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The influence of SO$_2$ on the tolerable water content to avoid pipeline corrosion during the transportation of supercritical CO$_2$

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Abstract
A systematic study is undertaken to establish the influence of sulphur dioxide (SO$_2$) concentration on the critical water content required to avoid substantial levels of internal corrosion during the transport of supercritical CO$_2$ for carbon capture and storage (CCS) applications. Corrosion experiments were performed on X65 carbon steel in autoclaves containing supercritical CO$_2$ at 80 bar and 35°C in the presence of 0, 50 and 100 ppm (mole) SO$_2$. General and localised corrosion rates were determined over a period of 48 hours through the implementation of gravimetric analysis and surface profilometry, respectively. Analysis of corrosion products formed on the steel surface was performed using x-ray diffraction, Raman spectroscopy and scanning electron microscopy. The results indicate that the presence of SO$_2$ reduces the critical water content required to maintain a general corrosion rate below 0.1 mm/year. Furthermore, the water content required to avoid excessive localised corrosion is far less than that to prevent significant general corrosion. Localised corrosion rates close to 1 mm/year were observed in the absence of SO$_2$ when the CO$_2$ system was water-saturated, but below water contents of ~1800 ppm (mole) and ~500 ppm, general and localised corrosion rates (respectfully) were found to be below 0.1 mm/year even in the presence of 100 ppm SO$_2$. The research presented highlights that reducing water content is a more favourable option compared to reducing SO$_2$ content to minimise internal pipeline corrosion during transportation. Consideration is also afforded to the consumption of impurities in the closed system experiments.

Keywords: corrosion, pitting, CO$_2$ transport, iron carbonate, iron sulphite

1. Introduction
The widespread implementation of Carbon Capture and Storage (CCS) technology would enable the continued use of fossil fuels through the abatement of CO$_2$, preventing emissions
into the atmosphere. Currently, CCS is the only technology which has the potential to make a significant and immediate impact on reducing the CO$_2$ level in the environment.

CCS involves capturing CO$_2$ from large point sources (e.g. power generation, refineries and other industrial applications), compressing the gas into a liquid or supercritical state and transporting it to geological reservoirs or depleted oil and gas reservoirs for sequestration or enhanced oil recovery (EOR) purposes.

It is predicted that, for the abatement of climate change, approximately 10 Gt/year of CO$_2$ will need to be transported and sequestered in 2050\[1\]. Dugstad et al.\[1\] estimated that this would require the construction of 3000 twelve-inch (or 1000 twenty-inch) pipelines under the assumption of a flow velocity of 1.5 m/s. They suggested that the only logical choice to achieve such enormous levels of abatement would be to have an extensive pipeline network constructed from carbon steel.

The transportation of CO$_2$ has been practiced for over 30 years and currently, over 6000 km of pipeline exist for EOR purposes. The majority of these pipelines are located in the USA and Canada, with some projects also being undertaken in Norway. Most of these pipelines transport CO$_2$ from natural sources, with a few pipelines carrying anthropogenic CO$_2$ as shown in Table 1.

Although the composition of CO$_2$ streams is not readily available in open literature, Table 1 provides a summary of information compiled from various sources\[2, 3, 4, 5, 6, 7, 8\]. CO$_2$ from natural sources is typically high purity and will require minimal gas treatment prior to injection. Only impurities such as CO$_2$, N$_2$, CH$_4$, H$_2$O and H$_2$S are to be expected\[9\]. Considering anthropogenic sources, there can be a distinct difference in fluid composition, as the stream can become further contaminated as a result of the presence of flue gas impurities (SO$_x$, NO$_x$ and O$_2$ in particular). Regrettably, this is not reflected in the list of anthropogenic sources in Table 1, and it is unclear from open literature whether this is because these components are not present in the CO$_2$ stream or that the process fluid was not analysed for these particular compounds.

Nonetheless, there will be significant differences between the transport of natural CO$_2$ and CO$_2$ from anthropogenic sources. Flue gas impurities are to be expected and will vary depending upon the type of capture process, the source and the level of gas treatment applied. Table 2 is adapted from the work of Lee et al.\[10\] who considered five different scenarios of post processing methodologies for a coal-fired power station with different levels of proposed contaminants. The table provides an example of the significant variations in impurity levels depending upon the amount of post processing involved in terms of coal combustion.
As shown in Table 1, it can be observed that the water contents within each CO\(_2\) stream vary from ~20 ppm (mole) to ~630 ppm (mole), with the exception of Sleipner which could be regarded as an anomaly in that it carries water-saturated supercritical CO\(_2\) using pipelines constructed from corrosion resistant alloys. Unfortunately, little information has been published on the rationale behind these imposed concentration limits.

If the water content within the CO\(_2\) stream exceeds the solubility limit locally, a separate aqueous phase will exist. If such a phase were to form on the pipeline wall, it will invariably become saturated with CO\(_2\), forming carbonic acid (H\(_2\)CO\(_3\)), lowering the pH of the aqueous phase (to pH ~3.3 at 80 bar) and posing a threat to pipeline integrity, even without the presence of additional flue gases such as SO\(_x\) and NO\(_x\).

It is worth noting in Table 1 that the two anthropogenic sources from gasification plants possess some of the lowest water specifications to prevent the break-out of water and the potential onset of corrosion. The introduction of impurities such as SO\(_x\), O\(_2\), and NO\(_x\) from flue gases can pose a significant problem for the transportation of anthropogenic CO\(_2\) streams in terms pipeline integrity when a sufficient level of water is present in the system to generate an aqueous phase\[1\]. When SO\(_2\) and O\(_2\) in particular are all present in the system, they can segregate into the aqueous phase forming sulphurous (H\(_2\)SO\(_3\)) and/or sulphuric acid (H\(_2\)SO\(_4\)), further lowering the pH and potentially increasing the corrosivity of the environment\[1\].

Consequently, to mitigate against the inherent risk associated with corrosion, pipeline operators set their own limits for water content in CO\(_2\) streams. According to Aspelend et al.\[12\] and Dugstad et al.\[1\] 500 ppm was considered to be the accepted limit in literature, although little reasoning exists behind this specific value. Kinder Morgan set a concentration limit of approximately 600 ppm\[13\], the CO\(_2\) stream at Weyburn is dehydrated down to 20 ppm whilst the pipelines at Sleipner transport water-saturated CO\(_2\) but use a corrosion resistant alloy as the pipeline material, as previously mentioned\[14\].

