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The role of Ca^{2+} ions on Ca/Fe carbonate products on X65 carbon steel in CO_2 corrosion environments at 80 and 150°C

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Abstract

The role of Ca^{2+} ions on the corrosion behaviour of carbon steel in CO_2-corrosion environments was evaluated at 80°C and 150°C. In the presence of Ca^{2+} ions there was a more significant effect on the general corrosion rate at the lower temperature of 80°C where the protection afforded by the corrosion product layer was reduced. The extent of localised/pitting corrosion increased through the addition of Ca^{2+} ions indicating that Ca^{2+} plays a role in promoting localised corrosion. XRD based calculations, along with focused ion beam EDX-line scans confirmed that the mixed Ca/Fe carbonates precipitated with concentration gradients across their thicknesses.

Key words: CO_2 corrosion, high temperature, iron carbonate, calcium carbonate, mixed carbonate

1.0 Introduction

The formation of protective surface films such as iron carbonate ($FeCO_3$) are of great importance in the oil and gas industry as they can prolong the lifetime of downhole equipment or production lines manufactured from carbon steel through the mitigation of internal carbon dioxide (CO_2) corrosion (1). Numerous studies have alluded to the effects of $FeCO_3$ in relation to corrosion rate suppression of carbon steel in CO_2-containing environments. However, the analysis of pipeline scale specimens collected from the oil and gas industry have shown that calcium carbonate ($CaCO_3$) may co-exist with $FeCO_3$ in typical deposition products (2). Interestingly, despite its prevalence, the role of $CaCO_3$ deposition and the associated effects of calcium (Ca^{2+}) ions within brine solutions on the general and pitting corrosion characteristics of carbon steel in CO_2 environments have rarely been considered in literature. Most corrosion research focuses on sodium chloride (NaCl) based brines which restrict the possible varieties of corrosion products capable of forming to $FeCO_3$ and, in some cases, magnetite (Fe_3O_4) at elevated temperatures and pH (3).

Ca^{2+} ions are widely present in oil and gas formation brines. Typically the major dissolved inorganic constituent of oilfield brines is sodium chloride but may also contain 1-30g.L^{-1} calcium, 0.1-30g.L^{-1} magnesium, 0-3g.L^{-1} strontium, up to ≈ 0.1g.L^{-1} barium, 0.1-2g.L^{-1} bicarbonate and 0.4g.L^{-1} sulphate; their total dissolved inorganic content is in the range 100-350g.L^{-1} (4). The presence of Ca^{2+} ions can facilitate precipitation of $CaCO_3$, however Ca^{2+} ions have also been shown to result in the formation of mixed carbonates such as iron-calcium carbonate ($Fe_xCa_yCO_3$ – where x+y=1) when Fe^{2+} ions are also present in the production fluid (5). This results in a scale/corrosion product with different chemical and morphological properties in comparison to pure $FeCO_3$ and $CaCO_3$. Despite numerous reports of mixed carbonate formation in the field (6) there have been very few research papers directed towards understanding the chemistry and structure of complex scales, particularly in the context of co-precipitation onto a corroding carbon steel surface and the implications this holds for general and pitting corrosion in a CO_2 environment.

This paper focuses on understanding the role of Ca^{2+} ions on the development of such mixed carbonates and their effect on the corrosion behaviour of carbon steel at 80 and 150°C in a CO_2-saturated environment. The remainder of this section provides a review of relevant published literature.

In solely NaCl based brines, it is well known that $FeCO_3$ is one of the main corrosion products which can accumulate onto the surface of internal pipelines. Several studies have focused on evaluating the protectiveness of this corrosion product, spanning a wide range of operating and environmental conditions (7-11). The general consensus is that pH and temperature have the most substantial effect on $FeCO_3$ formation and protectiveness, with an increase in either parameter producing faster and more effective film formation (12-14). Despite a number of influential factors being investigated with regards to $FeCO_3$ formation and protection, the effect of brine chemistry and the formation of mixed carbonates has rarely been studied, especially in a systematic format. This is particularly true for the presence of Ca^{2+} in brines and the formation of $Fe_xCa_yCO_3$.

One of the first studies to consider co-precipitation of iron and calcium carbonates was that performed by Alsaiari et al. (15), although this work focused on understanding precipitation within a bulk solution using a continuous stirrer tanker reactor as opposed to the mixed carbonate forming as a corrosion product onto a corroding steel surface. The effect of Ca^{2+} ions on precipitation behaviour of both carbonates was assessed in supersaturated solutions (with respect to both $FeCO_3$ and $CaCO_3$) containing 0.5 mol L^{-1} NaCl at 55°C and pH values between 6.2 and 7.8. Ca^{2+} was observed to have a strong effect on increasing the solubility of $FeCO_3$, preventing its formation even at high levels of saturation. Interestingly, the presence of Fe^{2+} had no effect on the solubility of $CaCO_3$. Examination of the molar ratios of Ca^{2+} to Fe^{2+} in the solution and within the precipitate led to the conclusion that for supersaturated solutions, $CaCO_3$ has the greatest preference to precipitate from the solution across the conditions evaluated. Following on from this research, Alsaiari et al. (2) have shown that the introduction of Ca^{2+} ions in a Ca^{2+}:Fe^{2+} molar ratio in excess of 1:10 increased the solubility of Fe^{2+}, and such an increase was proportional to the concentration of Ca^{2+}. Alsaiari et al. (5) then developed a correlation which could be used to predict the stoichiometry of Fe and Ca in bulk precipitation of $Fe_xCa_yCO_3$ based on the bulk fluid properties.

