Corrosion in CO\textsubscript{2} transport pipeline

Formation of corrosive phases in dense phase CO\textsubscript{2}

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Bjørn H. Morland
Lillestrøm, October 2019
Summary

Carbon capture and storage is suggested as one of the solutions to reduce CO₂ emissions. Material choice is an important part for the total cost of the transport system for CO₂. Although cost-considerations make carbon steel a clear material candidate for construction of the transportation system, it is important to ensure that the integrity is maintained throughout the lifetime. Corrosion and certain chemical reactions must therefore be avoided. There are many suggested specifications and recommendations for how much impurities (additional components) can be allowed in the CO₂ to be transported, but most of the impurity limits are set from a health safety and environment point of view. Due to lack of data, almost no impurity limits have been set from a material integrity point of view. This gap of knowledge makes it difficult to make a specification that will ensure safe operation.

The present work comprises investigations of corrosive situations which could occur during CO₂ transport, in particular: 1) testing of existing CO₂ specification with the impurities like H₂O, H₂S, O₂, SO₂, and NO₂ at realistic conditions to identify reactions between impurities and verification of upper limits for the mention impurities in CO₂. 2) Determination of nitric and sulfuric acid solubility in CO₂. 3) Corrosion testing with fix concentration of NO₂ or SO₂ with various water concentrations in dense phase CO₂. 4) carbon steel corrosion in water saturated with CO₂, and water dissolved in CO₂, at various at various temperature and pressure. Corrosion flow loops and autoclaves were used for this purpose and effort was made to improve the experimental setup, especially the method to introduce water to the loop.

CO₂ with various combinations and concentrations of impurities were tested in a systematic manner. It was clearly shown that many impurity combinations were basically inert, while other resulted in chemical reactions and some combinations even resulted in formation of a separate aqueous phase that contained high concentrations of sulfuric and nitric acid. This aqueous phase was highly corrosive to carbon steel. Corrosion was also observed in certain situations even if a separate aqueous phase was not observed.

CO₂ with SO₂ (75 ppmv) and O₂ (up to 220 ppmv) is not corrosive if the water concentration is less than 1600 ppmv at 100 bar and 25 °C in CO₂ streams. The same applies for CO₂ with 70 ppmv NO₂ and up to 250 ppmv H₂O. However, corrosion rates as high as 0.57 mm/y was observed for CO₂ with 70 ppmv NO₂ when the water content was increased from 250 to 670 ppmv (100 bar and 25 °C). This
principally different behaviour between CO$_2$ with H$_2$O/SO$_2$/O$_2$ (negligible corrosion) and CO$_2$ with H$_2$O/NO$_2$ (high corrosion rate) has not been fully understood, but it is a good illustration on the need to keep the water content low and that different impurity combinations behave differently.

Testing of CO$_2$ with multiple impurities (H$_2$O, H$_2$S, O$_2$, SO$_2$ and NO$_2$) under realistic pipeline transport conditions showed that nitric and sulfuric acid was formed for impurity concentrations well within existing specifications. Thus, these specifications cannot be accepted for CO$_2$ transportation in carbon steel pipelines. It was furthermore shown that several combinations of the impurities were non-reactive, but reactions started once CO$_2$ streams with H$_2$S and NO$_2$ were mixed. This finding is particularly important for a future situation with a large CO$_2$ transport network where streams from different sources may be mixed in a hub.

When the H$_2$O, H$_2$S, O$_2$, SO$_2$ and NO$_2$ impurities were present together, it resulted in several chemical reactions, and sulfuric and nitric acid formed if the impurity content was high enough. The stochiometric ratio of the consumed components showed that H$_2$S and NO$_2$ reacted and formed SO$_2$, NO and H$_2$O, while O$_2$ reacted with NO and formed NO$_2$ again. Sulfuric acid was produced through the reaction of SO$_2$ and H$_2$O with the help of NO$_2$. Acids were formed at 30 ppmv of H$_2$S, NO$_2$, and SO$_2$, while 5 and 10 ppmv gave chemical reactions but no condensation of acids.

The solubility of nitric acid and sulfuric acid in dense phase CO$_2$ was measured. The solubility of nitric acid (~1000 ppmv) was about 3 order of magnitude higher than the solubility of sulfuric acid (~1 ppmv). The solubility increases slightly with increasing temperature, while pressure has a much larger effect, especially between 1 and 100 bar. The results from the acid solubility in CO$_2$ has been implemented in the OLI thermodynamic model.

The experiments with water as the only impurity in the CO$_2$, showed clearly how the corrosion rate varied 3 to 4 decades depending on the water content. For very high water concentrations, were the water was present as a separate aqueous phase saturated with CO$_2$, the corrosion rate varied from 2 to 24 mm/y. For low water contents, where the water was fully dissolved in the CO$_2$ phase, the corrosion rate was less than 0.002 mm/y. It was also demonstrated how this huge difference in corrosion rate could result in various experimental artefacts. Injection of liquid water at start-up and water condensation during depressurisation can contribute significantly to the total amount corrosion. Thus, these artefacts may give erroneous corrosion rates, particularly for conditions that otherwise have low corrosivity.
Altogether, the present work has identified many important aspects of corrosion and chemical reactions for CO₂ transport. This has resulted in a better understanding of the processes that lead to corrosion. This is important information that is needed for making a CO₂ specification which ensures the integrity of pipelines or ship. The concentration limits of the specification vary with which impurities are present together. It has been shown that the specification must be strict, about 20 ppmv, if all the investigated impurities (H₂O, H₂S, O₂, SO₂, and NO₂) are present together at the same time. The limits can be relaxed if fewer impurities are present, but this needs to be verified experimentally for each impurity combination. Other impurities than those who have been investigated may behave differently.
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### Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>bar</td>
<td>Pressure unit</td>
</tr>
<tr>
<td>CCS</td>
<td>Carbon capture and storage</td>
</tr>
<tr>
<td>CCUS</td>
<td>Carbon capture utilisation and storage</td>
</tr>
<tr>
<td>CR</td>
<td>Corrosion rate</td>
</tr>
<tr>
<td>CRA</td>
<td>Corrosion resistant alloys</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy-dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>HSE</td>
<td>Health safety and environment</td>
</tr>
<tr>
<td>IC</td>
<td>Ion chromatography</td>
</tr>
<tr>
<td>IFE</td>
<td>Institute for Energy Technology</td>
</tr>
<tr>
<td>IPCC</td>
<td>The Intergovernmental panel on climate change</td>
</tr>
<tr>
<td>mm Hg</td>
<td>Pressure unit</td>
</tr>
<tr>
<td>mm/y</td>
<td>Corrosion rate unit: Millimeters per year</td>
</tr>
<tr>
<td>MSE</td>
<td>Mixed-solvent electrolyte</td>
</tr>
<tr>
<td>Mt/y</td>
<td>Flow unit: million tons per year</td>
</tr>
<tr>
<td>MW</td>
<td>Molecular weight</td>
</tr>
<tr>
<td>NETL</td>
<td>National Energy Technology Laboratory</td>
</tr>
<tr>
<td>NORSOK</td>
<td>The Norwegian shelf’s competitive position</td>
</tr>
<tr>
<td>PEEK</td>
<td>Polyether ether ketone</td>
</tr>
<tr>
<td>ppmv</td>
<td>Concentration unit: Parts per million volume</td>
</tr>
<tr>
<td>ppmw</td>
<td>Concentration unit: Parts per million weight</td>
</tr>
<tr>
<td>RH</td>
<td>Relative humidity</td>
</tr>
<tr>
<td>SACROC</td>
<td>Scurry area canyon reef operators</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>μm/y</td>
<td>Corrosion rate unit: micrometers per year</td>
</tr>
</tbody>
</table>
List of publications


Chapter 1

Introduction

1.1 Background

The carbon dioxide (CO₂) concentration in the atmosphere has increased dramatically over the last century, and much of this increase is a direct consequence of the industrial revolution followed by increased emission of flue gases [1]. The Intergovernmental Panel on Climate Change (IPCC) has identified CO₂ as a greenhouse gas which significantly contributes to global warming. There is an international agreement to reduce emission of CO₂ [2], and several initiatives are necessary to achieve this goal. Carbon dioxide capture and storage (CCS) is expected to contribute to about 20% of the total reduction of the CO₂ emission. CCS consist of a capturing plant where CO₂ from flue gasses or industrial processes is trapped, a transportation system and a permanent storage site. Carbon capture, utilisation and storage (CCUS) is basically the same except that the CO₂ is applied to something useful, like production of chemicals of commercial benefit or enhanced oil recovery. CCUS may to some extent make these large investments economically feasible. However, the demand for CO₂ is not high enough to reach the planned capture, so permanent storage is needed. Pipelines and ships are needed for transporting the CO₂ from the capturing plant to the storage site. Ships will be preferred when the distance is long and the volume is low, while pipeline would be used for large volume and shorter distance [3]. Except for very short distances, pipelines of corrosion resistant alloys (CRA) would be too costly. The transportation pipelines will therefore most likely be made of carbon steel and be designed with a long life-time. However, CO₂ can cause corrosion of carbon steel under certain conditions. Having a good understanding of the corrosion processes is therefore a key element in the integrity management of CO₂ transport pipelines.

CO₂ from natural sources has been transported in pipelines for many decades without corrosion problems [4]. Field experience has shown that corrosion is not a problem as long as the CO₂ is dried sufficiently to prevent precipitation of liquid water [4]. However, the CO₂ captured from flue gases is likely to contain additional components like oxygen, nitrogen dioxide, sulfur dioxide, and hydrogen sulfide [5,6]. These species are expected to be present at very low concentrations in the captured CO₂, and they are therefore called impurities in the present work. Even at ppm-levels, these impurities can cause corrosion, and they may introduce dust and solid formation which may lead to
operational difficulties. Previous experiments have shown that corrosive acids, like sulfuric acid and nitric acid, may form in certain CO$_2$ blends [7].