Surprisingly, there is no general consensus on what the actual allowable water content should be in the transported CO\(_2\) stream\[1\]. Furthermore, limited information exists in literature relating to the impact of impurities (other than water) on the corrosion processes in supercritical CO\(_2\) systems where CO\(_2\) is the dominant phase. A review of the work by Dugstad et al.\[1, 15\], Hua et al.\[16, 17, 18\] and Sim et al.\[19\] indicates that localised corrosion of carbon steel is significant in dense phase CO\(_2\) with only water as impurity. Hua et al.\[16, 17\] indicated that no localised attack was observed at 300 and 1600 ppm of water in supercritical CO\(_2\) condition (35°C and 50°C and 80 bar, respectively).
Some other valuable work was performed by Choi et al. who considered the effect of impurities of 4% $O_2$ and 1% $SO_2$ on the degradation of carbon steel in supercritical $CO_2$ at 80 bar and 50°C. Choi et al. evaluated the corrosion behaviour of X65 steel in both the water-saturated $CO_2$ phase and with the presence of only 650 ppm water. Their research highlighted that the corrosion rates could reach ~7 mm/year in the most severe conditions tested (water-saturated with the addition of 4% $O_2$ and 1% $SO_2$).

Dugstad and co-workers performed long durations experiments (7 and 30 days) to evaluate the susceptibility of X65 steel to corrosion in the presence of $O_2$ (0-200 ppm) and $SO_2$ (0-1000 ppm) at 100 bar and 20°C. Their findings indicated that the combined presence of $O_2$ (100 ppm) and $SO_2$ (200 ppm) induced small levels of corrosion (~0.01 mm/year) at water contents of 488 ppm, whilst no corrosion was observed at a higher water content of 1220 ppm when $O_2$ and $SO_2$ were absent from the system.

Farelas et al. considered the influence of a phase change of $CO_2$ from a supercritical fluid to liquid on the corrosion of X65. They determined that at 80 bar in static, liquid $CO_2$ conditions (25°C) corrosion was much more prevalent with the addition of 650 ppm water and 0.05% $SO_2$ than at supercritical conditions (50°C) with the same levels of impurities.

Finally, Xiang et al. have performed a handful of key studies which have considered the influence of $SO_2$ content (0.2-2 bar) on the corrosion rate of X70 carbon steel in water-saturated and under-saturated supercritical $CO_2$ as well as the influence of exposure time and water content. A summary of the aforementioned results were compiled by Hua et al. and are provided in another publication.

Although one particular publication by Xiang et al. involved assessing the corrosion behaviour of X70 carbon steel through varying water content in the presence of 2% $SO_2$ in supercritical $CO_2$ at 100 bar and 50°C, no systematic study has been conducted currently in literature to attempted to establish whether the same behaviour observed (in terms of the critical water content required to induce corrosion) extends to lower impurity systems, nor has the corrosion rate been quantified through localised corrosion measurements in such environments.

The research presented in this study has two key goals; firstly, to determine the influence of $SO_2$ contents typical of the $CO_2$ stream on the susceptibility of carbon steel to both general and localised corrosion in supercritical environments both under-saturated and saturated with water; and secondly, to determine the role of $SO_2$ content on the critical water content required to ensure no appreciable levels of corrosion are observed. For the purposes of this work, the threshold for the water content is defined as the point below which the corrosion rate (general or localised) is below 0.1 mm/year.
General and localised corrosion rates reported in this study are evaluated through a combination of the weight loss method and surface profilometry, respectively. Furthermore, a detailed analysis of the corrosion products formed in each environment is not presented here, although a selection of SEM images and XRD patterns are provided to show the morphology and composition of the corrosion products in specific experiments and how these are influenced by the presence of SO$_2$.

2. Experimental procedure

2.1 Materials and preparation

Test specimens were machined from carbon steel bars (API 5L X65) into discs of diameter 25 mm and thickness of 6 mm. The chemical composition of the X65 steel is provided in Table 3. Surface preparation consisted of wet-grinding the entire sample up to 800 grit using silicon carbide abrasive paper, rinsing with distilled water, followed by acetone, high purity ethanol and drying gently with compressed air. Samples were then stored in a desiccator until needed and weighed immediately before the experiment on an electronic balance with an accuracy of 0.001 mg before suspending inside the autoclave. Two samples were placed within the autoclave for each individual test, generating a total surface area of approximately 27 cm$^2$ exposed to the dense-phase CO$_2$.

2.2 Autoclave testing procedure

Figure 1 provides a schematic representation of the experimental system layout. The entire system consists of a 1 litre capacity autoclave, temperature controller, a CO$_2$/SO$_2$/O$_2$ mixed cylinder, a series of valves for CO$_2$ flow control and a waste gas treatment system. The distilled water used in each experiment was de-aerated by saturating the solution with CO$_2$ in a separate container for a minimum of 12 hours prior to testing. The specimens were suspended within the autoclave on a non-conducting wire whilst also ensuring they were not in contact with the walls of the cylinder to prevent galvanic effects. The prepared, required amount of CO$_2$-saturated water was carefully delivered into the autoclave at ambient pressure and temperature and sealed. All lines to the autoclave were purged with CO$_2$ and evacuated to ensure removal of O$_2$ within the system. The required CO$_2$/SO$_2$/O$_2$ mixture was then transferred into the autoclave and heated and pressurised to the required temperature and pressure. The starting point of the test is taken from the time at which the autoclave reached the required temperature and pressure. At the end of each experiment, the exhaust gas was filtered through an alkali solution to prevent release into the environment.
Based on the model by Spycher et al.\textsuperscript{26} the saturated water concentration in supercritical CO\textsubscript{2} at 35°C and 80 bar is 3437 ppm. In order to ensure the water-saturated CO\textsubscript{2} condition, 34000 ppm of water was introduced to the autoclave for the water-saturated tests (i.e. approximately 10 times the saturation limit). For experiments performed in under-saturated conditions, the exact volume of water was determined to achieve each required ppm concentration and this was injected into the bottom of the autoclave using a pipette.

