Corrosion behaviour of X65 steels in water-containing supercritical CO₂ environments with NO₂/O₂

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ABSTRACT

Corrosion experiments were performed on X65 carbon steel in water-saturated supercritical CO₂ (SC-CO₂) and under-saturated SC-CO₂ conditions at 80 bar and 35°C in the absence and presence of various combinations of NO₂ and O₂ ranging from 0-100 ppm and 0-1000 ppm, respectively. The purpose of the experiments was to understand the implications of the presence of these two species on both general and localized corrosion in likely conditions encountered during CO₂ transport.

The presence of 100 ppm NO₂ and 1000 ppm O₂ in water-saturated SC-CO₂ resulted in general corrosion rates reaching 0.3 mm/year after 48 hours and a localized corrosion rate of 6.8 mm/year, compared to 0.1 and 0.92 mm/year, respectively in the absence of both species. The final stages of testing considered corrosion rates in under-saturated SC-CO₂ with 100 ppm NO₂ and 1000 ppm O₂ at water contents between 0 and 1770 ppm. Although no corrosion occurred in dry conditions, increasing water concentration from 300 to 1770 ppm resulted in the general corrosion rates rising from 0.05 to 0.68 mm/year. However, there was no significant difference in the extent of localized corrosion observed with changing water content over this range, with values ranging between 0.5 and 0.6 mm/year.

Key words: corrosion, NO₂, O₂
INTRODUCTION

The corrosion in carbon steel pipelines transporting anthropogenic CO$_2$ from large sources has received considerable attention from many researchers.\textsuperscript{1, 2, 3, 4, 5, 6} The possible presence of contaminants such as O$_2$, SO$_x$ and NO$_x$ in the CO$_2$ stream can influence and potentially accelerate the corrosion process.\textsuperscript{1, 2, 3, 7, 8, 9, 10, 11, 12} Although carbon steels is a common and cost-effective pipeline material, it is highly susceptible to attack by corrosive impurities such as H$_2$O, CO$_2$, SO$_2$ and O$_2$.

With reference to literature within this subject area, most research efforts have been directed towards understanding the corrosion behaviour of X65 in dense phase CO$_2$ containing combinations of water, SO$_2$ or O$_2$ as impurities. Studies considering the effect of NO$_2$ individually or combined with O$_2$ on the corrosion behaviour of carbon steel in dense phase environments are rare and results have only been considered by a limited number of researchers.\textsuperscript{2, 9, 13} The purpose of this work is to determine the susceptibility of UNS G15130 steels to water-containing supercritical CO$_2$ environments in the presence of NO$_2$ (50 or 100 ppm) and O$_2$ (1000 ppm) by measuring the general corrosion rates through the implementation of the weight loss method and surface profilometry to quantify the localized corrosion behaviour. Focus is directed towards three key areas; synergistic effects of NO$_2$ and O$_2$ in water-saturated conditions, the effects of solution replenishment on the corrosion rates determined in autoclave experiments, and the influence of water content in under-saturated conditions. A combination of Scanning Electron Microscopy (SEM), Raman spectroscopy and X-Ray Diffraction (XRD) is also implemented to understand the morphological and compositional changes in the corrosion products produced in the presence of NO$_2$ and O$_2$.

EXPERIMENTAL PROCEDURE

Test specimens were machined from carbon steel (UNS G15130) bar into discs with diameter of 25 mm and thickness of 6 mm. The chemical composition of the steel is provided in Table 1. Surface preparation consisted of wet-grinding the entire sample with up to 800 grit silicon carbide (SiC) 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 required 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.