In relation to the study of co-precipitation onto corroding surfaces, Ding et al. (16) evaluated the corrosion of carbon steel at 10 bar CO_2 and 75°C in brine solutions with Ca^{2+} concentrations varying between 0 and 512 ppm. The addition of Ca^{2+} resulted in an increase in corrosion rate and the development of $Fe_xCa_yCO_3$ on the steel surface. Through interpretation of X-ray diffraction (XRD) patterns, the authors were able to show that the Fe^{2+} within the corrosion product was gradually replaced by Ca^{2+} with an increasing Ca^{2+} content in the brine. Such conclusions were made through the observations of shifts in the position of the $Fe_xCa_yCO_3$ peaks in the XRD patterns; this was attributed to a change in the unit cell of the corrosion product. In an alternative approach, Tavares et al. (17) made similar observations. Although general corrosion rate decreased in the presence of $CaCO_3$, a greater rate of localised corrosion was observed and attributed to the greater porosity of mixed carbonate films, making them more susceptible to chloride permeation (17).

More recently, Esmaeely et al. (18) conducted experiments over a range of Ca^{2+} concentrations (10 to 10,000 ppm Ca^{2+}) in order to determine the effect on both general and localised corrosion, as well as corrosion product characteristics for carbon steel in a 1 wt.% NaCl solution saturated with CO_2 at 80°C and pH 6.6. At elevated concentrations (1000 ppm or higher), Ca^{2+} had a significant effect on corrosion rate, changing the corrosion product into non-protective, porous $CaCO_3$. Further experiments by Esmaeely et al. (19) revealed that the localised corrosion rate was greater in the presence of the mixed corrosion product formed with greater mole fractions of Ca and it was therefore concluded that Ca^{2+} had induced localised corrosion rather than Cl^-.

Very little research has been directed towards to the precipitation of mixed iron-calcium carbonates in comparison to other carbonates within literature. This is surprising given that that the formation of $Fe_xCa_yCO_3$ has been observed in several water treatment plants and oil wells (6). It has been established that the presence of Ca^{2+} ions can result in the formation of a mixed carbonate scale which appears to influence both the general and localised corrosion behaviour of carbon steel, at least in low pressure environments. However, such characteristics have not been considered at elevated temperatures (beyond 80°C). It has been well documented that oil/gas reservoirs have average geothermal gradients of 25 to 35°C/km depending on their location. The depths of conventional and unconventional oil wells are typically 2 to 3 km and 3 to 5 km respectively (20). Consequently, this work focuses on the corrosion behaviour of X65 carbon steel, the characteristics of the surface corrosion products and their protective properties at 80 and 150°C in the absence and presence of 1.83 wt.% calcium chloride di-hydrate ($CaCl_2{\cdot}2H_2O$) to enhance understanding of CO_2 corrosion in more complex brine chemistries at elevated temperatures.

2.0 Experimental Procedure

2.1 Material preparation

X65 carbon steel specimens were machined into discs with a diameter of 25 mm and thickness of 6 mm. A 3 mm diameter hole was drilled into in the edge of each specimen for attachment onto the autoclave holder. The specimens were prepared no more than 30 minutes prior to each experiment. The preparation process consisted of wet-grinding each coupon successively with 120, 320 and 600 silicon carbide (SiC) grit paper, followed by rinsing with acetone and distilled water before drying gently with compressed air. Two specimens (total surface area of ~29 cm^2) were prepared for each experiment and were weighed after they had been wet-ground and degreased to enable corrosion rates to be determined via gravimetric analysis. The X65 carbon steel specimens were weighed using an electronic balance to within an accuracy of 0.01 mg. The manufacturer's elemental composition of X65 carbon steel is provided in Table 1, with the material possessing a ferritic-pearlitic microstructure (Figure 1).

Table 1: Elemental composition of X65 steel (wt.%)

C	**Si**	**Mn**	**P**	**S**	**Cr**	**Mo**	**Ni**
0.12	0.18	1.27	0.008	0.002	0.11	0.17	0.07
Cu	Sn	Al	B	Nb	Ti	V	Fe
0.12	0.008	0.022	0.0005	0.054	0.001	0.057	Balance

2.2 Solution preparation

For experiments performed in the absence of Ca^{2+}, a 3 wt.% NaCl solution was used. In experiments containing Ca^{2+}, the required wt.% of the divalent cation was achieved through the addition of $CaCl_2{\cdot}2H_2O$ salt to distilled water, with the appropriate amount of NaCl added to the solution to maintain a consistent chloride concentration at 1.83 wt.%. Each solution was prepared at least 24 h in advance with CO_2 bubbled into the solution to ensure saturation before every experiment. The full list of solution chemistries and temperatures considered is provided in the experimental test matrix in Table 2. Table 3 shows the measured total pressures and calculated partial pressure of CO_2 at each test temperature. The CO_2 partial pressures in Table 3 were calculated by subtracting the water vapour pressure from the total pressure.