Little is known about how much impurities that can be accepted without risking corrosion or solids formation in a CO$_2$ transportation system. Even though recommendations exist [8], the impurity limits are mostly based on HSE concerns in case of accidental spill, rather than pipeline integrity problems. It is of course possible to clean the captured CO$_2$ to near 100% purity, but it will be costly both from an economical and energy perspective. CO$_2$ specifications describing the acceptable amounts of impurities in the CO$_2$ from a corrosion perspective is therefore needed. To achieve this, experimental data is needed to identify reactions which can occur between the impurities in the CO$_2$ and determined the lowest possible concentration that can be accepted for without compromising the integrity of the carbon steel pipeline.

Due to lack of experimental data, it is currently not possible to predict when chemical reactions, corrosion and solids formation could be expected in a CO$_2$ transportation system. The final goal would of course be to develop a tool that can be used to predict such reactions. Development of such a tool is not part of the scope of the present work, but the results should be an important contribution to such development work. Crucial for making such a tool is knowledge about reactions, interactions, and solubility of the involved species. For example, no data exists on the solubility of sulfuric and nitric acid in dense phase CO$_2$, which might form under certain conditions. This information is important, since precipitation of strong acids will create a highly corrosive environment (risk of corrosion of carbon steel and formation of corrosion products). But if the acid remains dissolved in the dense phase CO$_2$, they can probably follow the stream without affecting the transportation pipeline. Therefore, the threshold when precipitation occurs (solubility limit is exceeded) needs to be known.

1.2 Objective

The main objective of this study is to carry out experimental testing to understand corrosion and chemical reactions in CO$_2$ transport system. The results will be important background information for determining a safe operation window for CO$_2$ transport when impurities are present. SO$_2$, NO$_2$, H$_2$O, O$_2$, and H$_2$S are selected as impurities to study since they are expected to be present in captured CO$_2$ and are known to be corrosive to carbon steel individually, and they may also react and form even more corrosive species. Particular focus is therefore put on identifying chemical reactions, reaction products and formation of separate liquid phases. The effect of impurity
concentrations is also studied as part of establishing a safe operation window. If reaction products remain dissolved in the bulk CO$_2$ phase, they can in principle follow the CO$_2$ stream without causing any damage. Sulfuric acid and nitric acid, which are known to form under certain conditions, is therefore studied in detail. Data from the present work will be shared with OLI Systems, who will implement them in their Mixed-Solvent Electrolyte (MSE) model. However, the thermodynamic modelling is outside the scope of the present PhD work.

1.3 Approach

The experimental approach will be to mimic the CO$_2$ transport conditions in the most realistic way as possible. Impurities will be continuously injected to ensure that the initial concentration stays constant, and that the impurities are not fully consumed through corrosion or reactions in the transported CO$_2$ to render possible stoichiometric calculations. The impurity concentrations will be monitored using various analytical techniques, and corrosion and chemical reactions will be determined from concentration differences between injected CO$_2$ and exhaust CO$_2$. The acid solubility in CO$_2$ will be examined near equilibrium in a steady state condition with slow flowing CO$_2$ through the representative acid. The experimental equipment will consist of corrosion loops, see-through and closed autoclaves, together with advanced injection and analysing equipment.

1.4 Thesis structure

The thesis consists of six individual papers. Five papers have been published and one has been submitted for publication. An overview of work on CO$_2$ transport corrosion and reactions published in the literature is given in Chapter 2. The experimental setups are thoroughly described in the articles they were used (Chapter 3 through 8), and some repetition could therefore not be avoided.

Chapter 3 reports a study of corrosion of carbon steel exposed to liquid water with high CO$_2$ pressures. Chapter 4 reports corrosion experiments where the water was fully dissolved in the CO$_2$ phase (no liquid water present). Chapter 5 studied reactions that took place in CO$_2$ blends with impurity concentrations well within established CO$_2$ specifications. The solubility of nitric and sulfuric acid in dense phase CO$_2$ is reported in Chapter 6. Corrosion of carbon steel in dense phase CO$_2$ with SO$_2$ and NO$_2$ is reported in Chapter 7. Chapter 8 reports a series of experiments where multiple CO$_2$ blends were mixed. An overall discussion of all the results, and the literature from Chapter 2, is given in Chapter 9, with conclusions in Chapter 10 and suggestion for further work in Chapter 11.
1.5 References


Chapter 2

Literature review

This chapter gives an overview of published work on corrosion and reactions relevant for dense phase CO₂ transport in carbon steel pipelines. Papers on corrosion and reactions for ship transport conditions of CO₂ were also search for, but no one was found. CCS has got increasingly more attention during the last two decades, and most papers were therefore published after 2000. Prior to this, relevant corrosion research was mainly related to oil and gas systems, which usually has much lower CO₂ partial pressures. The main focus in this review has been to summarise the present knowledge and identify knowledge gaps, with particular focus on effects of water content and impurities on corrosion of carbon steel.

2.1 Corrosion

For corrosion in CO₂ transportation systems it is important to distinguish between the two principally different situations when water is present as a separate phase and when the water is fully dissolved in the CO₂ phase. The corrosion mechanism is most likely the same, but the rates will be significantly different since the amount of water differs by many orders of magnitude. The presence of liquid water is a key factor to drive the corrosion reactions and large quantities of water will result in high corrosion rates. In contrast, water can probably be a limiting reactant by itself, and for example a small water phase (thin surface film) will result in rapid saturation of corrosion products.

2.1.1 Corrosion in a free water phase

A free water phase is not expected in CO₂ transport pipelines under normal operation, but it could occur due to accidental water ingress, equipment malfunction, carry-over from the compression stage, or other types of operational errors. This occurred in the start-up in the SACROC CO₂ injection project where wellheads and tubing was subjected to alternating water and CO₂ slugs. [1].

It is well known that carbon steel will corrode in contact with water and CO₂, and numerous data from oil and gas research show that this may result in high corrosion rates. Most of these data were acquired for a CO₂ partial pressure in the 0.1 to 10 bar range. There are many papers that discusses the mechanisms for CO₂ corrosion of carbon steel, and only a brief summary will be given here. More details can be found elsewhere [2-6]. Aqueous CO₂ is formed when dissolved in the water
phase and reacts with water to form carbonic acid (Equation 2-1). The electrochemical reactions consist of dissolution of iron (anodic, Equation 2-2) and the reduction of hydrogen, carbonic acid and bicarbonate (cathodic, Equations 2-3, 2-4, and 2-5).

\[
\begin{align*}
\text{CO}_2^{(aq)} + \text{H}_2\text{O}^{(l)} &\rightarrow \text{H}_2\text{CO}_3^{(aq)} \quad (2-1) \\
\text{Fe}^{(s)} &\rightarrow \text{Fe}^{2+}_{(aq)} + 2e^- \quad (2-2) \\
2\text{H}^+_{(aq)} + 2e^- &\rightarrow \text{H}_2^{(g)} \quad (2-3) \\
2\text{H}_2\text{CO}_3^{(aq)} + 2e^- &\rightarrow \text{H}_2^{(g)} + 2\text{HCO}_3^-_{(aq)} \quad (2-4) \\
2\text{HCO}_3^-_{(aq)} + 2e^- &\rightarrow \text{H}_2^{(g)} + 2\text{CO}_3^{2-}_{(aq)} \quad (2-5) \\
\text{Fe}^{2+}_{(aq)} + \text{CO}_3^{2-}_{(aq)} &\rightarrow \text{FeCO}_3^{(s)} \quad (2-6)
\end{align*}
\]

Eventually, the iron-ion and carbonate-ion will react (Equation 2-6) and precipitate. The iron carbonate corrosion product may, depending on the morphology, provide a varying degree of protection for the steel substrate. There are some publications that address corrosion in water under high CO\textsubscript{2} pressures. The reported corrosion rates vary significantly, and rates from 0.2 to 50 mm/y has been reported [7-15]. This wide spread of corrosion rates can in many cases be explained by the differences in experimental methods, and it emphasises the importance of comparing results under similar conditions. Zhang et al. [14] showed that the corrosion rate increased with increasing temperature (from 50 to 80 °C) under stagnant conditions. Nor et al. [16] concluded that the corrosion rate increased with increasing flow rate and with increasing temperature. The partial pressure (fugacity) of CO\textsubscript{2} will also influence the corrosion rate, and Seiersten et al. [7] reported increasing rates with increasing CO\textsubscript{2} pressure up to 40 bar, from 14 mm/y to 23 mm/y, after this point the corrosion rate started declining. However, the latter experiments were conducted at stagnant condition without replenishment of the water and the highest CO\textsubscript{2} pressures were therefore carried out at a higher pH. It might be different for flowing condition when corrosion products are removed from steel surface and the transport of corrosive species to the surface is enhanced. The pH will increase when corrosion products are accumulated in the water phase, which will contribute to lower corrosion rates.

### 2.1.2 Corrosion in CO\textsubscript{2} with dissolved water

Normally, the transported CO\textsubscript{2} should only contain small amounts of water that will be fully dissolved in the CO\textsubscript{2} phase, because the presence of free water gives unacceptable high corrosion rates on carbon steel. For several years the understanding has been that exposure to CO\textsubscript{2} with fully dissolved water leads to very low corrosion rates [12,17-24]. These rates (less than 0.010 mm/y) are so low that they are not of technological interest. However, during the last decade, significantly
higher corrosion rates in the range of 0.5 to 3 mm/y have been reported for conditions where the water nominally should be fully dissolved in the CO₂ phase [25-28]. Hua et al. [29] reported that the corrosion rate was about 0.1 mm/y with 80 bar CO₂ and 35 °C when the water content was 3400 ppmv, i.e. at the solubility limit. Furthermore, the localised (pitting) corrosion in that experiment was claimed to be as high as 0.9 mm/y. Even when the water content was reduced to 700 ppmv the pitting corrosion rate was as high as 0.2 mm/y. Similar pitting corrosion was also observed by Sim et al. [30] when they had a general corrosion of 0.03 mm/y for a large range of water contents (from 244 to 3670 ppmv water at 80 bar and 40 °C). These relatively high corrosion rates are in contrast with the previous work, which reported negligible corrosion rates as long as the water was fully dissolved in the CO₂ phase. Thus, there are conflicting results for conditions where the water is dissolved in dense phase CO₂. A summary of published corrosion values is listed in Table 2-1.