<table>
<thead>
<tr>
<th>Element</th>
<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>C</td>
<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>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>

A schematic representation of the experimental system layout has been shown in a previous paper.\textsuperscript{14} The entire system consists of a 1 liter capacity autoclave, temperature controller, a CO$_2$/NO$_2$/O$_2$ mixed cylinder, a liquid CO$_2$ cylinder and a series of valves for CO$_2$ flow control. All tests were conducted in static conditions in either water-saturated supercritical CO$_2$, or with the water content below the calculated solubility limit (under-saturated) based on the work of Spycher et al.,\textsuperscript{15} (i.e. the saturated water concentration in supercritical CO$_2$ at 35°C and 8 MPa is 3437 ppm (in
mole)). In order to ensure the water-saturated CO\textsubscript{2} condition, 34000 ppm of water was introduced to the bottom of the autoclave (not in direct contact with the sample and approximately 10 times the saturation limit). Replenishment of the test fluid was achieved by releasing the solution from the autoclave and replacing the exact initial CO\textsubscript{2}/NO\textsubscript{2}/O\textsubscript{2}/H\textsubscript{2}O mixture within the autoclave. This required de-pressurizing the system and re-pressurizing).

In terms of the autoclave operating procedure, distilled water was initially de-aerated by saturating the solution with CO\textsubscript{2} in a separate container for a minimum of 12 hours prior to testing. All 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, CO\textsubscript{2}-saturated water was then delivered into the bottom of the autoclave at ambient pressure and temperature and sealed. All lines to the autoclave were then purged with CO\textsubscript{2} and evacuated to ensure the removal of initial traces of O\textsubscript{2} within the system. The required technical grade of CO\textsubscript{2}/O\textsubscript{2}/NO\textsubscript{2} mixture and liquid CO\textsubscript{2} was then transferred into the autoclave, heated and then pressurized to the correct temperature and pressure. The starting point of the test was taken from the time at which the autoclave reached the required temperature and pressure (35°C and 8 MPa in this particular study).

At the end of each experiment, 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\textsuperscript{1} Standard G1-03. This was followed by rinsing the samples with distilled water and 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 using Equation (1):

$$V_c = \frac{876000\Delta m}{\rho A t}$$

where $V_c$ is the corrosion rate of the sample in mm/year, $\Delta m$ is the mass loss in grams, $\rho$ is the density of the sample in g/cm\textsuperscript{3}, $A$ is the exposed area in cm\textsuperscript{2} and $t$ is the immersion time in hours.

Profilometry measurements were performed on samples after cleaning (scanning a 3 x 3 mm\textsuperscript{2} area at a time) using a NP\textsubscript{FLEX} 3D Surface Metrology System to quantify localized attack. The objective used was 2.5x with approximately a 3.5 mm working distance. The pit depth analysis was conducted in alignment with ASTM\textsuperscript{1} Standard G46- 94.\textsuperscript{17} The standard stipulates that an average of the 10 deepest pits should be used for pit damage characterization of the sample area. In some instances, samples were not cleaned with Clarke’s solution and kept for analysis using either Scanning Electron Microscopy (SEM), Raman Spectroscopy or X-ray Diffraction (XRD).

As mentioned, three different stages of experimental tests were conducted. These comprised the following conditions:

- Stage 1: Examining the effect of individual impurities in the water-saturated environment (0-100 ppm NO\textsubscript{2} and 0-1000 ppm O\textsubscript{2} for 48 h)
- Stage 2: The process fluid replenishment (50 or 100 ppm NO\textsubscript{2} with 1000 ppm O\textsubscript{2} for 96 h with replenishment after 48 h)
- Stage 3: Under-saturated tests (water content from 0 – 1770 ppm in the presence of 100 ppm NO\textsubscript{2} and 1000 ppm O\textsubscript{2} for 48 h)

\textsuperscript{1} ASTM International, 100 Barr Harbor Drive, West Conshohocken, PA 19428-2959.
The entire matrix of the experimental conditions for these three stages are provided in Table 2, 3 and 4. Table 2 (stage 1) studies the samples were exposed to water-saturated SC-CO\(_2\) with various concentrations of NO\(_2\) and O\(_2\) (either separately or combined).

The matrix of the experiments for stage 2 is provided in Table 3. For these tests, the sample was exposed to water-saturated CO\(_2\) environment in the presence of different concentrations of 50 or 100 ppm NO\(_2\) and 1000 ppm O\(_2\) as these were the most severe conditions encountered in the first stage of testing.