2.3 Experimental method

A full schematic representation of the autoclave setup is shown in Figure 2. Two X65 carbon steel specimens were attached to the non-conducting autoclave specimen holder using screws manufactured from high temperature resistant polymer. The specimens were placed away from the autoclave walls and other components to prevent any galvanic effects during the experiments. 750 ml of the prepared brine solution was then pumped into the autoclave through CO_2 purged lines to avoid oxygen ingress before sealing the fluid entry system. Inlet and outlet lines to and from the autoclave were then purged again with CO_2 to remove any potential residual traces of oxygen from the system. The autoclave was then heated to 25°C whilst being continuously purged at atmospheric pressure with CO_2, allowing the gas to vent through one exit fitting. Once the solution reached 25°C, the CO_2 bubbling was ceased and the autoclave system was shut in at room pressure. The autoclave was then heated to the desired experimental temperature (either 80 or 150°C in this instance). The starting point of the experiment was taken from the point at which the required operating temperature was reached. Once the experiment had finished, the autoclave was cooled down to 80°C and depressurised. The specimens were then removed from the autoclave, rinsed with distilled water and dried with compressed air. One specimen was preserved in a desiccator to allow for further analysis of the corrosion product, while the other specimen was used for mass loss/gain measurements. Experiments were repeated to allow for average mass loss measurements to be carried out across a minimum of three specimens. For mass loss/gain calculations, all the specimens were weighed before the experiment, after the experiment with the corrosion products on the surface and after the experiment in the absence of corrosion product. For the final mass measurement, the corrosion product was removed with the aid of Clarke's solution (20 g antimony trioxide + 50 g tin (II) chloride + 1000 ml hydrochloric acid) in accordance with ASTM Standard G1-03 (21). The mass measurements were then used to determine both the mass of corrosion product and the integrated corrosion rate over the duration of the experiment in units of mm/year (based on the specimen surface area exposed to the test solution). The solubility of CO_2 at 80 and 150°C was examined using Henry's law to help aid the interpretation of the corrosion rate data (Table 4).

Table 2: Experimental test matrix to evaluate the role of Ca^{2+} ions on corrosion product formation and corrosion behaviour of X65 carbon steel

Test Condition	NaCl content (wt.%)	Total Cl^- (wt.%)	$CaCl_2\cdot 2H_2O$ content (wt.%)	Temperature (°C)	P_{CO2} at 25°C (bar)	Time (h)
1	3	1.82	0	80 and 150	1	6, 24, 48 and 96
2	1.54	1.82	1.83			

Table 3: Measured total and calculated partial pressures in autoclave experiments

Test Condition	p_{CO2} at 25°C (bar)	p_{CO2} at 80°C (bar)	p_{Total} at 80°C (bar)	p_{CO2} at 150°C (bar)	p_{Total} at 150°C (bar)
1	0.98	1.43	1.9	1.44	6.17
2	0.98	1.43	1.9	1.44	6.17

Table 4: Calculated concentration of CO_2 in aqueous and gas phases

Temperature (°C)	Cco_2 in aqueous phase (mol)	Cco_2 in gas phase (mol)	Gas/aqueous Cco_2 ratio
25	0.02186	0.01022	0.467
80	0.01382	0.01242	0.899
150	0.00826	0.01044	1.264

2.4 Surface analysis methods

2.4.1 Scanning electron microscopy (SEM)/energy dispersive X-ray spectroscopy (EDX) and focused ion beam (FIB)

A Carl Zeiss EVO MA15 VP SEM was used which was integrated with an Oxford instruments AZtecEnergy energy dispersive X-ray (EDX) system to provide secondary and backscattered imaging, elemental mapping and line scans. This instrument was used to analyse both top view and cross-sections of specimens (to observe corrosion product thickness). For top view imaging, the disc shaped specimens from the autoclave experiments were carbon coated along the height of their circumference to eliminate any surface charging effect before being used for any analysis. For cross-sections, the disc shaped specimens were immersed in a resin. The resin was left to completely set for at least 24 h before cutting the specimen in half. Once the specimen had been cut, the cut surface was wet-ground with up to 600 SiC grit paper. The cross-section specimen was then rinsed with distilled water and dried with compressed air. The resin on the outside of the cross-sectioned specimen was then carbon coated and the cross-sectioned steel surface was iridium coated to reduce any surface charging effect. A FEI Nova200 dual beam FIB/SEM was used to provide SEM images with EDX linescans of cross-section specimens. Specimens were prepared by coating the corrosion product layer with a platinum coating before a trench was cut in the corrosion product. A voltage range of 5-30 kV was used along with a current range of 0.1-5 nA.

2.4.2 X-ray diffraction (XRD) and data processing of patterns

A Bruker D8 X-ray diffractometer was used for crystalline phase identification. The X65 carbon steel specimens required no preparation beforehand and could simply be inserted onto a holder prior to analysis. The incident rays provided a 10 x 10 mm surface coverage and scans ranged from a 20-70^{o} 2Θ position for total scan time of 50 minutes. The XRD results were used to identify the phases present along with the molar fraction of Ca in $Fe_xCa_yCO_3$ for experiments conducted in the presence of Ca^{2+}. An equation was derived to determine the molar fraction of Ca based on the d-spacing of the main peak for $Fe_xCa_yCO_3$ located at the (104) inter-planar d-spacing. The equation is derived in the following section.

Equation (1) represents the inter-planar spacing (d) for a hexagonal Bravais lattice (22). This equation was used as a basis for the derivation as $FeCO_3$ and $CaCO_3$ share a hexagonal lattice structure where h, k and l are the Miller indices. In Equation (1) a and c are the unit cell parameters, also known as the lattice constants.