![Table 2-1: Summary of reported corrosion rates for carbon steel coupons exposed to CO₂ with dissolved water.](image)

*Water added in excess to ensure that the CO₂ phase was fully saturated with water.

For atmospheric corrosion, it is often referred to 60% relative humidity (RH) as a starting point of corrosion [36]. The reason is that the thickness of the adsorbed water film on the metal surface increases with increasing humidity, and at about 60% RH the surface water film has exceeded a critical thickness (in the order of 5-6 monolayers) where it has got bulk water properties [37,38]. The
conditions in a system with liquid or supercritical CO\textsubscript{2} are probably quite different from atmospheric conditions, but it is not unlikely that the same principles with surface absorption of water will apply. If so, the water film will at some critical thickness achieve bulk water properties, after which it can absorb CO\textsubscript{2} and form carbonic acid, which again may lead to corrosion reactions as explained in Chapter 2.1.1. If this link between water content in the bulk phase and mono layers of surface water applies for dense phase CO\textsubscript{2} conditions is not known. However, Hua et al. [31] observed an increase in general corrosion when the water content was increased from 1300 to 1800 ppmv, which equals about 40 to 54\% of the solubility limits of water in CO\textsubscript{2}.

2.2 Corrosion effects of single impurities with water

There is consensus that little or nothing happen with single impurity system without dissolved water present. Corrosion with dissolved water and other impurities are reviewed in the following chapters.

2.2.1 O\textsubscript{2} – H\textsubscript{2}O

The published data on corrosion in CO\textsubscript{2} with H\textsubscript{2}O and O\textsubscript{2} as impurities reports a wide spread in corrosion rates, as summarised in Table 2-2. Ayello et al. [25] reported a corrosion rate of 2.3 mm/y with 2440 ppmv water and 100 ppmw O\textsubscript{2} with 76 bar of CO\textsubscript{2} at 40 °C, and Choi et al. [26] showed in 2010 corrosion rates around 1 mm/y when 2 to 6\% O\textsubscript{2} was present in water saturated CO\textsubscript{2}. While in 2011, the same group [39] reported insignificant corrosion rates with 3.3 bar (equals about 2.6 mol\%) O\textsubscript{2} and water concentrations of 650, 2000, and 3000 ppmv (80 bar and 50 °C). The latter water content is close to the saturation limit.

<table>
<thead>
<tr>
<th>Pressure (bar)</th>
<th>Temp (°C)</th>
<th>H\textsubscript{2}O (ppmv)</th>
<th>O\textsubscript{2}</th>
<th>Exposure Time (days)</th>
<th>CR (mm/y)</th>
<th>Reference</th>
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<tr>
<td>76</td>
<td>40</td>
<td>2440</td>
<td>100 ppmw</td>
<td>0.3</td>
<td>2.3</td>
<td>[25]</td>
</tr>
<tr>
<td>80</td>
<td>50</td>
<td>sat</td>
<td>2 %</td>
<td>1</td>
<td>0.6</td>
<td>[26]</td>
</tr>
<tr>
<td>80</td>
<td>50</td>
<td>sat</td>
<td>4 %</td>
<td>1</td>
<td>1.1</td>
<td>[26]</td>
</tr>
<tr>
<td>80</td>
<td>50</td>
<td>sat</td>
<td>6 %</td>
<td>1</td>
<td>0.9</td>
<td>[26]</td>
</tr>
<tr>
<td>80</td>
<td>50</td>
<td>650</td>
<td>3.3 bar (2.6%)</td>
<td>1</td>
<td>&lt;0.01</td>
<td>[39]</td>
</tr>
<tr>
<td>80</td>
<td>50</td>
<td>2000</td>
<td>3.3 bar (2.6%)</td>
<td>1</td>
<td>&lt;0.01</td>
<td>[39]</td>
</tr>
<tr>
<td>80</td>
<td>50</td>
<td>3000</td>
<td>3.3 bar (2.6%)</td>
<td>1</td>
<td>&lt;0.01</td>
<td>[39]</td>
</tr>
<tr>
<td>100</td>
<td>45</td>
<td>sat</td>
<td>1400 ppmv</td>
<td>5</td>
<td>0.04</td>
<td>[40]</td>
</tr>
<tr>
<td>100</td>
<td>50</td>
<td>sat</td>
<td>2000 ppmv</td>
<td>10</td>
<td>0.01</td>
<td>[41]</td>
</tr>
<tr>
<td>100</td>
<td>20</td>
<td>1220</td>
<td>200 ppmw</td>
<td>30</td>
<td>Negligible</td>
<td>[17]</td>
</tr>
</tbody>
</table>

Both Sun et al. [41] and Zeng et al. [40] reported low general corrosion rates around 0.01 and 0.05 mm/y, respectively, for corrosion tests carried out under water-saturated conditions at 100 bar and
supercritical CO₂. However, Sun et al. also reported localised attacks and suggested that it might be connected to precipitation of water. Dugstad et al. [17] found no corrosion with 1220 ppmw O₂ (100 bar, 20 °C). It seems like water saturated conditions increases the corrosion rates and contribute to the discrepancy.

### 2.2.2 SO₂ – H₂O

There are several papers which address corrosion in dense phase CO₂ with SO₂ and H₂O, usually compared with and without O₂. Table 2-3 summarises the data without O₂. Ayello et al. [25] studied the effect of SO₂ and H₂O, they reported a corrosion rate of 4.6 mm/y with 2440 ppmv of water and 100 ppmw of SO₂ at 76 bar and 40 °C. Choi et al. [10,39] studied corrosion in CO₂ with 650 ppmv water and in water-saturated CO₂ with 0.8 bar (about 0.7%) SO₂ at 80 bar and 50 °C. They reported a corrosion rate of 3.5 and 5.6 mm/y, respectively. The same group [42] carried out tests with 0.05% (0.04 bar) and 0.1% (0.08 bar) of SO₂, but the corrosion rate was only 0.05 and 0.03 mm/y, respectively, for the same pressure and temperature at 650 ppmv of H₂O. They also tested at 25 °C and found 0.1 mm/y at 650 ppmv of water and 0.08 bar of SO₂. Due to density increase of the CO₂ when the temperature was lowered to 25 °C, the SO₂ concentration was only 0.025% and this could indicate that it is neither the temperature nor the amount of SO₂ that decides the corrosion rate, but rather how much water is present in the CO₂. With 650 ppmv water at 25 °C, the saturation ratio of water is higher than at 50 °C due to an increase in solubility with increasing temperature. They also found localised attacks in form of pits.

<table>
<thead>
<tr>
<th>Pressure (bar)</th>
<th>Temp (°C)</th>
<th>H₂O (ppmv)</th>
<th>SOx</th>
<th>Exposed (days)</th>
<th>Flow/mixing</th>
<th>CR (mm/y)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>25</td>
<td>650</td>
<td>0.08 bar (0.025%)</td>
<td>1</td>
<td>No</td>
<td>0.1 (pits)</td>
<td>[42]</td>
</tr>
<tr>
<td>60</td>
<td>25</td>
<td>650</td>
<td>0.08 bar (0.025%)</td>
<td>1</td>
<td>Yes</td>
<td>0.013</td>
<td>[42]</td>
</tr>
<tr>
<td>75.8</td>
<td>40</td>
<td>2440</td>
<td>100 ppmw</td>
<td>0.3</td>
<td>No</td>
<td>4.6</td>
<td>[17]</td>
</tr>
<tr>
<td>80</td>
<td>50</td>
<td>650</td>
<td>0.08 bar (0.1%)</td>
<td>1</td>
<td>No</td>
<td>0.03</td>
<td>[26]</td>
</tr>
<tr>
<td>80</td>
<td>50</td>
<td>650</td>
<td>0.04 bar (0.05%)</td>
<td>1</td>
<td>No</td>
<td>0.05</td>
<td>[26]</td>
</tr>
<tr>
<td>80</td>
<td>50</td>
<td>Sat</td>
<td>0.8 bar</td>
<td>1</td>
<td>No</td>
<td>5.6</td>
<td>[26]</td>
</tr>
<tr>
<td>80</td>
<td>50</td>
<td>650</td>
<td>0.8 bar</td>
<td>1</td>
<td>No</td>
<td>3.48</td>
<td>[34]</td>
</tr>
<tr>
<td>95</td>
<td>35</td>
<td>Sat</td>
<td>500 ppm</td>
<td>17</td>
<td>Yes</td>
<td>0.02</td>
<td>[43]</td>
</tr>
<tr>
<td>95</td>
<td>35</td>
<td>Sat</td>
<td>500 ppm</td>
<td>46</td>
<td>Yes</td>
<td>0.08</td>
<td>[43]</td>
</tr>
<tr>
<td>100</td>
<td>25</td>
<td>488</td>
<td>145 ppmw</td>
<td>14</td>
<td>Yes</td>
<td>&lt;0.005</td>
<td>[34]</td>
</tr>
<tr>
<td>100</td>
<td>25</td>
<td>488</td>
<td>500 ppmw</td>
<td>14</td>
<td>Yes</td>
<td>&lt;0.01</td>
<td>[34]</td>
</tr>
<tr>
<td>100</td>
<td>25</td>
<td>1220</td>
<td>500 ppmw</td>
<td>14</td>
<td>Yes</td>
<td>0.02</td>
<td>[34]</td>
</tr>
</tbody>
</table>

Dugstad et al. [33,34] reported low general corrosion rates (<0.02 mm/y) when the water was fully dissolved in the CO₂ phase and the SO₂ concentration was below 500 ppmw (100 bar and 25 °C).
They commented that the corrosion occurred in several spots and therefore the corrosion rates could be higher at these areas. Possibly the corrosion coupon might have been hit by the liquid water when it was introduced in the system. However, these findings are supported by Patchigolla et al. [43] who found corrosion rates from 0.02 to 0.08 mm/y in a flow loop with water saturated CO₂ and 500 ppm SO₂ (unclear if this is volume or weight) at 95 bar and 35 °C.