The final stage of testing considers the effect in the presence of 100 ppm NO\(_2\) and 1000 ppm O\(_2\) in an effort to determine the water content threshold required to avoid corrosion. For these series of tests, the last matrix of the experimental conditions is provided in Table 4. In these experiments the sample was exposed to under-saturated supercritical CO\(_2\) conditions in the presence of 100 ppm NO\(_2\) and 1000 ppm O\(_2\) with water contents controlled at 1770, 1200, 650, 300 and 0 ppm. Baseline tests were also performed in the absence of NO\(_2\) and O\(_2\).

### Table 2: Test matrix for studying the effect of individual impurity corrosion tests

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Pressure (MPa)</th>
<th>NO(_2) ppm</th>
<th>O(_2) ppm</th>
<th>H(_2)O (ppm (mole))</th>
<th>Materials</th>
<th>Immersion time (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>8</td>
<td>0</td>
<td>0</td>
<td>Water-saturated</td>
<td>X65</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>0</td>
<td>(34000 ppm water</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>100</td>
<td>0</td>
<td>added into the</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0</td>
<td>1000</td>
<td>autoclave)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>1000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>100</td>
<td>1000</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table 3: Test matrix for replenished solution corrosion tests

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Pressure (MPa)</th>
<th>H(_2)O (ppm (mole))</th>
<th>NO(_2) (ppm (mole))</th>
<th>O(_2) (ppm (mole))</th>
<th>Immersion time (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>80</td>
<td>Water-saturated</td>
<td>50</td>
<td>1000</td>
<td>96</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(34000 ppm water</td>
<td>(mole))</td>
<td>(mole))</td>
<td>Total Replenishment</td>
</tr>
<tr>
<td></td>
<td></td>
<td>added into the</td>
<td></td>
<td></td>
<td>time</td>
</tr>
<tr>
<td></td>
<td></td>
<td>autoclave)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1000</td>
<td></td>
<td></td>
<td>Not replenished</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Replenished after</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>48 hours</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Not replenished</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Replenished after</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>48 hours</td>
</tr>
</tbody>
</table>

### Table 4: Test matrix for under-saturated corrosion tests

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Pressure (MPa)</th>
<th>NO(_2) ppm</th>
<th>O(_2) ppm</th>
<th>H(_2)O ppm</th>
<th>Materials</th>
<th>Immersion time (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>80</td>
<td>0</td>
<td>0</td>
<td>1770</td>
<td>X65</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100</td>
<td>0</td>
<td>1200</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>650</td>
<td>300</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>300</td>
<td>0</td>
<td></td>
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</tbody>
</table>
RESULTS

Stage 1: The effect of individual and combined impurities on the corrosion behavior of carbon steel in water-saturated SC-CO$_2$ environments

Figure 1 provides the general corrosion rate and the profilometry measurements (in the form of a localized corrosion rate) extracted from the samples exposed to the water-saturated CO$_2$ environment at 35°C and 8 MPa with various concentrations of NO$_2$ and O$_2$ present in the system for 48 h. The localized corrosion rates are based on the top 10 deepest surface pits, identified in alignment with ASTM Standard G46-94.$^{17}$

The general corrosion rate averaged 0.10 mm/year for samples exposed to the water-saturated environment in the absence of NO$_2$ and O$_2$, which can be considered as a baseline measurement. The addition of 50 and 100 ppm NO$_2$ only increased the corrosion rate to 0.17 and 0.23 mm/year, respectively. The introduction of 1000 ppm O$_2$ (no NO$_2$) reduced the general corrosion rate from the baseline test to 0.03 mm/year. The addition of both 50/100 ppm NO$_2$ and 1000 ppm O$_2$ increased the general corrosion rate in the system to around 0.29 and 0.30 mm/year, indicating that NO$_2$ can have an effect on the corrosion kinetics, even at low concentrations of 50 and 100 ppm. The results also indicate a notable synergistic effect between NO$_2$ and O$_2$ as the general corrosion rate in the presence of both species is greater than the sum of the corrosion rates when both are present individually.