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{(h^2 + hk + k^2)}{a^2}\right) + \frac{l^2}{c^2} \qquad (1)$$

Equation (2) is the unit cell volume equation for a hexagonal system. Equation (2) was rearranged before insertion into Equation (1) to produce Equation (3). Equation (2) was rearranged in order to eliminate the term a^2 once substituted to reduce error in the final derivation as unit cell parameter a is smaller than unit cell parameter c which could impose a greater error in the final equation.

$$V = a^2c(sin(60)) \qquad (2)$$

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{(h^2 + hk + k^2)c\sqrt{3}}{2V}\right) + \frac{l^2}{c^2} \qquad (3)$$

Davidson et al. (23) synthesised $Fe_xCa_yCO_3$ and together with data from other sources was able to present the unit cell volumes/parameters as a function of Fe and Ca mole fraction. This data was used to develop linear correlations for both the unit cell volume (*V*) and unit cell parameter *c* as a function of the molar fraction of Ca (*y*) within the mixed carbonate (Equations (4) and (5)).

$$c = 1.688y + 15.373 \qquad (4)$$

$$V = 74.107y + 291.340 \qquad (5)$$

Inserting Equations (4) and (5) into Equation (3) and also inserting *h, k* and *l* values for the [104] inter planar d-spacing produces Equation (6). The [104] inter-planar d-spacing was used as the most intense Bragg peaks for $CaCO_3$ and $FeCO_3$ are located at 2θ positions 29.42° and 32.07°, respectively, which correspond to the [104] inter-planar d-spacing (18);

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{2.924y + 26.626}{148.214y + 582.680}\right) + \frac{16}{(1.688y + 15.373)^2} \qquad (6)$$

Equation (6) was used to determine the mole fraction of Ca in $Fe_xCa_yCO_3$ using the d-spacing of the (104) peak as this was the most prominent peak for all patterns. Equation (6) was validated using the ICDD database (Ref: 04-019-9174) and yielded an error of <4% with regards to the mole fraction of Ca.

The introduction of Ca into $FeCO_3$ results in an increase in the d-spacing which represents a larger space between atoms. In terms of the peak positions associated with the diffraction patterns from such crystalline planes, the peaks will shift towards lower values of 2θ as the Ca molar fraction within the $Fe_xCa_yCO_3$ structure increases.. The aforementioned analysis enables the extent of this shift to be related to the stoichiometry of atoms within $Fe_xCa_yCO_3$.

2.4.3 NP_{FLEX} 3D surface profilometry

NP_{Flex} 3D surface profilometry was used to determine whether there was any form of localised attack/pitting on the carbon steel specimens. The specimens used for this type of analysis were cleaned of corrosion product before analysis using Clarke's solution. This was necessary for identification of any pits, as the localised areas of pitting corrosion could have been filled with corrosion products during the experiment. Two 3 x 3 mm regions were scanned on each specimen (two coupons for each experimental time and condition). A 2.5x objective was used with a working distance of approximately 3.5 mm. The results gathered were then analysed using Vision64 software. The top 10 deepest pits were selected across all regions and an average was determined to represent the severity of pitting attack.

3.0 Results

3.1 3 wt.% NaCl with 0 wt.% Ca^{2+} at 80 and 150°C

Corrosion rates as a function of time determined from mass loss measurements, as well as the transient response of corrosion product mass and the mass loss values themselves are provided in Figure 3, for both 80 and 150°C experiments in the 3 wt.% NaCl solution. A reduction in corrosion rate with time is observed at both temperatures. The corrosion rate after 6 h is higher at 150°C (9.8 mm/year) compared to 80°C (8.6 mm/year), although this is not significant based on experimental error. The final corrosion rates after 96 h are suppressed to 0.59 and 2.53 mm/year for 150 and 80°C, respectively.

The rate of reduction in corrosion rate is noticeably faster at higher temperature (150°C) and can be attributed to the faster kinetics and development of a more compact corrosion product layer, as will be discussed later. However it may also be partly attributed to an increase in the bulk pH. Mass gain measurements in Figure 3(b) indicate that at 80°C and 6 h, there is minimal corrosion product on the steel surface. The low mass gain measurement is supported by the top-view SEM image of the steel surface in Figure 4(a), where no crystalline corrosion product is evident after 6 h, only the presence of a porous iron carbide (Fe_3C) structure as a result of the selective dissolution of the ferrite phase within the steel microstructure. Consequently, the corrosion rate recorded after 6 h can be regarded as the anticipated dissolution rate in the absence of a protective layer.

As the test progresses at 80°C, a reduction in corrosion rate occurs in conjunction with an increase in the mass of the corrosion product, which appears to decline in growth rate towards the end of the 96 h experiment. The resulting corrosion layer after 96 h is shown in the SEM images within Figures 4(b) and (c) (top view) and Figure 5(a) (cross-section), depicting a crystalline layer with a thickness exceeding 30 μm.