2.2.3 H₂S – H₂O
There are only a few experiment with H₂S and water, Schremp and Roberson [22] reported that 1000 ppmv of water with 800 ppmv of H₂S was not corrosive for carbon steel (X-60) in 138 bar CO₂ at 3 and 22 °C. The steel also passed a sulfide cracking test (stress corrosion cracking test). El Alami et al. [35] reported corrosion rates up to 0.3 mm/y on L80 carbon steel at 150 bar and 80 °C in water saturated CO₂ with 3 mol% H₂S, and they also reported localised attacks. Wei et al. [44] found the same corrosion rate as El Alami. However, Zeng and co-workers reported corrosion rates around 0.07 mm/y with 50 and 100 ppmv H₂S at saturated water conditions [40]. This corresponds with Sun et al. [41], who published a corrosion rate of 0.05 mm/y when 2000 ppmv H₂S was present at same conditions and they reported only general corrosion. Both, Zeng and Sun, found higher corrosion rates (about 0.3 mm/y) when O₂ was introduced, and localised attacks was observed. Several years with field experience in US [45] has shown that the present of H₂S in CO₂ transport pipelines do not lead to severe corrosion and the specification allows up to 1500 ppmw of H₂S to be transported with the CO₂.

2.2.4 NO₂ – H₂O
Nitrogen dioxide is very interesting since it known to be strongly oxidising and together with other impurities reactions might occurs to produce other corrosive species. Dugstad et al. [33,34,46] reported that the corrosion increased when the concentration of NO₂ was increased from 200 to 500 ppmv, with a water concentration of 1220 ppmv. When the water concentration was reduced from 1220 to 488 ppmv, the corrosion rate decreased to 0.06 mm/y. The corrosion rate was also strongly affected by exposure time, which might be linked to consumption of impurities. When the impurities are partly or fully consumed through corrosion, maximum corrosion rate is achieved in the beginning of the experiment while during the rest of the exposure time the corrosion rate might be very low.
Table 2-4: Published corrosion data with the present of NO\textsubscript{2} and H\textsubscript{2}O.

<table>
<thead>
<tr>
<th>Pressure (bar)</th>
<th>Temp (°C)</th>
<th>H\textsubscript{2}O (ppmv)</th>
<th>NO\textsubscript{x}</th>
<th>Exposed (days)</th>
<th>Flow/mixing</th>
<th>CR (mm/y)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>76</td>
<td>40</td>
<td>2440</td>
<td>100 ppmw</td>
<td>0.3</td>
<td>No</td>
<td>11.6</td>
<td>[25]</td>
</tr>
<tr>
<td>100</td>
<td>25</td>
<td>1220</td>
<td>500 ppmw</td>
<td>10</td>
<td>Yes</td>
<td>1.6</td>
<td>[34]</td>
</tr>
<tr>
<td>100</td>
<td>25</td>
<td>1220</td>
<td>200 ppmw</td>
<td>10</td>
<td>Yes</td>
<td>0.7</td>
<td>[33,34,46]</td>
</tr>
<tr>
<td>100</td>
<td>25</td>
<td>488</td>
<td>200 ppmw</td>
<td>20</td>
<td>Yes</td>
<td>0.06</td>
<td>[34]</td>
</tr>
<tr>
<td>100</td>
<td>25</td>
<td>488</td>
<td>100 ppmw</td>
<td>3</td>
<td>Yes</td>
<td>0.17</td>
<td>[34]</td>
</tr>
</tbody>
</table>

2.3 Corrosion in CO\textsubscript{2} with multiple impurities

The limited number of papers that is has been found showed that in general, the corrosion rates are strongly affected by the type of impurities, combination of impurities and concentration of impurities. Certain combinations are reported to give only negligible corrosion while other combinations may result in severe corrosion. When SO\textsubscript{2}-H\textsubscript{2}O and SO\textsubscript{2}-O\textsubscript{2}-H\textsubscript{2}O was compared at the same conditions, a moderate increase in corrosion rates was observed when O\textsubscript{2} was present [10,17,29,39,47]. Xiang et al. [48-50] preformed a series of SO\textsubscript{2}-O\textsubscript{2}-H\textsubscript{2}O experiments with 20000 ppmv of SO\textsubscript{2} and found that the corrosion rates increased with increasing water content, similar to what Hua et al. [29] reported. The corrosion rates ranged from 0.04 to 0.87 mm/y [48]. They also observed a temperature effect and an exposure time effect. The corrosion rate increased from 1.1 to 3 mm/y when the temperature was increased from 25 °C to 75 °C, while at 93 °C, the corrosion rate dropped to 1.2 mm/y [50]. The corrosion rate decreased from 1.95 to 0.75 mm/y when the exposure time was increased from 1 day to 8 days [49], and the authors related this effect of the build-up of protective surface layers. Build-up of surface layers that can provide a varying degree of protection is well known for corrosion processes, and in the oil and gas industry where free water usually is present, precipitation of iron carbonate or iron sulfide creates a protective film [2,5]. This also shows that short exposure time would present the worst-case corrosion rate while long term might give more realistic values of the corrosion. However, this would require the experimental conditions to be kept constant without consumption of the impurities due to corrosion or chemical reactions. This will be further discussed in Chapter 9.

There was not found any data that shows the effect of NO\textsubscript{2}-O\textsubscript{2}-H\textsubscript{2}O combination. However, Dugstad et al. [34] observed lower corrosion (0.017 mm/y) with SO\textsubscript{2}-NO\textsubscript{2}-H\textsubscript{2}O combination than with only NO\textsubscript{2}-H\textsubscript{2}O present (0.17 mm/y). They commented; “Whether the lower corrosion rate is attributed to less available impurities in the short autoclave, protective corrosion product film formed on the steel surface or consumption of impurities due to impurity reactions in the bulk phase can be questioned”. 
The reported corrosion rates are surprisingly low, for the few reported multiple impurities experiment [51-56] compared to many of the reported rates with water or only two impurities present. The main reason might be related to the control of the water concentration, since all experiments were performed with water concentration at 1000 ppmv and lower, and all corrosion rates were lower than 0.1 mm/y in both static and mixing situation.

2.4 Reactions between impurities

When certain impurities are present simultaneously in the CO2 phase they can react and form new reaction products. Several "common" impurities are regarded as oxidising agents (O2, NO2, and SO2). The focus of reactions in CO2 transport systems has mainly been directed towards carbon steel corrosion and type of corrosion products that forms on the steel surface. For example, NO2 and SO2 was reported to react (absorb, dissolve) with the surface water film on carbon steel [26,29,47]. It was suggested that the reactions were essentially similar as for atmospheric corrosion:

Dissolution of SO2 in water film at the steel surface [57]:

\[
\text{SO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \leftrightarrow \text{HSO}_3^- (\text{aq}) + \text{H}^+_\text{(aq)}
\]  
\[
\text{HSO}_3^- (\text{aq}) \leftrightarrow \text{SO}_3^{2-} (\text{aq}) + \text{H}^+_\text{(aq)}
\]  

If oxygen is present, sulfate could form [58]:

\[
\text{SO}_3^{2-} (\text{aq}) + \frac{1}{2} \text{O}_2 (\text{g}) \leftrightarrow \text{SO}_4^{2-} (\text{aq})
\]  

In presence of SO2, O2, and H2O, the corrosion products of carbon steel would then be either ferrous sulphite (FeSO3) or ferrous sulphate (FeSO4) depending on the amount of oxygen present. If the excess of oxygen is high, the ferrous sulphate could be converted to ferric oxyhydroxide (FeOOH) [59].

Formation of nitric acid was reported to proceed by dissolution of NO2 in the surface water film [60]:

\[
3\text{NO}_2(\text{g}) + \text{H}_2\text{O} (\text{l}) \rightarrow 2\text{HNO}_3(\text{l}) + \text{NO}(\text{g})
\]  

When NO2 is present, there are numerous reaction routes, which can result in formation of nitric acid or other oxidising substances, also in the gas phase [61-64]. Graedel et al. [58] commented that nitrates are seldom found on the surface as corrosion products and the reason might be that the
nitrate salts are highly soluble and can follow the flowing media (CO₂) away from the surface, instead iron oxide is detected.

Dugstad et al. [56] reported formation of acids in dense phase CO₂ when H₂O, SO₂, H₂S, O₂, and NO₂ were present. They suggested that several chemical reactions took place in both the CO₂ phase. Paschke et al. [51] found nitric acid when NO₂ and H₂O was present, but concluded that sulfuric acid did not form when SO₂, O₂, and H₂O was present because the oxidisation of SO₂ to SO₃ with O₂ was not possible at CCS condition (4 to 50°C and 60 to 200 bar), due to the pressure and temperature. This is also in accordance with findings of Torrente-Murciano et al. [65] who found that SO₂ was not oxidised by NO₂ in the CO₂ gas phase at low pressure (5 to 15 bar), they also confirmed that NO₂ and SO₂ dissolved in water and created sulfuric and nitric acid in the water phase. This result is in contrast with Paschke et al., who found sulfuric acid when NO was added, and suggested that the lead chamber reaction took place:

\[
\text{NO}_2(g) + \text{SO}_2(g) + \text{H}_2\text{O}(l) = \text{H}_2\text{SO}_4(aq) + \text{NO}(g)
\]  

There are no available data in the literature on solubility of nitric and sulfuric acid in the CO₂ phase. The solubility of these acids is important for predicting if acid producing reactions can result in precipitation of a separate phase with acids. The corrosion situation would be totally different if a second phase is formed instead of the acid remaining dissolved in the CO₂ phase. The acid solubility has been measured in air, Gimtro et al. [66] reported a vapour pressure of sulfuric acid to be \(10^{-3}\) mm Hg (\(~1.3\) ppmv) and \(10^{-2}\) mm Hg (\(~13\) ppmv) at 25 °C and 50 °C, respectively. Sproesser et al. [67] reported vapour pressures for nitric acid of 6.2 (\(~8200\) ppmv) and 13.7 (\(~18300\) ppmv) mm. Hg at 35 °C and 50 °C, respectively. Thus, in air the vapour pressure of nitric acid in air is about three orders of magnitude higher than for sulfuric acid. Although these vapour pressures were found at ambient pressures in air, it would not be surprising if there was a significant difference in acid solubility limits in CO₂ as well.