\section*{2.3 Determining the test matrix for SO\textsubscript{2}/CO\textsubscript{2}/H\textsubscript{2}O experiments}

There are currently no recognised specifications for the CO\textsubscript{2} quality required for transportation\textsuperscript{1}. It is envisaged that the main technical constraint imposed will be the maximum allowable impurity content from the perspective of storage or from a corrosion and safety standpoint during transportation.

A number of tentative CO\textsubscript{2} specifications exist in literature, two of which are provided in Table 4 and where used as the basis for selecting the SO\textsubscript{2} concentrations studied within this work. The information within Table 4 was compiled from the European project ‘ENCAP – ENhanced CAPture of CO\textsubscript{2}’ from the DYNAMIS project\textsuperscript{7} and a set of data from Alstom adapted from the work of Dugstad et al.\textsuperscript{15}

Although a large variation is observed in tolerated impurity concentrations in Table 2, it is clear that the low limit for SO\textsubscript{2} content is below 100 ppm and is controlled from a health and safety perspective in both specifications. To represent the conditions likely to be encountered in CO\textsubscript{2} streams, SO\textsubscript{2} contents of 0, 50 and 100 ppm were selected in this study.

The complete matrix of tests performed within this paper is provided in Table 5, which outline the variations in water content that were also assessed.

At the end of each test conducted within this matrix, the specimens were dried thoroughly and photographed. The samples were subsequently chemically cleaned to remove all traces of corrosion products before weighing. The cleaning process consisted of wiping the surface with a cotton pad soaked in Clarke’s solution (20 g antimony trioxide + 50 g stannous chloride + 1000 ml hydrochloric acid) in accordance with ASTM Standard G1-03\textsuperscript{27}. This was followed by rinsing the samples with distilled water, followed by drying with compressed air.

The mass loss due to corrosion was determined from the weight difference before exposure and after cleaning. The corrosion rates were calculated by using Equation (1):

\begin{equation}
CR = \frac{87600 \times \Delta m}{\rho \times A \times T}
\end{equation}
Where $CR$ is the corrosion rate of the sample in mm/y, $\Delta m$ is the weight loss in grams, $\rho$ is the density of the sample in g/cm$^3$, $A$ is the exposed area in cm$^2$ and $T$ is the immersion time in hours.

### 2.4 Interferometry

The profilometry measurements were performed on samples (scanning a 3 x 3 mm$^2$ area at a time) using a NP$\text{FLEX}$ 3D Surface Metrology System to quantify localised attack. The objective used was 2.5X with a 3.5 mm working distance. All samples that were analysed by profilometry were first cleaned thoroughly with Clarke’s solution to remove any traces of corrosion product to enable the pits to be accurately quantified. The pit depth analysis was conducted in accordance with ASTM Standard G46-94$^{[28]}$. The standard stipulates that an average of the 10 deepest pits and the maximum pit depth should be used for pit damage characterisation of the sample area.

### 2.5 X-ray diffraction

The XRD patterns for each sample were collected using a PANalytical X’pert multipurpose diffractometer (MPD), employing Cu K$\alpha$ radiation with an active area of 10 x 10 mm$^2$. Scans were performed over a range $2\theta = 20$ to 80$^\circ$ using a step size of 0.033 per second, with a total scan time of approximately 50 minutes.

### 2.6 Scanning electron microscopy

SEM was carried out on samples using a Carl Zeiss EVO MA15 SEM to assess coverage and topography of corrosion product. All images were collected at an accelerating voltage of 20 kV and at a working distance of around 8 mm.

### 2.7 Raman spectroscopy

Raman spectra were collected by employing 488 nm radiation from an Ar ion laser (1% and 5%). The exposure time for each sample was recorded at between 5 and 30 minutes, with a total scan time of approximately 10 to 50 minutes. Raman spectroscopy was used to identify the nature of corrosion products locally on the surface and to detect the presence of potentially amorphous products not recorded by XRD.

### 3. Results and Discussion

#### 3.1 General corrosion behaviour of X65 in CO$_2$/SO$_2$/H$_2$O system with varying concentrations of SO$_2$ and H$_2$O

Figure 2 shows the general corrosion rates (determined from mass loss measurements) of X65 samples exposed to the water-saturated and under-saturated supercritical CO$_2$ phase at
35°C and 80 bar, containing 0, 50 and 100 ppm of SO₂ for an immersion time of 48 hours. The corrosion rates are represented on both a logarithmic scale as well as a continuous scale to enable better interpretation of the data.

Figure 2 indicates that the general corrosion rate of X65 is low (<0.01 mm/year) in the presence of all three different concentrations of SO₂ when the water content is below 700 ppm. No corrosion was recorded in tests performed in dry, impure CO₂ i.e. with a water content of 0 ppm, as expected.

Referring to Figure 2, as the water concentration is increased, the general corrosion rate in each environment also rises. In all three conditions, an increase in water content from 300 to 1770 ppm resulted in an increase in general corrosion rate of ~0.003 to 0.07 mm/year. However, the increase in water content from 1770 ppm to water-saturated conditions caused more substantial rates of increase in corrosion rate. In tests containing 0, 50 and 100 ppm SO₂, general corrosion rates in the water-saturated environment reached 0.10, 0.37 and 0.72 mm/year, respectively. The effect of the presence of SO₂ becomes distinctly more noticeable as the water content in the system rises.

Referring to literature, the tests which are most comparable with the data produced here are those performed by Dugstad et al. [21] who evaluated the corrosion behaviour of carbon steel exposed to supercritical CO₂ at 20°C and 100 bar. In the presence of 200 ppm SO₂, 100 ppm O₂ and 488 ppm water, a general corrosion rate below 0.01 mm/year was recorded over 7 days of testing. This observation aligns well with the results in Figure 2, but it must be noted that there are differences in operating conditions and impurity concentrations between the two experiments.

In an additional publication, Dugstad et al. [1] conducted tests on X65 steel at 20°C and 100 bar in supercritical CO₂ for 14 days in a rotating system at 3 rpm. No attack was observed in the absence of SO₂ and O₂ at water contents of 488 and 1220 ppm water. However, the introduction of 100 ppm SO₂ at a water content of 488 ppm resulted in corrosion rates of <0.005 mm/year. Increasing SO₂ content further to 344 ppm and maintaining water content at 488 ppm resulted in the same general corrosion rate. Finally, a SO₂ content of 344 ppm and a higher water concentration of 1220 ppm increased the general corrosion rate to 0.02 mm/year. All these values align well with the observations recorded in Figure 2, despite the slight differences in operating temperature, pressure and impurity content.