At 150°C after 6 h there is a considerable amount of corrosion product (0.1 g) on the X65 steel surface based on mass gain measurements in Figure 3(b). The top view SEM image of the steel surface after 6 h (Figure 4(d)) can be contrasted with those on the carbon steel surface at 80°C after the same exposure period in Figure 4(a). At 150°C, a 10-15 μm thick film has already developed compared to no protective film formation at the lower temperature. Figure 3(b) shows that the corrosion product mass on the steel surface remains relatively constant throughout the duration of the experiment at 150°C, demonstrating that the majority of precipitation occurs within the first 6 h. Such observations highlight that the precipitation is much more rapid at 150°C, but also that the corrosion rate of 9.8 mm/year is not an accurate reflection of the corrosion rate for X65 in the absence of a protective corrosion product film; i.e. the corrosion rate under these conditions is under-estimated. After 96 h exposure to the test solution, there is no significant change in the corrosion product thickness (Figure 5(b)) – which is representative of all cross-sections examined between 6 and 96 h) or mass (Figure 3(b)). However, the crystal size has increased dramatically based on the top view images (Figure 4(e)). Given that the mass of corrosion product remains stable throughout the entire test, yet the crystal size increases, this perhaps indicates that some crystals are growing on the surface at the expense of others.

The corrosion product present at 150°C after 96 h offers superior protection to the steel substrate compared to that formed at 80°C after the same exposure time. However, after 4 days of immersion in the test solution the corrosion product layer formed at 150°C possesses half the mass and half the thickness of the film precipitated at 80°C, which corresponds to approximately the same average film porosity in both experiments, yet the film formed at 150°C is substantially more protective. Figure 6 shows the XRD patterns of corrosion products at each temperature as a function of time, highlighting that both corrosion products possess the same composition (purely $FeCO_3$) and that the difference in protectiveness is not attributed to different film chemistries in this instance.

3.2 1.54 wt.% NaCl and 1.83 wt.% $CaCl_2{\cdot}2H_2O$ at 80 and 150°C

Mass loss experiments were conducted using the same methodology adopted for the 3 wt.% NaCl solution tests, however, 1.83 wt.% of *$CaCl_2{\cdot}2H_2O$* in the form of $CaCl_2{\cdot}2H_2O$ was added and the NaCl concentration was reduced accordingly to maintain a constant Cl^- content. The mass loss results and their values expressed as integrated corrosion rates along with the mass of corrosion product and mass attributed to dissolution as a function of time at both temperatures are shown in Figures 7(a) and 7(b), respectively.

In comparison to the experiments performed in 3 wt.% NaCl, the initial corrosion rates after 6 h at 80°C were lower in the presence of 1.83 wt.% *$CaCl_2{\cdot}2H_2O$*. Furthermore, the corrosion product film formed at 80°C resulted in a less protective layer after 96 h (3.6 mm year^{-1} in comparison to 2.5 mm year^{-1} in pure NaCl), which precipitated more slowly over the first 48 h, but ultimately possessed a greater mass by the end of the 96 h experiments. The slower kinetics of film formation over 48 h may be attributed to the effect of Ca^{2+} on the solubility of the formed precipitate, as discussed and observed by Alsaiari et al. (15), or it could be partly caused by the lower corrosion rate over the first 24 h of the experiments compared to tests in the absence of Ca^{2+} (as shown in Figure 3) which would delay Fe^{2+} saturation of the test solution and hence, the onset of precipitation. However, after 48 h, total mass loss of carbon steel is higher in the presence of Ca^{2+} compared to that in the NaCl solution over the same time period *but* the inverse relationship is observed with regards to the corrosion product mass i.e. the amount of precipitation relative to the corrosion rate is lower in the presence of Ca^{2+}. This observation of a lower precipitation rate relative to the overall dissolution rate of the steel over the first 48 h suggests that less corrosion product layer is retained at the steel surface. Given that no bulk precipitation was observed at the end of any of the experiments performed in this study (i.e. the solution appeared completely clear upon immediate opening of the autoclave), it is suggested that Ca^{2+} does play a role in increasing the solubility of the overall corrosion product within the system.

The greater mass of the corrosion product after a duration of 96 h in the presence of Ca^{2+} can be attributed to the reduction in corrosion rate compared to tests in the pure NaCl system which provides a greater flux of Fe^{2+} ions into the bulk solution to facilitate further precipitation back onto the specimen surface.

The film formed at 150°C in the presence of Ca^{2+} resulted in a final corrosion rate of 0.5 mm/year for the underlying steel which is similar to the 0.6 mm/year recorded in the 3 wt.% NaCl solution. The kinetics of corrosion product formation were rapid and indistinguishable at 150°C in both the presence and absence of Ca^{2+}. However, the mass of corrosion product on the steel surface when Ca^{2+} was present in the brine was half that of the layer generated in the pure NaCl solution, yet offered similar levels of protection towards general corrosion. The low corrosion rate after 96 h of exposure at 150°C may once again be partly attributed to an increase in the bulk pH of the solution brine. However in both the presence and absence of calcium ions at 150°C there was a rapid reduction in the corrosion rate and together with the calculated molar concentrations of CO_2 (Table 4) it can be concluded that the CO_2 partial pressure at the beginning of the corrosion tests was sufficient to maintain the corrosion process for the 96 h test durations.

Across all these environments there was an inverse relationship between corrosion product mass and the corrosion rate of the underlying steel, with the greatest mass of corrosion product providing the least protection to the substrate after 96 h. This indicates that a large mass or thick corrosion product does not necessarily ensure efficient suppression of general corrosion rate for carbon steels.