2.5 Expected impurity concentrations and existing CO₂ specifications

There are numerous types of capturing techniques [68] which each have different efficiencies on various types of impurities. Furthermore, there are various types of flue-gas sources which again will have different types and concentrations of impurities. In summary this means that the captured CO₂ will have a wide range of different types and concentrations of impurities. An example of expected impurity content after oxy-fuel, pre- and post-combustion capturing together with a specification from natural formation is shown in Table 2-5.
Table 2-5: The concentrations of impurities from different capturing sources and natural formation.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Oxy-fuel [69]</th>
<th>Pre-combustion [70]</th>
<th>Post-combustion [71]</th>
<th>Natural formation Weyburn [72]</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O (ppmv)</td>
<td>100</td>
<td>600</td>
<td>100</td>
<td>&lt;20</td>
</tr>
<tr>
<td>SO₂ (ppmv)</td>
<td>70</td>
<td>0</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>O₂ (ppmv)</td>
<td>100</td>
<td>0</td>
<td>150</td>
<td>&lt;50</td>
</tr>
<tr>
<td>NO₃ (ppmv)</td>
<td>100</td>
<td>0</td>
<td>20</td>
<td>-</td>
</tr>
<tr>
<td>H₂S/COS (ppmv)</td>
<td>0</td>
<td>&lt;100</td>
<td>0</td>
<td>9000</td>
</tr>
<tr>
<td>CO (ppmv)</td>
<td>50</td>
<td>400</td>
<td>10</td>
<td>1000</td>
</tr>
<tr>
<td>Ar, N₂, H₂ (ppmv)</td>
<td>300</td>
<td>20000</td>
<td>450</td>
<td>&lt;300</td>
</tr>
<tr>
<td>Hydrocarbons (vol. %)</td>
<td>-</td>
<td>0.02</td>
<td>-</td>
<td>2.3</td>
</tr>
</tbody>
</table>

There are many suggested specifications and recommendations in the literature for the maximum allowed impurity content in CO₂. An extensive report from the National Energy Technology Laboratory (NETL), where 55 different specification were summarised [73], showed that there is a wide spread of the number of impurities expected to be present in the CO₂ after capture. Table 2-6 shows the impurities that will be focus on in this thesis and their concentration range based on the report from NETL.

Table 2-6: Expected concentration ranges for impurities [73] transported in pipeline, CO₂ is the balance.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration (ppmv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>20 – 650</td>
</tr>
<tr>
<td>O₂</td>
<td>10 – 40000</td>
</tr>
<tr>
<td>SO₃</td>
<td>10 – 50000*</td>
</tr>
<tr>
<td>H₂S</td>
<td>20 – 13000*</td>
</tr>
<tr>
<td>NO₃</td>
<td>20 – 2500*</td>
</tr>
<tr>
<td>N₂</td>
<td>100 – 7000</td>
</tr>
<tr>
<td>Ar</td>
<td>100 – 4000</td>
</tr>
<tr>
<td>CH₄</td>
<td>100 – 4000</td>
</tr>
<tr>
<td>H₂</td>
<td>100 – 4000</td>
</tr>
<tr>
<td>CO</td>
<td>10 – 5000</td>
</tr>
<tr>
<td>NH₃</td>
<td>0 – 50</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>0 – 1000</td>
</tr>
<tr>
<td>C₃+</td>
<td>0 – 1000</td>
</tr>
<tr>
<td>Glycol</td>
<td>0 – 0.174</td>
</tr>
<tr>
<td>Particles</td>
<td>0 – 1</td>
</tr>
</tbody>
</table>

*Often given as 100 ppmv for HSE concern.

The final recommendation made from all these reviewed specifications is summarised in Table 2-7 and compared with the Dynamis [72] recommendation which is one of the most referred to in the
Due to the lack of experimental data, the both recommendations had to use HSE concern to set the limits, and for this reason they might not be the best for the integrity of the carbon steel pipeline. The NETL report pointed out that most of these concentration levels are not based on experimental data but rather set by health, safety and the environmental (HSE) concerns and stressed that the experimental base for making specification was too thin and for design of transport systems more experimental results are needed in several areas. The shaded impurities in Table 2-7 are the ones investigated in this thesis. They are of most concern for corrosion of carbon steel, while the other impurities would be more interesting when it comes to flow properties inside the pipeline.

Table 2-7: Comparison of the NETL and the Dynamis recommendation.

<table>
<thead>
<tr>
<th>Compound</th>
<th>NETL [73] (ppmv)</th>
<th>Dynamis [72] (ppmv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>500</td>
<td>500</td>
</tr>
<tr>
<td>O₂</td>
<td>10</td>
<td>&lt;4000</td>
</tr>
<tr>
<td>SOx</td>
<td>100*</td>
<td>100*</td>
</tr>
<tr>
<td>H₂S</td>
<td>100*</td>
<td>200*</td>
</tr>
<tr>
<td>NOx</td>
<td>100*</td>
<td>100*</td>
</tr>
<tr>
<td>N₂</td>
<td>4000</td>
<td>&lt;4000</td>
</tr>
<tr>
<td>Ar</td>
<td>4000</td>
<td>&lt;4000</td>
</tr>
<tr>
<td>CH₄</td>
<td>4000</td>
<td>&lt;4000</td>
</tr>
<tr>
<td>H₂</td>
<td>4000</td>
<td>&lt;4000</td>
</tr>
<tr>
<td>CO</td>
<td>35</td>
<td>2000</td>
</tr>
<tr>
<td>NH₃</td>
<td>50</td>
<td>-</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>1000</td>
<td>-</td>
</tr>
<tr>
<td>C₃+</td>
<td>&lt; 1000</td>
<td>-</td>
</tr>
<tr>
<td>Glycol</td>
<td>0.046</td>
<td>-</td>
</tr>
<tr>
<td>Particles</td>
<td>1</td>
<td>-</td>
</tr>
</tbody>
</table>

*Often given as 100 ppmv for HSE concern.

2.6 Experimental methods and equipment

Essentially all papers on corrosion in liquid and supercritical CO₂ (see chapter 2.1, 2.2, and 2.3) have used autoclaves for the experimental testing. There are many different variants of the setups, but they typically consist of; an autoclave with heating jacket, a temperature transmitter (TT), a pressure transmitter (PT), one or multiple holders for hanging corrosion coupons, and one or several valves for loading and relief, see example in Figure 2-1.
Figure 2-1: Simple sketch of a typical autoclave system with hanging coupons and injected water at the bottom. Pressure transmitter (PT) and temperature transmitter (TT) is fitted.

There are also large variations in the start-up procedures, but it usually consists of the following sequence of actions: mounting the specimens, deaerate the autoclave, injection of liquid water, deaerate, injection of impurities, and finally pressurising with CO₂. The autoclave was then kept closed throughout the experiment, and there was usually no analyses of the impurities or water content before, during, or after the experiment. The water was always added as liquid water directly in the autoclave in the beginning, either as a small amount for under-saturated experiments (water fully dissolved in the CO₂ phase) or as a large amount for water saturated experiments (water added in excess, may replenish if water is depleted from the CO₂ phase).

Information on how fast the CO₂ was loaded into the autoclave or how fast the depressurisation process was at the end of the experiment was not reported in any of the papers. Apparently, all papers assumed that the liquid water dissolved rapidly into the CO₂ bulk phase, but it was not possible to find any experiments that actually had measured the dissolution rate. Slow dissolution of liquid water was indirectly reported in a paper from Thodla and Ayello [25,27], they used electrochemical impedance spectroscopy (EIS) to study the corrosion in pressurised CO₂. One droplet of water, equal 100 ppmw if dissolved in the bulk CO₂ phase, was still present after 6 hours in the CO₂ at 76 bar.

Several experiments were conducted with a relatively short exposure time [9,26,31,39,74], even as short as 6 hours [25,27]. For a closed autoclave system with on-going corrosion processes, it is reasonable to keep the test time short to prevent that the impurities will be fully consumed. On the other hand, it is well known that many corrosion processes need longer time (weeks) to reach a
steady rate, and thus the relevance of the very short experiments could be questioned. Hua and colleagues [29] concluded that the amount of corrosion compared with the amount of consumed impurities was negligible for their experiments with low corrosion rates.