Similarly, Choi and Nesic [20] performed tests with X65 steel exposed to supercritical CO₂ at 50°C and 80 bar for 24 hours in the presence of only 650 ppm water. They reported a corrosion rate below 0.01 mm/year, which aligns with the reported values here of ~0.004 mm/year at 700 ppm water under identical temperature and pressure.
3.2 Analysis of corrosion product morphology and composition

Figure 3 presents the scanning electron microscopy (SEM) images of the corroded X65 steel samples exposed to a selected number of conditions tested within the matrix in Table 5. Images of the steel surface exposed to 700 ppm water (Figures 3(a), (d) and (g)) showed minimal signs of corrosion on the steel surface. As water content is increased, the quantity of visible corrosion product on the steel surface became noticeably larger.

In the system exposed to supercritical CO$_2$ without the presence of SO$_2$ or O$_2$ (Figures 3(a) – (c)), an increase in water content resulted in the formation of cubic crystals on the steel surface. These crystals were confirmed as FeCO$_3$ by XRD analysis. The resulting patterns can be observed in Figure 4 and the formation of such crystals is consistent with the observations of numerous authors [13, 16, 18, 25] in very similar environments.

In terms of the reaction mechanisms associated with the formation of FeCO$_3$, three series of reactions are capable within steel pipelines which transport supercritical CO$_2$ when water condenses onto the steel surface. These reactions are:

a) The saturation of the condensed water with CO$_2$, its association to produce carbonic acid and its subsequent partial homogenous dissociation in two steps to form bicarbonate and carbonate ions:

\[
\text{CO}_2(g) \leftrightarrow \text{CO}_2(aq) \quad (2)
\]

\[
\text{CO}_2(g) + \text{H}_2 \text{O}(l) \leftrightarrow \text{H}_2\text{CO}_3(aq) \quad (3)
\]

\[
\text{H}_2\text{CO}_3 \leftrightarrow \text{H}^+ + \text{HCO}_3^- \quad (4)
\]

\[
\text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^{2-} \quad (5)
\]

b) In the next stage of reactions, the cathodic reaction can occur either by direct reduction of hydrogen ions, or the reduction of carbonic acid or carbonate ions:

\[
2\text{H}^+ + 2e^- \leftrightarrow \text{H}_2 \quad (6)
\]

\[
2\text{H}_2\text{CO}_3 + 2e^- \rightarrow \text{H}_2 + 2\text{HCO}_3^- \quad (7)
\]

\[
2\text{HCO}_3^- + 2e^- \rightarrow \text{H}_2 + 2\text{CO}_3^{2-} \quad (8)
\]

c) The final stage is the anodic dissolution of iron:
Which can be followed by the precipitation of FeCO$_3$ via a one stage reaction with carbonates, or via a two stage reaction with bicarbonates:

$$\text{Fe}^2+ + \text{CO}_3^{2-} \rightarrow \text{FeCO}_3$$  \hspace{1cm} (10)

$$\text{Fe}^2+ + 2\text{HCO}_3^- \rightarrow \text{Fe(HCO}_3)_2$$  \hspace{1cm} (11)

$$\text{Fe(HCO}_3)_2 \rightarrow \text{FeCO}_3 + \text{CO}_2 + \text{H}_2\text{O}$$  \hspace{1cm} (12)

The introduction of both 50 and 100 ppm SO$_2$ with 20 ppm O$_2$ into the system resulted in the corrosion product morphology on the steel surface changing dramatically. Figures 3(e), (f), (h) and (i) indicate that the presence of SO$_2$ initiated the formation of a thin, sulphur-containing compound (confirmed via EDX measurements) across the steel surface (whilst at higher water contents, the presence of columnar crystals was also observed (Figures 3(f) and(i)) which also possessed a high sulphur content. Both these types of surface morphology have been observed by Choi et al. at operating conditions of 80 bar and 50°C in water-saturated supercritical CO$_2$ in the presence of 0.8 bar SO$_2$ and 0.8 bar SO$_2$ with 3.3 bar O$_2$. In addition, to these observations, Figure 3(i) shows that these particular tests produced globular crystals on the steel surface which possessed no trace of elemental sulphur.

The XRD patterns for the sample exposed to the water-saturated environments containing 50 and 100 ppm SO$_2$ provided in Figure 4 confirmed that the sulphur-containing crystals are hydrated iron sulphite (FeSO$_3\cdot$3H$_2$O). The presence of FeCO$_3$ was also detected on the steel surface through XRD measurements. The use of localised Raman spectroscopy at specific locations on the steel surface (Figure 5) confirmed that the globular crystals were FeCO$_3$ and that the columnar crystals were FeSO$_3\cdot$3H$_2$O. The strongest Raman peak observed at 1085 cm$^{-1}$ over the globular crystals in Figure 5 is representative of FeCO$_3$. Other peaks corresponding to the CO$_3^{2-}$ are located at 735 cm$^{-1}$ and 1500 cm$^{-1}$.

The strongest Raman peak observed from the scan over the globular crystals exists at 954 cm$^{-1}$ for crystal FeSO$_3$ and the vibrational wavenumbers between ~3200 and 3400 cm$^{-1}$ are related to the degree of hydration. As mentioned, the detection of FeSO$_3$ crystals is consistent with Choi et al. In their specific tests, no presence of FeCO$_3$ was recorded (potentially due to the high SO$_2$ content of 1% which may have preferred to form FeSO$_3$ in comparison to the formation of FeCO$_3$). The tests performed here have shown that the lower
The formation of FeSO₃ can be described by the following reactions:

a) Firstly, SO₂ is believed to dissolve into the condensed water film on the surface and subsequently becomes ionised:

\[
H_2O + SO_2 \rightarrow H^+ + HSO_3^- \quad (13)
\]

\[
HSO_3^- \rightarrow H^+ + SO_3^{2-} \quad (14)
\]

b) The cathodic reaction then occurs through the direct reduction of hydrogen ions:

\[
2H^+ + 2e^- \leftrightarrow H_2 \quad (15)
\]

c) FeSO₃ then forms via a precipitation process:

\[
Fe^{2+} + SO_3^{2-} \rightarrow FeSO_3 \quad (16)
\]

Both Choi et al. and Xiang et al. have observed FeSO₃ in experiments involving SO₂, however, in tests containing O₂ (1000 ppm in a 100 bar CO₂ system in the case of Xiang et al. and 3.3 bar partial pressure in a 80 bar CO₂ system in the case of Choi et al.), iron sulphate (FeSO₄) was also detected. It was suggested that the addition of O₂ not only results in an additional cathodic reaction, but it also enables the oxidation of sulphite ions to sulphate ions, allowing FeSO₄ to form via a precipitation reaction. It is apparent that the low concentration of 20 ppm O₂ administered in these tests was not sufficient enough to form appreciable amounts (if any) of FeSO₄ as it could not be detected through XRD or Raman spectroscopy.