The top-view SEM image corresponding to the specimen exposed to the 1.54 wt.% NaCl solution with 1.83 wt.% $CaCl_2{\cdot}2H_2O$ in Figure 8(a) shows that at 80°C a seemingly amorphous layer (which was very thin due to the low mass gain value recorded and rich in iron and calcium based on EDX measurements) had precipitated after 6 h of exposure. This can be contrasted with the absence of a layer on X65 steel in the 3 wt.% NaCl solution (Figure 4(a)). In the presence of Ca^{2+}, the formation of the initial amorphous layer was followed by the precipitation of a crystalline corrosion product (also rich in iron and calcium – confirmed later as $Fe_xCa_yCO_3$) exhibiting a different morphology to that of $FeCO_3$ in the pure NaCl system (Figure 4(b)). After 96 h (Figure 8(b)), the deposition of calcium rich crystals (confirmed later as $CaCO_3$) had occurred on top of the already precipitated $Fe_xCa_yCO_3$ film. Higher magnification images of the mixed carbonate film (Figure 8(c)) indicate that this layer is substantially more porous than that of the film formed in the presence of purely NaCl after 96 h, correlating with its poor ability to inhibit general corrosion. FIB-SEM images in Figures 8(d) and (e) also indicate $CaCO_3$ precipitation on top of the mixed carbonate layer.

At 150°C, $Fe_xCa_yCO_3$ crystals and $CaCO_3$ crystals were evident on the steel surface after 6 h of exposure (Figure 8(f)). However, unlike the calcium-rich crystals that had precipitated at 80°C after 96 h, these appeared to be embedded within the mixed iron-calcium layer, although it is not clear as to whether these crystals were in contact with the steel substrate.

The cross-sectional SEM images shown in Figure 9 show that the corrosion product layer at 80°C after 96 h is 50 μm thick, which is around twice the thickness of that in the 3 wt.% NaCl solution. However, the layer appears to be less well adhered to the substrate in comparison to the one formed in the pure NaCl experiment at the same temperature. Furthermore, the layer formed in the presence of Ca^{2+} is known to be very porous, as shown in Figure 8(c) where some areas exist on the steel surface that are completely absent of corrosion product. Both these observations correlate with the poor protection offered by the film in the presence of Ca^{2+}.

Conversely, the corrosion film formed at 150°C with 1.83 wt.% $CaCl_2{\cdot}2H_2O$ after 96 h (Figure 9b) is more compact and protective than that formed in the pure NaCl solution at the same temperature (Figure 5b), although not as uniform in thickness. This indicates that the uniformity of coverage is affected by the presence of Ca^{2+} in the brine.

Figure 10 shows the XRD patterns of the precipitated films in the presence of Ca^{2+} at both operating temperatures as a function of time. The results at 80°C (Figure 10(a)) confirm that a crystalline layer of $Fe_xCa_yCO_3$ had precipitated after 24 h of exposure and that $CaCO_3$ was present on the surface after 96 h of exposure. The results also show that the main (104) peak for $Fe_xCa_yCO_3$ shifts to the right towards that associated with the same miller plane for $FeCO_3$, whist also increasing in intensity with exposure time. The Bravais lattices for $CaCO_3$ and $FeCO_3$ are located at 2θ angles of 29.42° and 32.07°, respectively, and a shift can be observed from the latter to the former with increased exposure time within Figure 10(a) (and also within Figure 11 which provides a magnified version of the (104) peaks at 80°C in both environments as a function of time).

The XRD results at 150°C (Figure 10(b)) confirmed that both $Fe_xCa_yCO_3$ and $CaCO_3$ were present on the steel surface within the first 6 h of exposure to the 1.83 wt.% $CaCl_2\cdot 2H_2O$ solution and remained present throughout the 4 day experiment.

Using the previously derived Equation (6), the mole fraction of Ca within the precipitated mixed carbonate was determined for experiments at 80°C and 150°C. Firstly, Figure 11 shows a magnification of the main (104) peak for $Fe_xCa_yCO_3$ (in the case of Ca^{2+} containing solutions) and $FeCO_3$ (for NaCl solutions) at exposure times of 24, 48 and 96 h at 80°C as this was shown to vary with exposure time, unlike tests at 150°C.

For the mixed carbonate corrosion product which develops in the presence of 1.83 wt.% of $CaCl_2\cdot 2H_2O$ there is a shift in the 2θ position of the (104) peak by 1.31, 1.61 and 1.91° from that of the $FeCO_3$ (104) peak located at 32.07° between 24 and 96 h. Moreover, the peak shifts from left to right (i.e. from near the (104) peak associated with pure $CaCO_3$ towards the (104) peak associated with pure $FeCO_3$ with time. Such shifts signify that the average mole fraction of Ca within the corrosion product reduces with time. For the 3 wt.% NaCl experiments, there is no gradual shift in the (104) peak, with the corrosion product remaining as $FeCO_3$.

It is possible to calculate the mole fraction of Ca within the $Fe_xCa_yCO_3$ based on the shift in the (104) peak. Such calculations are outlined in Section 2.4.2, providing the derivation of Equation (6). Calculations were performed using Equation (6) and are provided in Table 5 for all test temperatures, conditions and exposure times. The results were correlated with EDX measurements which evaluate the ratio between the atomic wt.% of Ca to the combined atomic wt.% of Fe and Ca.