2.7 Summary

The present literature study has identified that the amount - and state - of water is extremely important for carbon steel corrosion in dense phase CO₂ systems. The corrosion rate is several decades higher when carbon steel is exposed to a free water phase (20 to 50 mm/y) compared to exposure to CO₂ with fully dissolved water (0.001 to 0.1 mm/y). Experiments with corrosion coupons exposed to water-saturated CO₂, usually reports higher corrosion rates (0.1 to 1.5 mm/y) than similar experiments with exposure to undersaturated CO₂. Collier et al. reported a high degree of scatter in the corrosion data and concluded that there are several limitations in the experimental method. They found essential the same corrosion rate, about 0.02 mm/y, in pure and water-saturated CO₂.[32] Although the corrosion rates probably would increase when the water content approaches saturation, it is not clear if the this increase should be just slightly or several decades since the amount water dissolved in the CO₂ phase is small. However, essentially all water-saturated experiments have applied an excess of water in the autoclave, which increases the chances of accidental spilling of liquid water to the corrosion coupons – especially during pressurising and depressurisation. Furthermore, for a fully water saturated CO₂ phase, small temperature and pressure fluctuations may cause intermittent periods with water condensation. In almost every corrosion experiment with water dissolved in the CO₂ phase, the water was injected in liquid state before the system was pressurised with CO₂. It was therefore, implicitly, assumed that the dissolution rate of liquid water in dense phase CO₂ is fast, but experiments that measured the dissolution rate were not found. Thus, there are some uncertainties around these experiments, especially those with very short exposure time.

The review identified several components that is expected to be present at low concentrations in the captured CO₂ (often referred to as impurities). Of most interest with respect to corrosion are SO₂, NO₂, H₂S, H₂O, and O₂. The presence of impurities had very varying effects on corrosion and chemical reactions, depending both on the combination and concentration of impurities. According to the literature, certain impurity combinations are non-reactive while other may result in chemical reactions and corrosion. For example, H₂S and O₂ will alone not cause corrosion. However, the results with H₂S and O₂ (present individually and together) are somewhat contradictive, which could
most likely be connected to the presence of excess/liquid water rather than the impurities itself. For example it was reported it was reported up to 1 mm/y with O2 and water-saturated condition [26], while others [40,41] reported 0.01 to 0.04 mm/y. The review also identified that SO2 and NO2 may result in corrosion either by direct reactions or due to formation of acids, especially if present together with water and O2.[51,55] Both, Dugstad et al.[55] and Paschke et al.[51], suggested that the lead chamber reaction might occur and NO2 could be the catalysing part to form sulfuric acid.

Several corrosion reactions have been proposed in CO2 with dissolved water, and the general opinion is that the thin water film on the steel surface could attract impurities like SO2 and NO2 to create acids.[75] Thus, the main understanding has been that these reactions occur on the steel substrate and typically corrosion products would be FeCO3, FeSO4, FeSO3, and FeOOH. A normal operation situation for CO2 transport will occur with water fully dissolved (and much lower than the solubility limit) in the CO2, and it might be that there is not enough water to produce a water film thick enough to allows these surface reactions to proceed. In a fully water-saturated condition, the water surface film may be thicker, which possibly could let such reactions occur without too much hinderance. There is however indication that some reaction is occurring in the CO2 phase creating aggressive species that could attack carbon steel. [51,55]

Some papers reported that sulfuric and nitric acid could form from reaction of certain impurities. These acids are very corrosive to carbon steel, and it is therefore important to know if these acids will precipitate or dissolve in the CO2 phase. The literature search did not find any solubility data for sulfuric and nitric acid in dense phase CO2. However, ambient pressure experiments showed several decades difference in solubility between nitric acid and sulfuric acid in air, the latter had the lowest value.

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Chapter 4

Corrosion of carbon steel in dense phase CO$_2$
with water above and below the solubility
limit

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Corrosion of carbon steel in dense phase CO₂ with water above and below the solubility limit

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Abstract

Few experimental studies have addressed corrosion under dense phase CO₂ transport conditions and very different corrosion rates (CR) are reported for apparently the same concentration of impurities (i.e. water) in the CO₂ stream. The differences reflect shortcomings in the experimental methodology and demonstrate the need for a commonly agreed test approach.

An experimental set up allowing accurate control of the water concentration was developed and used in the present work, which provides a more realistic condition mimicking the situation in the operating pipelines. Five corrosion experiments were conducted at 95 bar to determine the corrosion rate of carbon steel in CO₂ with various concentration of dissolved water. The water concentration was increased stepwise from 100 ppmv to the solubility limit and the limit was also exceeded in one of the experiment. The temperature was varied between 8 °C and 35 °C.

The general corrosion rates determined by weight loss were around 1.0 μm/y and no localised attacks were observed as long as the water content was below the solubility limit or exceeding the solubility limit with 10 percent for 400 hours. The results indicate that the corrosion rate of carbon steel will be negligible in the CO₂-water system as long as the water is kept below the solubility limit. The presence of other impurities than water will change the condition for precipitation of corrosive aqueous phases.

Keywords: CCS; dense phase CO₂; corrosion; dissolved water; carbon steel; saturation degree; entrained water
1. Introduction

The CO₂ concentration in the atmosphere has increased dramatically over the last century, and much of this increase is a direct consequence of human activities. Being a greenhouse gas, CO₂ significantly contributes to global warming, and there is an international agreement to reduce emission of CO₂ [1]. One method of reducing the CO₂ release is carbon dioxide capture and storage (CCS).

In CSS, the site of storage could be quite far from the site of capture, thus transport of the captured CO₂ will be necessary. CO₂ can be transported by ships, pipelines or a combination of both. However, for large volume and short to medium distances, pipeline transport is usually the most cost effective means of transportation. For a number of countries, including Norway, the preferred storage locations will be offshore, necessitating offshore pipelines between the capture and the storage facilities. USA has routinely transported CO₂ in land based pipelines for over 30 years, giving rise to the assumption that CO₂ transport in CCS will not involve corrosion challenges, and that research on this topic is of less importance [2, 3]. Although valuable data can be acquired from the existing CO₂ transport pipelines, CCS pipelines will deal with different challenges since the captured CO₂ may contain other components (impurities), including water, at varying concentrations. Limited amount of water will be present after the capture process, but water may also enter the CCS pipelines in response to accidents or operational errors. Water flooding might increase the corrosion rate considerably, and reduce the lifetime of the pipeline [4].

It is very important to distinguish between water present as a separate aqueous phase and water dissolved in the CO₂. It is well known that a free water phase under the high CO₂ pressures expected in CCS pipelines will result in unacceptably high corrosion rates, which can range from 0.2 to 40 mm/y depending on pressure, temperature and flow rate [4-13].

Most of the published CO₂ transport specifications have a recommended maximum water concentration between 20 and 650 ppmv [14]. In a pure water-CO₂ system, this water range is far below the solubility limit indicated in Figure 1 and the water will therefore not precipitate as a separate phase in the given temperature range. When the water concentration is below the solubility limit, most labs find the corrosion rate to be insignificant for pure CO₂-H₂O systems [4, 8, 15-21] (Table 1). However, some researchers have reported higher corrosion rates, even above 3 mm/y in lab experiments [22-24] for the same content of dissolved water. There have also been reported localised attacks up to 1.4 mm/y [25, 26]. In summary the effect of water on the corrosion rate is an important parameter, but it is not consensus on how it affects the corrosion of carbon steel.

![Figure 1. Solubility of water in pure CO₂ as a function of temperature at a pressure of 100 bar [3].](image-url)
Table 1. Summary of lab experiments with dissolved water in CO2 at stagnant condition.

<table>
<thead>
<tr>
<th>H2O (ppmv)</th>
<th>Pressure (bar)</th>
<th>Temp (°C)</th>
<th>Exposed days</th>
<th>CR (mm/y)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>79</td>
<td>31</td>
<td>0.25</td>
<td>1.1</td>
<td>[24]</td>
</tr>
<tr>
<td>240</td>
<td>80</td>
<td>40</td>
<td>7</td>
<td>0.08</td>
<td>[27]</td>
</tr>
<tr>
<td>244</td>
<td>76</td>
<td>40</td>
<td>0.25</td>
<td>1.2</td>
<td>[22]</td>
</tr>
<tr>
<td>300</td>
<td>80</td>
<td>35</td>
<td>2</td>
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<td>[25]</td>
</tr>
<tr>
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<td>80</td>
<td>40</td>
<td>7</td>
<td>0.07</td>
<td>[27]</td>
</tr>
<tr>
<td>610</td>
<td>63</td>
<td>22</td>
<td>42</td>
<td>No</td>
<td>[16]</td>
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<tr>
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<td>80</td>
<td>35</td>
<td>2</td>
<td>0.004</td>
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<td>[27]</td>
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<td>40</td>
<td>7</td>
<td>0.08</td>
<td>[27]</td>
</tr>
<tr>
<td>998</td>
<td>63</td>
<td>22</td>
<td>21</td>
<td>Slight</td>
<td>[16]</td>
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<tr>
<td>1000</td>
<td>79</td>
<td>31</td>
<td>0.25</td>
<td>2.5</td>
<td>[24]</td>
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<tr>
<td>1220</td>
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<td>30</td>
<td>No</td>
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<tr>
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<td>80</td>
<td>35</td>
<td>2</td>
<td>0.01</td>
<td>[25]</td>
</tr>
<tr>
<td>1200</td>
<td>80</td>
<td>40</td>
<td>7</td>
<td>0.07</td>
<td>[27]</td>
</tr>
<tr>
<td>1770</td>
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<td>35</td>
<td>2</td>
<td>0.03</td>
<td>[25]</td>
</tr>
<tr>
<td>2440</td>
<td>76</td>
<td>40</td>
<td>0.25</td>
<td>2.3</td>
<td>[22]</td>
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<tr>
<td>2650</td>
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<td>50</td>
<td>2</td>
<td>0.014</td>
<td>[25]</td>
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<tr>
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<td>2</td>
<td>0.07</td>
<td>[25]</td>
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<tr>
<td>3670</td>
<td>80</td>
<td>40</td>
<td>7</td>
<td>0.08</td>
<td>[27]</td>
</tr>
<tr>
<td>4880</td>
<td>76</td>
<td>40</td>
<td>0.25</td>
<td>2.5</td>
<td>[22]</td>
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<tr>
<td>4880</td>
<td>130</td>
<td>40</td>
<td>0.25</td>
<td>3.5</td>
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<td>80</td>
<td>35</td>
<td>0.6</td>
<td>0.11</td>
<td>[25]</td>
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<tr>
<td>Sat</td>
<td>80</td>
<td>35</td>
<td>1</td>
<td>0.11</td>
<td>[25]</td>
</tr>
<tr>
<td>Sat</td>
<td>80</td>
<td>35</td>
<td>2</td>
<td>0.10</td>
<td>[25]</td>
</tr>
<tr>
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<td>[27]</td>
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<tr>
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<td>80</td>
<td>40</td>
<td>7</td>
<td>0.11</td>
<td>[27]</td>
</tr>
<tr>
<td>Sat</td>
<td>80</td>
<td>50</td>
<td>0.6</td>
<td>0.09</td>
<td>[25]</td>
</tr>
<tr>
<td>Sat</td>
<td>80</td>
<td>50</td>
<td>1</td>
<td>0.03</td>
<td>[25]</td>
</tr>
<tr>
<td>Sat</td>
<td>80</td>
<td>50</td>
<td>2</td>
<td>0.02</td>
<td>[25]</td>
</tr>
<tr>
<td>Sat</td>
<td>80</td>
<td>50</td>
<td>1</td>
<td>0.4</td>
<td>[23]</td>
</tr>
<tr>
<td>Sat</td>
<td>150</td>
<td>80</td>
<td>28</td>
<td>0.1</td>
<td>[28]</td>
</tr>
</tbody>
</table>