### 3.3 Localised corrosion measurements

Figure 6 provides examples of the profilometry measurements from the sample surfaces exposed to the under-saturated and water-saturated environment at 35°C and 80 bar with concentrations of 0, 50 and 100 ppm SO₂ present in the system. The images indicate that the presence of SO₂ has a significant effect on the extent of localised attack and is capable of initiating more severe degradation at lower water contents than that in the absence of SO₂ and O₂. Profilometry measurements such as those displayed in Figure 6 were performed numerous times on the surface of each steel sample. In some instances (e.g. under-saturated conditions) all regions of localised attack could be easily focused on by the
profilometer. In other experiments where the surface degradation was more extensive, multiple measurements were performed on randomly chosen areas of the corroded steel surface in order to help accurately quantify the extent of localised attack. From all the profilometry scans collected on each sample surface, a multi-region analysis technique was employed to determine the top 10 deepest surface pits in accordance with ASTM Standard G46-94. The pit depths were then converted to pitting rates based on exposure time to provide a quantitative assessment of the extent of localised attack.

The pitting rates produced from the profilometry assessment are provided in Figure 7 on both a logarithmic scale (Figure 7(a)) and a continuous scale (Figure 7(b)). The results show that localised corrosion rates can become appreciably high (in excess of 1 mm/year) if enough water is present in the system, even in the absence of SO\(_2\) and O\(_2\). In all three environments evaluated, corrosion rates exceeded 0.1 mm/year at a water content of 700 ppm. Only tests performed at 0 and 300 ppm water content produced no measurable localised attack on the steel surface. Interestingly, the most significant increase in pitting rate was observed between 1200 and 1770 ppm, whilst the largest increase in general corrosion was from 1770 ppm to water-saturated conditions.

These observations suggest that the minimum water content to produce acceptable levels of general corrosion differs dramatically from that required to prevent significant localised attack.

### 3.4 Establishing a critical water content – general vs localised corrosion assessment

Figure 8 shows 3D surface plots to indicate the variation in general and localised corrosion of X65 as a function of SO\(_2\) and water content at 35°C and 80 bar. Both plots clearly indicate that increasing concentrations of SO\(_2\) and water results in an increase in degradation rate. It is also clear that adhering to a maximum critical water content over a range of SO\(_2\) concentrations is more effective than limiting SO\(_2\) content, as degradation rates can still be excessive in high water contents without the presence of any SO\(_2\).

Both Figures 8(a) and 8(b) show that a critical water content does exist, below which no substantial level of general or localised corrosion occurs. However, it is obvious that the critical water content required to minimise localised attack is considerably lower than that to reduce general corrosion to acceptable levels demonstrating that evaluating pitting rates is crucial in determining the safe conditions for CO\(_2\) transport.
Figure 9 considers the water content required to reduce general and localised corrosion to below 0.1 mm/year based on the trends observed on the surface plots. These values were obtained through linear interpolation between the two measurements and as such, should not be regarded as exact values. Nonetheless, they illustrate an important point. The critical water content required to evaluate pitting rates is crucial in determining the safe conditions for \( \text{CO}_2 \) transport.

In all three conditions, the water content required to prevent significant localised attack was established at approximately 500 ppm. However, the critical water content to reduce general corrosion to 0.1 mm/year varied and reduced significantly from 3400 to 1850 ppm as \( \text{SO}_2 \) content was increased from 0 to 100 ppm.

It is believed that for metals in corrosive environments, a critical relative humidity exists above which metal corrosion rate would experience a dramatic increase. The value of the critical humidity at atmospheric pressure is believed to be around 60-70\%\cite{29, 30} and is potentially the reason behind some experts recommending an upper humidity level of 60\% for supercritical \( \text{CO}_2 \) as a worst case scenario\cite{7}.

The only currently published study to consider this critical water content in high pressure \( \text{CO}_2 \) is that performed by Xiang et al.\cite{24} who identified the critical relative humidity for the corrosion of X70 carbon steel in supercritical \( \text{CO}_2 \) at 100 bar and 50\(^\circ\)C over 5 day experiments. These experiments were performed in the presence of 2\% (2 bar) \( \text{SO}_2 \) and 1000 ppm \( \text{O}_2 \) at a rotation speed of 120 rpm. From mass loss measurements, Xiang et al.\cite{24} determined the general corrosion rate of X70 as a function of humidity and established a very similar trend to that observed in Figure 2(b) consisting of low corrosion rates at low humidity, followed by a rapid rise once a critical water content was reached. Xiang et al.\cite{24} reported that the critical humidity was approximately 50-60\% based on the general corrosion rates determined from mass loss measurements. According to Figure 2(b), the general corrosion rate measurements tend to agree with the observation of Xiang et al.\cite{24}, whereas the localised corrosion rates present a different perspective by suggesting a considerably lower critical humidity.

It is important to state that it is unclear whether the pitting rates determined over 48 hours continue at this rate indefinitely. i.e. remain constant for the duration of the experiment. However, the measurements of high localised corrosion rates are in agreement with the observation by Farelas et al.\cite{22} who recorded initial localised corrosion rates in excess of 2.4 mm/year for X65 samples exposed to liquid \( \text{CO}_2 \) at 25\(^\circ\)C and 80 bar for 24 hours in under-saturated conditions in the presence of 650 ppm water and 0.05-0.1\% \( \text{SO}_2 \). The growth of surface pits in such conditions will be the subject of further studies.
3.5 Fluids velocity

The velocity of the process fluid in dense phase CO\textsubscript{2} systems has been shown to influence the corrosion behaviour of materials\textsuperscript{[31]} and it is perhaps worth commenting on the difference between the static tests performed in this study and how this compares to a dynamic system.