![Image](image_url)

Figure 1: Average general corrosion and pitting rates of X65 carbon steel in water-saturated supercritical CO$_2$ environments containing varying concentrations of NO$_2$ and O$_2$ at 35°C and 8 MPa for 48 hours

$^{1}$ ASTM International, 100 Barr Harbor Drive, West Conshohocken, PA 19428-2959.
Figure 2: 2D profilometry images of X65 carbon steel exposed to water-saturated supercritical CO₂ environments containing varying concentrations of NO₂ and O₂ at 35°C and 8 MPa for 48 hours (a) 0 ppm NO₂ and 0 ppm O₂, (b) 50 ppm NO₂ and 0 ppm O₂, (c) 100 ppm NO₂ and 0 ppm O₂, (d) 0 ppm NO₂ and 1000 ppm O₂ and (e) 100 ppm NO₂ and 1000 ppm O₂

In terms of the localized corrosion rates, the penetration from pitting or localized attack is over one order of magnitude greater than the general corrosion rates calculated through the implementation of
mass loss measurements. Examples of the profilometry images extracted are provided in Figure 2. The most severe localized attack was when NO₂ and O₂ were combined at a concentration of 100 ppm and 1000 ppm, respectively. This produced a penetration rate of 6.8 mm/year compared to 0.9 mm/year in the absence of both NO₂ and O₂.

Figure 3 provides the SEM images of the sample surfaces exposed to water-saturated supercritical CO₂ environments containing different levels of NO₂ and O₂ after 48 hours. In each instance the steel surface was found to be locally covered by various corrosion products. Figure 4 indicates the XRD patterns acquired through scans of over 1 cm² in area from each sample surface.

In the absence of NO₂ and O₂ in the system, the surface of the steel was locally covered by large, cubic crystals (Figure 3(a)) which were identified as FeCO₃ based on the XRD pattern shown in Figure 4. The addition of 1000 ppm O₂ inhibited the formation of crystalline FeCO₃ and formed an amorphous layer as shown in Figure 3(b). This layer mainly comprised of iron oxides and hydroxides which was identified in a previous study through the implementation of X-ray Photoelectron Spectroscopy (XPS).¹⁴

Addition of solely 50 or 100 ppm NO₂ changed the morphology of FeCO₃ and produced a corrosion product layer consisting of a large number of voids, as shown in Figure 3(c) for 100 ppm NO₂. Finally, the introduction of both 50 or 100 ppm NO₂ with 1000 ppm O₂ resulted in the formation of FeCO₃ covered by an amorphous top layer.

Figure 3: SEM images of surface morphology of corrosion products formed on X65 exposed to water-saturated CO₂ at 35°C and 8 MPa after 48 hours for various impurities concentration (a) only water, (b) 1000 ppm O₂, (c) 100 ppm NO₂ and (d) 100 ppm NO₂ and 1000 ppm O₂.
Stage 2: Effect of replenishing impurities in water-saturated CO\textsubscript{2} conditions

Another issue associated with experiments in closed vessels with low impurity concentrations is that significant levels of depletion (resulting in lower corrosion rates being observed) can occur in the system over the course of the experiment. To investigate the effect of impurity depletion, a series of tests were performed over 96 h in which the solution was or was not replenished.

The general and localized corrosion rates for the second stage of testing are provided in Figure 5 to indicate the effect of impurity replenishment. It is clear that replenishing the NO\textsubscript{2} and O\textsubscript{2} results in increased general corrosion rates. For the system containing 50 ppm NO\textsubscript{2} and 1000 ppm O\textsubscript{2}, general corrosion rates increased from 0.17 to 0.26 mm/year by replenishing the solution, and the general corrosion rate in the system containing 100 ppm NO\textsubscript{2} and 1000 ppm O\textsubscript{2} increased by 40% from 0.19 to 0.32 mm/year. However, the localized corrosion rates showed no significant change as a result of renewing the solution. The localized corrosion rates provided in Figure 5 are approximately 3.1-3.3 mm/year in the presence of 50/100 ppm NO\textsubscript{2} and 1000 ppm O\textsubscript{2}. This also indicates that, when compared with the localized corrosion rates after 48 h in Figure 1 under the same test conditions that the local penetration rate reduces markedly over the 96 h test duration. Example profilometry images are again provided in Figure 6 which show the high degree of localized attack.