Most of the published papers discussing corrosion in dense phase CO2 with dissolved water are based on stagnant autoclave experiments where water is injection before the addition of CO2. Very few paper actually analyses of the water content in the CO2 during the experiment. Thus it is possible that the water was unevenly distributed inside the test equipment or that part of the water was consumed. The present work was carried out in an advanced loop
The results presented in this paper were produced in a recent master thesis at IFE and the University of Oslo [29].

2. Experimental

2.1. Loop/reaction chamber

The experiments were carried out in a high pressure loop built in Hastelloy C276, a highly corrosion resistant material. The loop is designed for a pressure up to 500 bar and is placed inside a ventilated cabinet for HSE reasons (see Figure 2). A cooling unit and heating clamps controlled the loop temperature in the range 0 °C to 60 °C. The loop volume was 2.15 L. There was an inlet for CO₂ pre-mixed with water and an outlet for CO₂ that was routed to the analyser where the water concentration was measured.

Figure 2. The high pressure CO₂ impurity loop. The test section is on the top where the carbon steel sample can be placed. Bypass of the test section is in the middle, temperature sensor, two pressure transmitters, and a coriolis massflow meter are placed as indicated on the figure. The inlet for the CO₂ with pre-mixed levels of water is indicated with “1”, and the outlet from where CO₂ can be sent to the analyser for the determination of water concentration in CO₂ is indicated with “2”.

The carbon steel test coupon was placed in the test section before the loop was flushed with CO₂ to make sure that no oxygen was present. A booster pump was then used to fill the loop, with dry CO₂ until the pressure reached 95 bar. The test section which was closed before the feeding of wet CO₂, was by-passed until the required water level was reached. The circulation pump was adjusted to give a flow velocity of 0.4 m/s.
2.2. Water dosing unit

Accurate water dosing was acquired by adjusting the flow ratio of dry CO\textsubscript{2} and water saturated CO\textsubscript{2} using mass flow meters (see Figure 3). The water saturated CO\textsubscript{2} was produced by letting dense phase CO\textsubscript{2} flow slowly through a tank with liquid water (wetting chamber). The saturation concentration of water in CO\textsubscript{2} is temperature dependent (Figure 1), so the temperature of the wetting chamber will affect the amount of water in the wet CO\textsubscript{2}. The temperature was fixed at 20 °C in the present study. Since the system was continuously dosed, the wet CO\textsubscript{2} was possibly not in complete equilibrium, but this was compensated for by adjusting the mixing ratios of dry and wet CO\textsubscript{2}. The dosing unit could deliver water concentration range from 10 ppmv to about 2500 ppmv at 20 °C, depending on the flow rate. Higher flow gives less time to saturate the CO\textsubscript{2}.

2.3. Analysing module

There are several techniques for measuring water concentration in gases, but the high pressure makes it difficult to measure the water content of the dense phase CO\textsubscript{2} directly. Therefore the pressure was reduced from 95 bar to 2 bar in the venting line, after which the CO\textsubscript{2} entered the analysing module as a gas phase. This module consist of various instruments for measuring impurity concentrations, but only the water analyser (a tunable diode laser) and the oxygen analyser (a zirconia sensor) were used in the present work. The gas flow to the analysers was controlled by a mass flow controller to ensure a stable gas flow rate.
2.4. Corrosion rate

The corrosion rate was determined from weight loss after the corrosion products sticking to the steel surface were removed in an inhibited HCl solution. Since one mole of iron consumes one mole of water when the steel corrodes the corrosion rate can also be calculated from the water consumption rate according to equation 1. The sensitivity is about 0.5 mm/y during continuously dosing of CO2 and water. A higher sensitivity can be achieved by closing both the dosing and venting system for a certain period of time, allowing the water in the closed system to be consumed by corrosion and then measure the decrease in water concentration.

\[ CR = \frac{\text{CH}_2\text{O} \cdot \rho_{\text{CO}_2} \cdot V_{\text{CO}_2} \cdot \text{MW}_{\text{Fe}}}{A_{\text{Fe}} \cdot \rho_{\text{Fe}} \cdot \text{MW}_{\text{CO}_2}} \text{100} \]  

where, \( CR \) is the corrosion rate (mm/y), \( \text{CH}_2\text{O} \) is the consumed water (ppmv/y), \( V_{\text{CO}_2} \) is the volume of dense phase \( \text{CO}_2 \) in the loop (L), \( \rho_{\text{CO}_2} \) is the density of \( \text{CO}_2 \) (g/cm\(^3\)), \( \text{MW}_{\text{CO}_2} \) is the molar mass of \( \text{CO}_2 \) (g/mol), \( A_{\text{Fe}} \) is the area of the carbon steel sample (cm\(^2\)), \( \rho_{\text{Fe}} \) is the density of iron (g/cm\(^3\)), \( \text{MW}_{\text{Fe}} \) is the molar mass of iron (g/mol).

2.5. Materials

The corrosion coupons were cut from carbon steel foils. The chemical composition of the steel which is denoted S355J2 (a type of mild steel equivalent to St52-3N) is shown in Table 2. Shavings from the same material were packed in a mesh cylinder and placed in the test section to increase the exposed steel surface area.

Table 2. The chemical composition (wt. %) of the carbon steel grade S355J2.

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Cu</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>S355J2</td>
<td>≤0.2</td>
<td>≤1.6</td>
<td>≤0.55</td>
<td>≤0.030</td>
<td>≤0.030</td>
<td>≤0.55</td>
<td>Balance</td>
</tr>
</tbody>
</table>

The coupons were first washed in acetone and then in isopropanol, wiped with a lint free tissue and ground by hand with a 600 grit abrasive paper.

High purity (5.0) CO2 from a bottle with riser was used in this work.

3. Results

One blank test (without corrosion coupons) and five corrosion experiments were performed. Test conditions and results are summarised in Table 3.

Table 3. Test conditions and corrosion rate for the experiments performed in the loop at pressure of 95 bar with the flow rate of 0.4 m/s.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Temperature, (°C)</th>
<th>Water conc. (ppmv)</th>
<th>Exposure (h)</th>
<th>Sample surface area (cm(^2))</th>
<th>Corrosion rate (μm/y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp1 (blank)</td>
<td>25</td>
<td>150 – 2360*</td>
<td>362</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Exp2</td>
<td>25</td>
<td>570 – 2380*</td>
<td>422</td>
<td>1246</td>
<td>0.8</td>
</tr>
<tr>
<td>Exp3</td>
<td>27 → 12**</td>
<td>2300</td>
<td>189</td>
<td>1252</td>
<td>1.4</td>
</tr>
<tr>
<td>Exp4</td>
<td>8 → 14**</td>
<td>2300</td>
<td>551</td>
<td>1254</td>
<td>1.0</td>
</tr>
<tr>
<td>Exp5</td>
<td>35</td>
<td>2500</td>
<td>334</td>
<td>233</td>
<td>N/A</td>
</tr>
<tr>
<td>Exp6</td>
<td>25</td>
<td>100</td>
<td>890</td>
<td>251</td>
<td>0.2</td>
</tr>
</tbody>
</table>

* Ramping of concentration to five different water levels.
** Temperature ramping, constant water levels.
3.1. Ramping water concentration

The blank test (Exp1) was performed in order to fine tune the water dosing system and to see how the system reacted when dry CO₂ was injected (referred to as a dry-up period) in the loop that was full of moist CO₂. As the water concentration in Exp1 never reached the solubility limit, no pool of precipitated water is expected in the loop. Injection of dry CO₂ will therefore decrease the measured water concentration according to a first-order system if there is not too much adsorption and desorption of water on the loop walls [29]. The dry up rate which is shown in Figure 6 (green line) was used for comparison with dry up lines in experiments where the solubility limit of water was exceeded and where the shift in the dry up curve depended on the amounts of precipitated water.

Exp2 (Figure 4) was carried out in the same manner as the blank test, but with carbon steel coupons present. The corrosion rate was so low that it could not be detected from water consumption (equation 1) when water was continuously replenished. Therefore, the system was closed for three different periods of time (grey area in Figure 4, CO₂ routed directly to the analyser) to measure the decrease of the water concentration. These closed periods did not give a significant decrease of the water concentration, indicating again that the corrosion rate is very low. The average corrosion rate measured by weight loss after the exposure was 0.8 μm/y.