Table 5: Calculated mole fraction of Ca present in the $Fe_xCa_yCO_3$ corrosion product layers developed on X65 carbon steel as a function of exposure time at both 80 and 150°C. Calculations are based on XRD and EDX analysis and specimens were exposed to a CO_2-saturated 1.54 wt.% NaCl solution with 1.83 wt.% $CaCl_2\cdot 2H_2O$

Temperature (°C)	Exposure time (h)	Mole fraction of Ca from XRD	Mole fraction of Ca from EDX
	6	Amorphous	

80	24	0.68	0.68
	48	0.57	0.57
	96	0.46	0.36
150	6	0.55	0.50
	24	0.52	0.56
	48	0.58	0.47
	96	0.54	0.38

Table 5 shows that calculated mole fraction of Ca within the corrosion product layer decreased with exposure time at 80°C. These observations suggest that the corrosion product at 80°C has different iron and calcium compositions along its thickness. An extended 192 h experiment was conducted at 80°C to further observe the decrease in the mole fraction of Ca with time. The results show that the average mole fraction of Ca decreased further to 0.17. Table 5 also shows that at 150˚C (unlike 80˚C) the mole fraction of Ca remains constant with time. However due to extremely fast kinetics at 150˚C most of the corrosion product had precipitated within the first 6 h of exposure and ceased to continue developing which meant that mole fraction determined at 6, 24, 48 and 96 h of exposure were in fact the same corrosion product.

Figure 12 shows EDX line scan results of the two corrosion product layers formed in the presence of Ca^{2+} at 80 and 150°C. The images indicate the variability in Ca concentration through the film. The variation at 80°C (Figure 12(a)) shows a higher concentration closer to the steel surface, although this line scan does not extend all the way to the substrate. At 150°C (Figure 12(b)), the opposite trend is observed whereby the Ca concentration reduces closer towards the steel surface.

3.4 Localised corrosion behaviour

Figure 13 shows the uniform thickness loss, localised/pit depth relative to the corroded surface and total penetration depth as a function of time for the carbon steel surfaces exposed to 80 and 150°C environments in the absence and presence of Ca^{2+}. The uniform thickness loss was calculated from the total mass loss measurements, while the pit depth relative to the corroded surface was extracted from profilometry measurement. The top 10 pits recorded across multiple

3x3 mm^2 measurements on at least two carbon steel specimens taken from separate experiments were used to express the pit depth relative to the corroded surface. The error bars denote the range of the top 10 pit depths. The penetration depth provided is the summation of the uniform thickness loss and the pit depth relative to the corroded surface (Equation (7)), with the cumulative error taken into account.

$$Penetration_{Total} = Penetration_{Uniform} + Penetration_{Pit} \qquad (7)$$

Figures 13(a) and (b) relate to experiments at 80°C and make for an interesting comparison. The pit depth relative to the corroding surface increases steadily in both the presence and absence of Ca^{2+}, with no discernible difference being evident between the two, suggesting that Ca^{2+} does not influence the pitting kinetics in this environment. However, there is a difference in the level of uniform thickness loss between the two experiments as a function of time towards the latter stages of each test, with the rate of thickness loss reducing more significantly in the absence of Ca^{2+} due to the more protective nature of the film formed.

When considering the combined effect of uniform thickness loss and pit depth relative to the corroded surface, a total penetration depth can be quantified, and here lies a distinction between the specimens exposed to each environment. The higher uniform thickness loss in the presence of Ca^{2+} towards the end of the experiments creates a more discernible difference between the two total penetration depths in Figures 13(a) and (b). It could be argued that the higher uniform thickness loss in the presence of Ca^{2+} somewhat masks the true pit growth kinetics as the area surrounding the pits are receding at a comparatively substantial rate. As an example, the uniform thickness loss comprises over 40% of the total penetration depth after 96 h in the presence of Ca^{2+}. These results lead to the conclusion that Ca^{2+} does appear to promote pit growth in the 80°C environment, however, this is overshadowed somewhat by the ion's additional effect of maintaining a higher uniform corrosion rate due to the establishment of a less protective corrosion product layer compared to the environment in the absence of Ca^{2+}.

In addition to accentuating the pitting kinetics at 80°C, the presence of Ca^{2+} influences the topography of the corroded surface at the end of the experiment and the morphology of the form of attack. Figure 14 shows the surface characteristics of the carbon steel surfaces after removal of the corrosion product using surface profilometry. The addition of Ca^{2+} changes the topography significantly and the form of attack changes from a very non-uniform/locally corroded surface, to one with clearly distinguishable micro-pits.

Referring back to Figure 13, the latter two Figures of 13(c) and (d) relate to experiments performed at 150°C in the absence and presence of Ca^{2+}. Across all time periods, there is no significant difference between either the uniform thickness, localised/pit depth relative to the corroding surface, or the total penetration depth. The kinetics of pit initiation and propagation at 150°C are significantly quicker than at 80°C, with a pit penetration depth reaching in excess of 30 μm after only 6 h in both 150°C environments. This depth is twice that of the values obtained at 80°C after the same time period. However, unlike the experiments at 80°C, pit propagation completely ceases after 6 h at 150°C, regardless of the presence of Ca^{2+}. The highly protective nature of both films formed at 150°C completely prevents pit propagation and also minimises the extent of general corrosion. These results indicate that protective film formation is possible in the presence of Ca^{2+} containing brines and that $Fe_xCa_yCO_3$ layers can offer just as much protection to steel surfaces as $FeCO_3$ when formed at higher temperatures (150°C). This is true not only from the perspective of general corrosion, but also localised corrosion. Profilometry images of the steel surface after exposure to the 150°C solutions for 96 h are provided in Figure 15 after removal of corrosion products.