Figure 4: XRD patterns of X65 steel samples after exposure to water-saturated supercritical CO\textsubscript{2} phase at 35°C and 8 MPa containing different concentrations of NO\textsubscript{2} and O\textsubscript{2}
Figure 5: Average general corrosion and pitting rates of X65 carbon steel in the water-saturated CO\textsubscript{2} phase at 8 MPa and 35°C for an exposure time of 96 hours, containing NO\textsubscript{2} (50 and 100 ppm) and 1000 ppm O\textsubscript{2}, with and without impurity replenishment every 48 hours.

Figure 6: 2D profilometry images of X65 carbon steel exposed to water-saturated supercritical CO\textsubscript{2} environments at 35°C and 8 MPa for 96 hours with or without replenishing solution after 48 hours containing (a) 100 ppm NO\textsubscript{2} and 1000 ppm O\textsubscript{2} – solution not replenished (b) 100 ppm NO\textsubscript{2} and 1000 ppm O\textsubscript{2} – solution replenished.
The morphology and the level of visible corrosion product formed on the surface are similar with or without replenishing the impurities. Figure 7 shows an example of the SEM images for samples exposed to water-saturated supercritical CO₂ environments with replenishing 100 ppm NO₂ and 1000 ppm O₂ over 96 hours. It is interesting to note that the corrosion product are not uniformly distributed and the localized attack was clearly observed on the surface.

The XRD pattern of the samples exposed to the second stage of test environments is provided in Figure 8. A slight reduction in intensity for FeCO₃ was observed as a result of replenishing the impurities. The reduced intensity for FeCO₃ might indicate a lower quantity of FeCO₃ on the surface for the sample exposed to the replenished impurity and also suggest that the NO₂ and O₂ together can inhibit the formation of crystalline FeCO₃ on the surface, either due to increasing acidity of the condensed solution on the surface (as in the case of NO₂), or through oxidising ferrous ions into ferric ions (as in the case of O₂).²

![Figure 7: SEM images of surface morphology of corrosion products formed on X65 exposed to water-saturated CO₂ at 35°C and 8 MPa for 96 hours with replenishing 100 ppm NO₂ and 1000 ppm O₂ after 48 hours.](image)
Figure 8: XRD patterns of samples exposed to water-saturated supercritical CO\(_2\) phase at 35°C and 8 MPa for 96 hours with and without replenishing 50/100 ppm of NO\(_2\) and 1000 ppm of O\(_2\) after 48 hours.

Stage 3: Evaluation of general and localized corrosion in under-saturated CO\(_2\) conditions for 100 ppm NO\(_2\) and 1000 ppm O\(_2\)

When water is present in a SC-CO\(_2\) system, either water-saturated conditions are created when the water content is above the solubility limit or the dense phase is under-saturated with water when the water content is below the solubility limit. One of the critical factors which influences the level of corrosion observed in an under-saturated system is the dissolved water content. Considering the conditions during the transport of CO\(_2\) in pipelines, operators tend to dehydrate the CO\(_2\) stream to specified levels below the solubility of water prior to transport. Therefore, it is also important to study the corrosion behaviour of X65 when exposed to under-saturated conditions in the supercritical CO\(_2\) phase. This stage of testing considers this effect in the presence of 100 ppm NO\(_2\) and 1000 ppm O\(_2\) in an effort to determine the water content threshold required to avoid corrosion. For these series of tests, the last matrix of the experimental conditions is provided in Table 4. In these experiments the sample was exposed to under-saturated supercritical CO\(_2\) conditions in the presence of 100 ppm NO\(_2\) and 1000 ppm O\(_2\) with water contents controlled at 1770, 1200, 650, 300 and 0 ppm. Baseline tests were also performed in the absence of NO\(_2\) and O\(_2\).
The measured general and localized corrosion rates of X65 when exposed to the under-saturated conditions at 35°C and 8 MPa in the presence of 100 ppm NO₂/1000 ppm O₂ and 0 ppm NO₂/0 ppm O₂ are provided in Figure 9. For both environments, no measureable general and localized corrosion was recorded in dry conditions, while general and localized corrosion rates were 0.05 and 0.51 mm/year at a water content of 300 ppm for the 100 ppm NO₂/1000 ppm O₂ solution, respectively. In contrast to the tests without NO₂ and O₂, general corrosion rates were below 0-0.005 mm/year and no localized corrosion could be identified on the surface. This shows that a higher water content can be tolerated by the pure SC-CO₂ system compared to the system with NO₂ and O₂ impurities.

