaCl solution.

Figure 2: Variation of pH, Fe^{2+} and $\text{SR}_{(\text{FeCO}_3)}$ during the exposure of 1Cr steel: (a) at $T=80^{\circ}\text{C}$ and (b) $T=40^{\circ}\text{C}$ in 1wt.% NaCl solution.

Figure 3: Results of Electrochemical impedance measurements: Nyquist plot (a) at T=80°C and (b) T=40°C ; Bode plot $|Z|$ vs frequency (c) at T=80°C and (d) T=40°C ; Bode plot Phase vs frequency (e) at T=80°C and (f) T=40°C.

Figure 4: Schematic representation of the adaptation of the equivalent circuit used for numerical simulation of the EIS data

Figure 5

Figure 6: Results from ex-situ X-ray tomography analysis of 1Cr steel exposed to 1wt.% NaCl solution at T=80°C: (a) volumetric representation, (b) volumetric representation without showing the corrosion scale, (c) ortho slice in XZ direction,(d) ortho slice in XY direction.

Figure 7: : Results from ex-situ X-ray tomography analysis of CT scanning for the 1Cr steel exposed to 1wt.% NaCl solution at T=40°C: (a) volumetric representation, (b) volumetric representation without showing the corrosion scale,(c) ortho slice in XZ direction,(d) ortho slice in XY direction.

Figure 8: SEM and X-ray mapping results of sample exposed to 1wt.% NaCl solution at $T=80^{\circ}\text{C}$: (a) surface morphology of the corrosion product, (b) cross section, (c) X-ray mapping of the cross section.

Figure 9: SEM and X-ray mapping results of sample exposed to 1wt.% NaCl solution at $T=40^{\circ}\text{C}$: (a) images of the surface morphology of the corrosion product, (b) cross section, (c) X-ray mapping of the cross section.

Journal Pre-proof

Table captions

Table 1 Chemical composition in wt.% of the 1Cr carbon steel material

Material	C	Cr	Mn	Mo	P	Si	S
1Cr	0.40%	1.10%	0.75%	0.20%	≤0.035%	0.20%	≤0.040%

Table 2 Experimental conditions used for electrochemical experiments

Parameter	Condition
Material	1Cr
Rotation	300 rpm
Solution	1 wt.% NaCl in Deionized water
Temperature	40 °C, 80°C
CO ₂ partial pressure	0.93 bar (at 40 °C) and 0.5 bar (at 80°C) at atmospheric pressure
Initial pH	Free to settle

Table 3: Electrochemical impedance parameters obtained from the measured EIS data circuit fitting for 1Cr steel immersed in 1wt.% NaCl solution at T=80°C.

Day	C _{sc}	R _{po}	C _{dl}	R _{ct}
	mF/cm ²	Ω·cm ²	mF/cm ²	Ω·cm ²
1	2.4	21.4	76.8	10.8
5	15.9	21.9	201.4	14.4
8	20.6	21.1	155.9	18.8
9	18.8	25.0	122.1	35.8
10	17.6	29.9	49.9	85.8
11	14.4	37.5	45.6	126.9
15	8.4	57.5	27.9	132.1
18	8.0	62.6	27.8	136.0

Table 4: Electrochemical impedance parameters obtained fitted from the measured EIS data circuit fitting for 1Cr steel immersed in 1wt.% NaCl solution at T=40°C.

Day	C_{sc}	R_{po}	C_{dl}	R_{ct}
	mF/cm ²	$\Omega \cdot \text{cm}^2$	mF/cm ²	$\Omega \cdot \text{cm}^2$
1	6.7	32.1	365.4	15.2
2	8.4	32.7	399.4	15.6
5	13.5	34.8	497.0	13.8
8	17.9	38.7	395.8	14.1
11	20.9	40.1	249.9	14.9
15	22.6	36.2	70.5	24.2
20	24.7	32.4	45.6	33.8