In fact, specific research\textsuperscript{[31]} has suggested that the presence of flow within the system reduces the amount of water condensed onto the steel surface through entrainment back into the bulk solution and subsequently minimises the level of corrosion. Consequently, the results presented in this study in static conditions could be regarded as providing a worst case scenario in terms of corrosion rates, although this required further study.

In terms of supporting the theory of the surface velocities potentially producing lower corrosion rates, the work of Farelas et al.,\textsuperscript{[31]} demonstrated that the presence of flow (1000 rpm sample rotation speed) reduced corrosion rates of X65 steel by around an order of magnitude in specific dense phase CO\textsubscript{2} environments. Farelas et al.,\textsuperscript{[31]} performed tests at 80 bar in both liquid (25°C) and supercritical (50°C) conditions with the addition of 650 ppm water and 0.08 bar (0.1 %) SO\textsubscript{2}. General corrosion rates reduced as the transition was made from static to dynamic from 0.03 to 0.02 mm/year in supercritical conditions and from 0.1 to 0.01 mm/year in liquid CO\textsubscript{2}.

3.6 Consumption of impurities

One final point to note is that one of the issues associated with experiments in closed systems with low impurity concentrations is that significant levels of depletion can occur in the system over the course of the experiment. Based on the assumption that 1 mole impurity (water or SO\textsubscript{2}) reacts with 1 mole Fe, the depletion of impurity can be estimated from the sample corrosion rate. The calculation requires the assumption that all corrosion is attributed to SO\textsubscript{2} and not carbonic acid. With this in mind, the rate of impurity depletion for SO\textsubscript{2} and water is provided in Figure 10.

Figure 10 indicates that significant consumption of the SO\textsubscript{2} occurred in tests where the water content was high. This poses the possibility that the corrosion rates recorded from mass loss measurements and surface profilometry did not provide a ‘worst case scenario’ corrosion rate in terms of CO\textsubscript{2} pipeline transportation. As water content is reduced, the reduction in corrosion rate of the X65 steel results in the calculated loss of SO\textsubscript{2} in the system declining significantly. Below a water content of 700
ppm, the consumption of SO$_2$ was below 3%. Therefore, confidence exists in the accuracy of
the critical water contents stated in this study to minimise localised corrosion as at low water
contents, the level of depletion of impurities is reduced significantly.

In a publication by Dugstad et al.[1] it was stated that the actual consumption of impurities
had been studied in autoclave experiments by IFE. They suggested that typically, the
consumption of less than 5% impurities was sufficient to influence the corrosion rate.
Consequently, understanding the consumption of impurities in closed systems is imperative
in order to define acceptable CO$_2$ specifications with the utmost confidence.

### 4. Conclusions

The extent of general and localised corrosion of X65 steel in pure and impure supercritical
CO$_2$ is reviewed. Tests were performed in dense phase CO$_2$ containing small concentrations
of water (0 ppm to water-saturated CO$_2$), SO$_2$ (0-100 ppm) and O$_2$ (0-20 ppm) at 35°C and
80 bar for 48 hours in an effort to determine the effect of impurities on the critical water
content required to avoid significant levels of general and localised corrosion. The main
conclusions from this study are:

1. Corrosion of carbon steel can take place in conditions where the water content is well
below the solubility limit of water in supercritical CO$_2$ (300 ppm within this study) in
the presence of 0, 50 and 100 ppm SO$_2$. From this perspective, the molar
concentration limit of 500-650 ppm (DYNAMIS/Kinder Morgan) would not be
sufficient to completely prevent corrosion in a system at 35°C, although general
corrosion rates would be very small in such environments (i.e. below 0.04 mm/year).

2. Increasing water content resulted in an increase in corrosion rate in all test
environments. In the absence of SO$_2$ and O$_2$, the critical water content at which a
general corrosion rate of 0.1 mm/year was reached was determined to be 3400 ppm,
which was very close to the solubility limit of water in CO$_2$ under the given conditions.

3. The introduction of 50 ppm SO$_2$ and 20 ppm O$_2$ resulted in a significant reduction in
the critical water content required to stay below a general corrosion rate of 0.1
mm/year, reducing it to ~2120 ppm. Further increase in SO$_2$ content to 100 ppm,
reduce the critical water content to ~1850 ppm.

4. Profilometry measurements indicated significant levels of localised attack on the steel
surface, predominantly in the form of pitting. The attack became more prominent with
increasing SO$_2$ and water content.

5. The critical water content required to minimise significant level of localised attack was
substantially lower than that required to prevent general corrosion (0.1 mm/year) and
was determined to be approximately 500 ppm, irrespective of SO$_2$ content (0, 50 or 100 ppm).

6. The results indicated that minimising water content is a better strategy compared to reducing SO$_2$ content as a method to reduce both general and localised corrosion as substantial corrosion was still observed at high water contents in the absence of SO$_2$ and O$_2$.

7. Calculations of impurity consumption indicated that water and SO$_2$ consumption was excessive in high humidity environments. However, consumption was below 5% in conditions near the critical water content to minimise localised corrosion. Therefore, this promoted confidence in the results at low water content, but suggested the values obtained at high water content may not reflect the ‘worst case scenario’ corrosion rate.

5. References


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sulphur dioxide, carbon dioxide, and suspended particles on the rusting of iron).

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2012: Salt Lake City, UT:NACE.