Figure 9: Average general corrosion rate and pitting corrosion rates of X65 carbon steel in under-saturated CO₂ phase at 8 MPa and temperature of 35°C for an exposure time of 48 hours in the presence of 100 ppm NO₂ and 1000 ppm O₂. Data is presented on (a) general corrosion rate and (b) localized corrosion rate.
Figure 10: SEM images of surface morphology of corrosion products formed on X65 exposed to under-saturated CO$_2$ at 35°C and 8 MPa after 48 hours in the presence of 100 ppm NO$_2$ and 1000 ppm O$_2$ (a) 1770 ppm, (b) 1200 ppm, (c) 650 ppm, (d) 300 ppm and (e) 0 ppm.

For the 100 ppm NO$_2$/1000 ppm O$_2$ system, the general corrosion rates increased from 0.05 mm/year to 0.68 mm/year as the water content rose from 300 ppm to 1770 ppm. However, the localized corrosion rate over this range did not change significantly averaging ~0.5 m/year, significantly lower than that recorded in the water-saturated system in Figure 1 by comparison.

SEM images of the sample surfaces provided in Figure 10 corroborate with the mass loss measurements in terms of the extent of corrosion product agreeing with the measured mass loss. For these experiments, the corrosion product was confirmed as Fe(NO$_3$)$_3$ according to the Raman measurements as shown in Figure 11. This suggests that the presence of NO$_2$ permits the formation of nitric acid within the condensed aqueous phase.

**The influence of NO$_2$ and O$_2$ on corrosion product formation**

Based on the collected XRD and Raman spectra from the steel surface in the collective presence and absence of NO$_2$ and O$_2$, it appears that two different corrosion products are predominately detected for water-saturated or under-saturated conditions.

For water-saturated environments, the XRD patterns showed only FeCO$_3$ crystals in the absence of 0 ppm NO$_2$ and 0 ppm O$_2$. The morphology of FeCO$_3$ crystals changed from cubic to globular through the addition of 50/100 ppm NO$_2$. Raman spectroscopy was used to provide the localized form of corrosion...
product analysis. The results showed the corrosion products are mainly FeCO$_3$ in the presence of 50 or 100 ppm NO$_2$ with or without 1000 ppm O$_2$.

![Figure 11: Raman spectra of samples exposed to (a) water-saturated and (b) under-saturated supercritical CO$_2$ phase at 35°C and 8 MPa containing 100 ppm NO$_2$ and 1000 ppm O$_2$. Areas scanned on the steel surface are representative of those depicted in (A).](image)

For under-saturated environments, in the system containing 100 ppm NO$_2$ and 1000 ppm O$_2$, no FeCO$_3$ crystals were detected by XRD or Raman. Instead the presence of Fe(NO$_3$)$_3$ was detected (peaks at 430 cm$^{-1}$, 720 cm$^{-1}$ and 1053 cm$^{-1}$ in Figure 11) and fully covered the entire steel surface. The possible reactions can be described by the following reactions:

The presence of CO$_2$ and NO$_2$ is believed to dissolve into the water rich phase to form carbonic acid and nitric acid which dissociated via the following reactions:
The possible cathodic reactions included the reduction of hydrogen ions (produced from both carbonic and nitric acid) and the reduction reaction of O$_2$ can accelerate the cathodic reactions:

\begin{align*}
H_2O + 3NO_2 &\rightarrow NO + 2HNO_3 \\
HNO_3 &\rightarrow H^+ + NO_3^- \\
CO_2 + H_2O &\rightarrow H_2CO_3 \\
H_2CO_3 + 2e^- &\rightarrow H_2 + 2HCO_3^- \\
2HCO_3^- + 2e^- &\rightarrow H_2 + 2CO_3^{2-}
\end{align*}