4.0 Conclusions

The role of Ca^{2+} ions on the corrosion behaviour of X65 carbon steel in a CO_2-containing sodium chloride solution was evaluated using the mass loss technique over periods from 6 to 96 h at both 80°C and 150°C. The addition of Ca^{2+} ions to $FeCO_3$ to form $Fe_xCa_yCO_3$ carbonate scale had a significant effect on both the uniform and localised corrosion behaviour at 80°C, where the addition of 1.83 wt.% of $CaCl_2{\cdot}2H_2O$ led to the formation of a thicker and less protective corrosion product layer consisting of $Fe_xCa_yCO_3$. The addition of Ca^{2+} at 80°C accelerated pit growth. Greater uniform corrosion rates were also observed, owing to the establishment of a less protective corrosion product layer. These effects were smaller at 150°C. This establishes that mixed carbonates such as $Fe_xCa_yCO_3$ can be as protective as $FeCO_3$ when precipitated at higher temperatures (150°C). The stoichiometry (x and y) of iron-calcium carbonate ($Fe_xCa_yCO_3$) can exist with concentration gradient across the thickness.

5.0 References

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Figure captions:

Figure 1: X65 carbon steel microstructure

Figure 2: Schematic of autoclave set-up for evaluation of X65 carbon steel corrosion in CO_2-containing environments at elevated temperature

Figure 3: (a) Mass loss measurements and the corresponding calculated corrosion rates in mm/year and (b) corrosion product mass determined from mass gain measurements as a function of time for X65 carbon steel exposed to a CO_2-saturated 3 wt.% NaCl solution at 80 and 150°C

Figure 4: Top view SEM images of X65 carbon steel after exposure to a CO_2-saturated 3 wt.% NaCl solution after (a) 6 h at 80°C; (b) 96 h at 80°C; (c) 96 h at 80°C at higher magnification; (d) 6 h at 150°C and (e) 96 h at 150°C

Figure 5: Cross-section SEM images of X65 carbon steel after exposure to a CO_2-saturated 3 wt.% NaCl solution after 96 h at (a) 80°C and (b) 150°C

Figure 6: XRD patterns collected from X65 carbon steel surfaces exposed to a CO_2-saturated 3 wt.% NaCl solution for different time periods between 6 h and 96 h at (a) 80°C and (b) 150°C

Figure 7: (a) Mass loss measurements and the corresponding calculated corrosion rates in mm year^{-1} and (b) corrosion product mass determined from mass gain measurements as a function of time for X65 carbon steel exposed to a CO_2-saturated 1.54 wt.% NaCl solution with 1.83 wt.% $CaCl_2{\cdot}2H_2O$ at 80 and 150°C

Figure 8: Top view SEM images of X65 carbon steel after exposure to a CO_2-saturated 1.54 wt.% NaCl solution with 1.83 wt.% $CaCl_2{\cdot}2H_2O$ after (a) 6 h at 80°C; (b) 96 h at 80°C; (c) 96 h at 80°C at higher magnification (d) FIB-SEM 96 h at 80°C; (e) FIB 96 h at 80°C; (f) 6 h at 150°C and (g) 96 h at 150°C

Figure 9: Cross-section SEM images of X65 carbon steel after exposure to a CO_2-saturated 1.54 wt.% NaCl solution with 1.83 wt.% $CaCl_2{\cdot}2H_2O$ after 96 h at (a) 80°C and (b) 150°C

Figure 10: XRD patterns collected from X65 carbon steel surfaces exposed to a CO_2-saturated 1.54 wt.% NaCl solution with 1.83 wt.% $CaCl_2{\cdot}2H_2O$ for different time periods between 6 h and 96 h at (a) 80°C and (b) 150°C

Figure 11: XRD patterns for X65 steel samples exposed to a CO_2-saturated solution containing either 3 wt.% NaCl or 1.54 wt.% NaCl with 1.83 wt.% $CaCl_2 \cdot 2H_2O$ at 80˚C after 24, 48 and 96 h of exposure

Figure 12: FIB section and EDX line scan of cross-section of X65 carbon steel after exposure to a CO_2-saturated 1.54 wt. % NaCl solution with 1.83 wt.% $CaCl_2 \cdot 2H_2O$ after (a) 96 h at 80˚C and (b) 96 h at 150˚C

Figure 13: Uniform thickness loss (calculated from mass loss measurements), average of the top 10 pit depths relative to the corroded steel surface (from profilometry analysis) and total penetration depth (summation of the two aforementioned measurements) on X65 carbon steel as a function of time for a CO_2-saturated solution containing (a) 3 wt.% NaCl at 80^{o}C; (b) 1.54 wt.% NaCl and 1.83 wt.% $CaCl_2 \cdot 2H_2O$ at 80^{o}C; (c) 3 wt.% NaCl at 150^{o}C; (d) 1.54 wt.% NaCl and 1.83 wt.% $CaCl_2 \cdot 2H_2O$ at 150^{o}C

Figure 14: Surface profilometry images of carbon steel surfaces after exposure to a CO_2-saturated solution for 96 h at 80˚C containing (a) 3 wt.% NaCl and (b) 1.54 wt.% NaCl and 1.83 wt.% $CaCl_2 \cdot 2H_2O$. Images are acquired after removal of the corrosion product layer

Figure 15: Surface profilometry images of carbon steel surfaces after exposure to a CO_2-saturated solution for 96 h at 150˚C containing (a) 3 wt.% NaCl and (b) 1.54 wt.% NaCl and 1.83 wt.% $CaCl_2 \cdot 2H_2O$. Images are acquired after removal of the corrosion product layer