32. I.S. Cole, D.A. Paterson, P. Corrigan, S. Sim, and N. Birbilis, State of the aqueous
phase in liquid and supercritical CO₂ as relevant to CCS pipelines. International
<table>
<thead>
<tr>
<th>Location</th>
<th>Operator</th>
<th>Length (km)</th>
<th>Capacity (Mt/y)</th>
<th>Source</th>
<th>(\text{CO}_2) (vol.%)</th>
<th>(\text{CH}_4) (vol.%)</th>
<th>(\text{N}_2) (vol.%)</th>
<th>(\text{H}_2\text{S}) (vol.%)</th>
<th>(\text{C}_2\text{+}) (vol.%)</th>
<th>(\text{CO}) (vol.%)</th>
<th>(\text{O}_2) (vol.%)</th>
<th>(\text{NO}_2)</th>
<th>(\text{SO}_2)</th>
<th>(\text{H}_2) (vol.%)</th>
<th>(\text{Ar}) (vol.%)</th>
<th>Water content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Canyon Reef Carriers</td>
<td>Kinder Morgan</td>
<td>352</td>
<td>4.4</td>
<td>Anthropogenic - Gasification Plant</td>
<td>85-98</td>
<td>2-15 ((\text{C}<em>6\text{H}</em>{14}))</td>
<td>&lt;0.5</td>
<td>&lt;260 ppm</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Not specified</td>
<td>Not specified</td>
</tr>
<tr>
<td>Central Basin Pipeline</td>
<td>Kinder Morgan</td>
<td>278</td>
<td>20</td>
<td>Natural</td>
<td>98.5</td>
<td>0.2</td>
<td>1.3</td>
<td>&lt;26 ppm</td>
<td>0.3-0.6</td>
<td>Trace</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.5-2.0 total hydrocarbons</td>
<td>Not specified</td>
</tr>
<tr>
<td>Sheep Mountain</td>
<td>BP</td>
<td>772</td>
<td>9.2</td>
<td>Natural</td>
<td>96.8-97.4</td>
<td>1.7</td>
<td>0.6-0.9</td>
<td>-</td>
<td>-</td>
<td>Trace</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Not specified</td>
<td>Not specified</td>
<td>315 ppm</td>
</tr>
<tr>
<td>Bravo Dome Source</td>
<td>BP</td>
<td>350</td>
<td>7.3</td>
<td>Natural</td>
<td>99.7</td>
<td>-</td>
<td>0.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Not specified</td>
<td>Not specified</td>
<td>Not specified</td>
</tr>
<tr>
<td>Cortez Pipeline</td>
<td>Kinder Morgan</td>
<td>803</td>
<td>19.3</td>
<td>Natural</td>
<td>95</td>
<td>1-5</td>
<td>4</td>
<td>-</td>
<td>Trace</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3-5 non-condensable</td>
<td>Not specified</td>
<td>Not specified</td>
</tr>
<tr>
<td>Weyburn</td>
<td>Dakota Gasification Company</td>
<td>328</td>
<td>5</td>
<td>Natural</td>
<td>96</td>
<td>0.7</td>
<td>&lt;300 ppm</td>
<td>20 ppm</td>
<td>-</td>
<td>2.3</td>
<td>&lt;70 ppm</td>
<td>-</td>
<td>-</td>
<td>0.5-2.0 total hydrocarbons</td>
<td>Not specified</td>
<td>Not specified</td>
</tr>
<tr>
<td>Jackson Dome</td>
<td>Denbury Resources</td>
<td>295</td>
<td>n/a</td>
<td>Natural</td>
<td>98.7-99.4</td>
<td>0.3</td>
<td>0.3</td>
<td>9000 ppm</td>
<td>-</td>
<td>3-5 non-condensable</td>
<td>Not specified</td>
<td>-</td>
<td>-</td>
<td>Not specified</td>
<td>Not specified</td>
<td>418 ppm</td>
</tr>
<tr>
<td>Sleipner</td>
<td>Statoil</td>
<td>153</td>
<td>0.7</td>
<td>Separation from Natural Gas</td>
<td>93-96</td>
<td>3-5 non-condensable</td>
<td>3-5 non-condensable</td>
<td>-</td>
<td>-</td>
<td>Not specified</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Not specified</td>
<td>Not specified</td>
<td>50 ppm</td>
</tr>
<tr>
<td>Snohvit</td>
<td>Statoil</td>
<td>160</td>
<td>1</td>
<td>Separation from Natural Gas</td>
<td>Not specified</td>
<td>Not specified</td>
<td>Not specified</td>
<td>-</td>
<td>-</td>
<td>Not specified</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Not specified</td>
<td>Not specified</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 2: Typical performance values for removal of flue gas components by \( \text{SO}_x \), \( \text{NO}_x \) and \( \text{CO}_2 \) control systems – adapted from Lee et al.\cite{10} and Cole et al.\cite{32}

<table>
<thead>
<tr>
<th>Contaminants</th>
<th>( \text{SO}_2 )</th>
<th>( \text{SO}_3 )</th>
<th>( \text{NO}_2 )</th>
<th>( \text{HCl} )</th>
<th>( \text{Hg}^{2+} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>No contaminant control</td>
<td>0.6-4.4 wt.%</td>
<td>42-579 ppm</td>
<td>24-111 ppm</td>
<td>36-835 ppm</td>
<td>23-261 ppm</td>
</tr>
<tr>
<td>( \text{SO}_2 ) control by a wet FGD scrubber</td>
<td>337-2403 ppm</td>
<td>21-302 ppm</td>
<td>18-87 ppm</td>
<td>2-44 ppm</td>
<td>2-27 ppm</td>
</tr>
<tr>
<td>( \text{NO}_x ) control by LNB/SCR</td>
<td>0.6-4.4 wt.%</td>
<td>42-579 ppm</td>
<td>10-44 ppm</td>
<td>36-835 ppm</td>
<td>23-261 ppm</td>
</tr>
<tr>
<td>( \text{NO}_x ) control by LNB/SCR plus ( \text{SO}_2 ) control by a wet FGD scrubber</td>
<td>337-2403 ppm</td>
<td>21-302 ppm</td>
<td>7-35 ppm</td>
<td>2-44 ppm</td>
<td>2-27 ppm</td>
</tr>
<tr>
<td>( \text{NO}_x ) control by LNB/SCR plus ( \text{SO}_2 ) control by a wet FGD scrubber, and also assuming MEAS-based ( \text{CO}_2 ) control unit is used to trap ( \text{CO}_2 )</td>
<td>34-135 ppm</td>
<td>(&lt;(21-302)) ppm</td>
<td>(&lt;(7-35)) ppm</td>
<td>(&lt;(2-44)) ppm</td>
<td>(&lt;(2-27)) ppb</td>
</tr>
</tbody>
</table>

Note: FGD = flue gas desulphurisation, LNB = low \( \text{NO}_x \) burner, SCR = selective catalytic reduction

Table 3: Elemental composition of X65 steel (wt. %)