FeCO$_3$ and Fe(NO$_3$)$_3$ can then form via their respective precipitation processes:

\begin{align*}
Fe^{2+} + CO_3^{2-} &\rightarrow FeCO_3 \\
Fe^{3+} + 3NO_3^- &\rightarrow Fe(NO_3)_3
\end{align*}

Sun et al.,$^9$ suggested that Fe(NO$_3$)$_3$ may exist as an unstable corrosion product and can facilitate the formation of iron oxide (Fe$_2$O$_3$) via the following reaction. However, this cannot be confirmed in this study:

\begin{equation}
4Fe(NO_3)_3 \rightarrow 2Fe_2O_3 + 12NO_2 + 3O_2
\end{equation}

However, the results here corroborate with Sun et al.,$^9,^{10}$ given the detection of FeCO$_3$ and Fe(NO$_3$)$_3$ despite their experiments being performed at much higher O$_2$ and NO$_2$ contents. In their tests, Fe(NO$_3$)$_3$ and Fe$_2$O$_3$ were reported to have formed on X65 in the presence of 1000 ppm NO$_2$ and 1000 ppm O$_2$ after 72 hours exposure time. However, Fe$_2$O$_3$ was not observed in this study possibly due to the lower NO$_2$ content (100 ppm). The results here also suggest that a noticeable synergy exists between the two species resulting in the slight enhancement of the rate of material dissolution, particularly at undersaturated conditions.

**CONCLUSIONS**

The research presented has focused towards quantifying the extent of the general corrosion and localized corrosion of X65 carbon steel in 3 different environments: water-saturated, replenished solution and under-saturated supercritical CO$_2$ environments containing various levels of nitrogen oxide (NO$_2$) and oxygen (O$_2$), representative of dense phase anthropogenic carbon dioxide (CO$_2$) transport. Tests were conducted at a pressure of 8 MPa and a temperature of 35°C for 48 hours in an effort to understand carbon steel performance/susceptibility, but also to identify the potential synergistic effect between NO$_2$ and O$_2$. From this study the following conclusions can be made:

- In water-saturated conditions containing various levels of NO$_2$ and O$_2$, general corrosion rates of carbon steel was 0.1 mm/year in the absence of NO$_2$ and O$_2$. The general corrosion rate of carbon steel increased from 0.1 to 0.3 mm/year by addition of 100 ppm NO$_2$ and 1000 ppm O$_2$.
- In water-saturated conditions containing 50 or 100 ppm NO$_2$ and 1000 ppm O$_2$, the highest localized corrosion rates with ranged between 6.6 and 6.8 mm/year. The localized corrosion
rates were over one order of magnitude higher than the general corrosion rates in all the environments, with a noticeable synergistic effect being observed between NO$_2$ and O$_2$ in terms of enhancing the localized dissolution of carbon steel.

- General corrosion rates increased with the replenishment of the process fluids, although the localized corrosion rates showed no significant change as a result of replacing the test solution.
- In under-saturated conditions containing 100 ppm NO$_2$ and 1000 ppm O$_2$, the general corrosion rates increased from 0 to 0.68 mm/year as the water content was increased from 0 to 1770 ppm. However, the localized corrosion rate was not influenced significantly by water content variation providing the water content was below the solubility limit.
- The formation of iron nitrate (Fe(NO$_3$)$_3$) as well as iron carbonate (FeCO$_3$) was detected on the steel surface in systems containing NO$_2$ and O$_2$, suggesting that NO$_2$ permits the formation of nitric acid within the condensed aqueous phase on the steel surface.

ACKNOWLEDGEMENTS
Special thanks go to Johnston Shaun from Wood Group Kenny and Alex Hunt from WOODVIEW Technology for their invaluable advice. This research was financially supported by innovate UK.

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