<table>
<thead>
<tr>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Mo</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.12</td>
<td>0.18</td>
<td>1.27</td>
<td>0.008</td>
<td>0.002</td>
<td>0.11</td>
<td>0.17</td>
<td>0.07</td>
</tr>
<tr>
<td>Cu</td>
<td>Sn</td>
<td>Al</td>
<td>B</td>
<td>Nb</td>
<td>Ti</td>
<td>V</td>
<td>Fe</td>
</tr>
<tr>
<td>0.12</td>
<td>0.008</td>
<td>0.022</td>
<td>0.0005</td>
<td>0.054</td>
<td>0.001</td>
<td>0.057</td>
<td>Balance</td>
</tr>
</tbody>
</table>
Table 4: DYNAMIS CO₂ quality recommendations and Alstom CO₂ quality tolerances (the reasons behind each limitation is also provided)

<table>
<thead>
<tr>
<th>Component</th>
<th>DYNAMIC CO₂ quality recommendations (adapted from de Visser et al.[7])</th>
<th>Alstom CO₂ quality tolerances (adapted from Dugstad et al.[15])</th>
<th>Concentration Limit</th>
<th>Reason for Limit</th>
<th>Low Limit</th>
<th>High Limit</th>
<th>Reason for Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>Balanced with other compounds in CO₂</td>
<td>&gt;9% vol.%</td>
<td>Low – Storage requirement</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>&gt;90% vol.% (storage)</td>
<td>High – EOR requirement</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>&gt;95% vol.% (EOR)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N₂/Ar/ H₂</td>
<td>&lt; 4 vol.%</td>
<td>As proposed in ENCAP</td>
<td>&lt;4 vol.%</td>
<td>EOR requirement</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O₂</td>
<td>Aquifer &lt; 4 vol.%, EOR 100 – 1000 ppm</td>
<td>Technical: range for EOR due to lack of practical experiments on effect of O₂ under ground</td>
<td>&lt;10 ppm</td>
<td>&lt;1000 ppm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₄</td>
<td>Aquifer &lt; 4 vol.%, EOR &lt; 2 vol. %</td>
<td>As proposed in ENCAP</td>
<td>&lt;4%</td>
<td>EOR requirement</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td>500 ppm</td>
<td>Technical: below solubility limit of H₂O in CO₂. No significant cross effect of H₂O and H₂S, cross effect of H₂O and CH₄ is significant but within limits for water solubility.</td>
<td>&lt;10 ppm</td>
<td>&lt;600 ppm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂S</td>
<td>200 ppm</td>
<td>Health and Safety</td>
<td>&lt;10 ppm</td>
<td>&lt;15000 ppm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>2000 ppm</td>
<td>Health and Safety</td>
<td>&lt;100 ppm</td>
<td>&lt;40000 ppm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO₂</td>
<td>100 ppm</td>
<td>Health and Safety</td>
<td>&lt;100 ppm</td>
<td>&lt;1500 ppm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NOₓ</td>
<td>100 ppm</td>
<td>Health and Safety</td>
<td>&lt;100 ppm</td>
<td>&lt;1500 ppm</td>
<td></td>
<td></td>
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</table>
Table 5: Test matrix for corrosion experiments

<table>
<thead>
<tr>
<th>Water-saturated CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Temperature (°C)</strong></td>
</tr>
<tr>
<td>35</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Under-saturated CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Temperature (°C)</strong></td>
</tr>
<tr>
<td>35</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>
Figure 1: Schematic of autoclave setup

Figure 2: Corrosion rates of X65 carbon steel in under-saturated and water-saturated CO\(_2\) phase at 80 bar and 35°C over an exposure time of 48 hours. SO\(_2\) in the gas phase is varied from 0 to 100 ppm. Data is presented on (a) a logarithmic scale and (b) a continuous scale.
Figure 3: SEM images of the X65 corroded samples exposed to under-saturated and water-saturated CO$_2$ at 35°C and 80 bar for 48 hours in the presence of various concentrations of impurities; (a)-(c) 0 ppm SO$_2$ and 0 ppm O$_2$ in the presence of 700, 1770 and 3437 ppm (water-saturated) water, respectively; (d)-(f) 50 ppm SO$_2$ and 20 ppm O$_2$ in the presence of 700, 1770 and 3437 ppm (water-saturated) water, respectively; (g)-(i) 100 ppm SO$_2$ and 20 ppm O$_2$ in the presence of 700, 1770 and 3437 ppm (water-saturated) water, respectively.
Figure 4: XRD spectra of samples exposed to water-saturated CO\textsubscript{2} phase at 35°C and 80 bar containing different concentration levels of SO\textsubscript{2} (0, 50 and 100 ppm) and O\textsubscript{2} (0 and 20 ppm) impurities.

Figure 5: Raman spectra of samples exposed to water-saturated supercritical CO\textsubscript{2} phase at 35°C and 80 bar containing 100 ppm SO\textsubscript{2} and 20 ppm O\textsubscript{2}. Areas scanned on the steel surface are representative of those depicted in Figure 3(i).
Figure 6: Example profilometry images of X65 steel surfaces after removal of corrosion products (a) 0 ppm SO$_2$, 0 ppm O$_2$, 1770 ppm water, (b) 0 ppm SO$_2$, 0 ppm O$_2$, water-saturated, (c) 50 ppm SO$_2$, 20 ppm O$_2$, 1770 ppm water, (d) 50 ppm SO$_2$, 20 ppm O$_2$, water-saturated, (e) 100 ppm SO$_2$, 20 ppm O$_2$, 1770 ppm water, (f) 100 ppm SO$_2$, 20 ppm O$_2$, water-saturated. All tests were performed at 35°C and 80 bar for 48 hours in supercritical CO$_2$.
Figure 7: Pitting corrosion rates of X65 carbon steel in under-saturated and water-saturated CO$_2$ phase at 80 bar and temperature of 35°C for an exposure time of 48 hours. SO$_2$ in the gas phase is varied from 0 to 100 ppm. Data is presented on (a) a logarithmic scale and (b) a continuous scale.
Figure 8: Surface plots to indicate the variation of (a) general and (b) pitting/localised corrosion rates as a function of SO$_2$ and water content. All tests were performed at 35 °C and 80 bar.
Figure 9: Critical water content at which 0.1 mm/year corrosion rate is reached from the perspective of general and localised corrosion for X65 steel. Conditions are 35°C and 80 bar in supercritical CO₂ for 48 hours.
Figure 10: (a) General corrosion rate and rate of consumption of (b) $\text{SO}_2$ and (c) water under different conditions at 80 bar and 35°C.