![Figure 4. The measured water level of the exhaust gas (purple line) of Exp2 plotted as a function of time. The grey area indicates closed loop with no dosing, the CO₂ would then bypass the loop and go directly to the analyser. Exp2 was performed at 25°C, 95 bar and 0.4 m/s flow velocity.](image)

3.2. Ramping temperature

To prevent liquid water precipitation and entrainment of droplets in the dosing lines, the dosing unit was not used to feed fully water saturated CO₂. To reach and exceed the water solubility limit the loop system was therefore cooled a few degrees (see Figure 1) in Exp3 and Exp 4. In Exp3 (Figure 5) the temperature was decreased stepwise from 27 °C to 12 °C. The injected CO₂ contained 2300 ppmv water, and the solubility limit was reached when the temperature became 15°C. This can be seen as a reduction in the dissolved water concentration at lower temperatures, i.e. water precipitation takes place (see also Exp4, Figure 6).

The saw tooth shape of both the temperature and the water concentration curves is due to the defrosting of the cooler. In an attempt of getting rid of these, the defrosting program of the cooler system was stopped when the temperature reached 16 °C. This worked fine until the cooler was blocked with ice at around 130 hours, leading to an increase in temperature, as shown in Figure 5.

![Figure 5. The temperature and water concentration as a function of time for Exp3 and Exp4.](image)
Figure 5. The Exp3 experiment was performed at the temperature 25°C, 95 bars of pressure, and with a flow of 0.4 m/s. The measured water level of the exhaust gas (purple line) and the temperature (orange line) are plotted as a function of time.

The mutually correlated relationship between the water and temperature curves is clearly observed in Figure 6, Exp4. Since the measured water concentration is lower than the actual dosing rate (about 10 percent), precipitation of water inside the loop system is occurring. This is also supported by the increase of water concentration seen when the temperature was increased to 25 °C. The water concentration should increase to 2300 ppmv which is the dosing rate, but instead it increased to 2800 ppmv. The CO₂ in the loop system is now dissolving the previously precipitated water.

When dry CO₂ was injected after 515 hours (see enlarged Figure 6), the measured water concentration did not follow the calculated diluting rate (red line) or the previously measured dry-up period from Exp1 (green line). Instead it forms a plateau, and when all of the precipitated water was dissolved all lines aligned to form the same trend. The corrosion rate in Exp3 was found to be 1.0 μm/y and in Exp4 1.4 μm/y by weight loss (shown in Table 3).
3.3. Steady temperature and water concentration

In Exp5 the carbon steel coupon was exposed to super critical CO$_2$ with about 2500 ppmv water, as shown in Figure 7 below. This is as the highest water content the wetting system could deliver. There are some periods in the beginning and in the end which has a lower content of water. In the beginning the system needed some time to achieve the right level and in the end of the experiment, the humidifier in the dosing unit ran out of water. Four closed loop periods (between the green and blue lines) was carried out to control and adjust the water level to about 2500 ppmv of water. After the third close period (230 - 255 hours) the water concentration decreased with about 100 ppmv in the loop. If this decrease in water concentration was caused by corrosion alone, it would correspond to a corrosion rate of 59 μm/y (calculated with equation 1).

The weight loss was too low to give a conclusive corrosion rate for Exp5.

Figure 7. Exp5 was performed at the temperature 35°C, 95 bar pressure, and a flow of 0.4 m/s. The measured water content of the exhaust gas (purple line) and the temperature (orange line) are plotted as a function of time.

Figure 8 shows Exp6, a long term experiment which started with about 130 ppmv and ended with about 100 ppmv of water in the CO$_2$. Corrosion rate determined by weight loss was found to be 0.2 μm/y.
3.4. Corrosion coupons

A small amount of corrosion products were found on all coupons (see Figure 9). There was more products on the specimens surfaces exposed in Exp3 and Exp4, than Exp2 and Exp5. This is expected since the corrosion rate of Exp3 and Exp4 was somewhat higher. Exp6 had most products on the surface, which cannot be explained from the corrosion rate alone. EDS investigation documented that the surface products contained a lot of sulphur, which was contamination from another experiment that was carried out with H2S and SO2.

The EDS analysis (Figure 11a) of the other coupons indicated iron carbonate on the surface. The thickness of the corrosion products was calculated by film weight to be around 100 nm thick if evenly distributed on the coupons. The similar was found by using a Monte-Carlo simulation (CASION[30]) compared to the EDS analysis (see Figure 10), assuming that all the substrate was iron carbonate [29]. The program can simulate a large amount of electron trajectories in a solid and intend to represent the actual interaction conditions in SEM. Iron carbonate was used as the substrate, and penetration depth at different acceleration voltages was studied. When the iron carbonate atomic ratio; FeCO3, 1:1:3 is moved towards an increasing level of iron in the EDS analysis, we can assume that the accelerating voltage is so high that it goes through the iron carbonate layer and into the carbon steel matrix underneath.
Figure 10. The measured element concentration (atomic per cent) and the simulated penetration depth versus acceleration voltage of the electron beam [29].

Figure 11. (a) An EDS analysis of Exp2. (b) A profile picture with extracted profile curve taken of Exp5.

The corrosion products were removed with inhibited HCl solution and a visual inspection show no localised attacks on the surface. The profilometer scan (Figure 11b) of the surface also verified this.

4. Summary and discussion

The present work has shown that a free water phase is essential for corrosion in dense phase CO₂. In the absence of free water the corrosion rate was less than 1 μm/y which is not regarded as a threat for the pipeline integrity. But it increased slightly (1.4 μm/y) when small amounts of water precipitated. It should be noted that the measured corrosion rates were (Table 3) close to the practical detection limit and the relative error might be high.

When free water is present, it is likely that the corrosion rate depends on the amount of liquid water that is present. The corrosion rate in Exp4 would therefore be higher if the injection rate of wet CO₂ had been higher (more liquid water would have precipitated in the loop). The presence of a bulk water phase will definitely increase the corrosion rate. It has been claimed that for more than three monolayers of water on the surface the properties
approach those of bulk water [31]. In atmospheric condition this happens around 60 to 80 percent of relative humidity (in air) [32]. Dense phase CO₂ with water is of course very different from air, but if it is assumed that the same principle applies, a few monolayers of water would form between 2000 and 2500 ppmv at 25 °C and 100 bar. This can explain the presence of the tiny amount of corrosion products that were found on the exposed steel surfaces. The average thickness of the corrosion product layer was about 100 nm. A much thicker iron carbonate film is usually required [33] to give good corrosion protection (passivation) in oil and gas pipelines. Therefore it is possible that the corrosion process was limited by water supply in the present experiments rather than a protective corrosion product film on the surface.

There are thousands of papers that report very high CO₂ driven corrosion rates (0.1 to 50 mm/y) when free water phase is present. Water did clearly precipitate in Exp3 and Exp4, but the resulting corrosion rate was still low (<< 0.1 mm/y), and more importantly it was much lower than what would be expected if all available free water was consumed by corrosion. Consumption of all free water would give an average corrosion rate of about 0.4 mm/y according to equation 1. How the free water phase is distributed in the CO₂ stream in the loop is not documented. It is possible that the precipitated water never reached the carbon steel coupons, but was adsorbed on the wall or was trapped in dead legs and crevices. The amount of precipitated water was calculated to be about five gram in Exp4.

An increasing flow rate can increase the corrosion rate by enhancing the transport of corrosive species toward, or remove protective product from, the surface. The flow rate and flow pattern also affect how water is entrained in oil phases[34] and it is assumed that free water can be entrained in a CO₂ in a similar way. It should be noted that the density difference between water and liquid CO₂ is less than between water and oil. The free water does not need to be lifted up by the flowing CO₂ if the water precipitates directly as droplets in the CO₂ bulk phase. So it could be likely that some, if not all, of the precipitated water is entrained and over saturation (super saturation) is need to get water on the carbon steel surface. No published data was found addressing entrainment of water in dense phase CO₂.

A wide range of corrosion rates in dense phase CO₂ has been reported in the open literature, from no corrosion [4, 8, 15-21] to 3.5 mm/y [22-24], depending on the water content, pressure, and temperature. The large spread in reported corrosion rates for apparently the same experimental conditions indicates the technical difficulties of such corrosion experiments and the importance of having full control of the water distribution in the system. The experimental setup used in the present work is the first of its kind allowing water injection to be droplet free since the water saturation is taking place outside the loop. In previous published work with dense phase CO₂ the water was typically injected as a liquid. When corrosion rates of 0.01 mm/y and higher were reported, the exposed samples had often droplet shaped attacks on the surface. This could indicate that the sample either had been hit by water droplets or that water had condensed on the surface during the experiment [29]. In the latter case, the situation changes and CO₂ corrosion in water (free water phase) will occur. It is well known in the literature that this type of corrosion will have high corrosion rates, even up to 40 mm/y until the water becomes saturated with corrosion products [4].

The corrosion process will continue until the water is consumed, leaving droplet-shaped corrosion product clusters with localised attacks underneath [29]. In such cases the transport of water to the surface is limiting the corrosion rate. As shown in Figure 9, the coupons exposed in Exp3 and Exp4 had most corrosion product on their surfaces. They also were exposed to higher degree of saturation, even though both Exp2 and Exp5 were exposed to a higher concentration level of ppmv (2300 and 2500 versus about 2000 ppmv). The duration of Exp3 was shorter than both Exp2 and Exp5, but still more visible corrosion products. It seems like the degree of saturation is the key factor here, which control the deposition on and the hydration of the surface. Further supporting this hypothesis is the observation made in Exp5, where the temperature was the highest, but the corrosion rate was below detection limit and low amounts of products were present on the surface. Normally in free water/CO₂ system, the corrosion rate increases with temperature [35]. The degree of saturation in Exp5 is among the lowest only Exp6 was lower, and this is probably the reason for the low corrosion rate. Unfortunately, no good conclusion can be drawn from Exp6, except for the low overall corrosion rate (0.2 μm/y), since it was contaminated with impurities from other experiments. It can of course be argued if the difference in corrosion rate is significant between the experiments, but the amount of products is clear. It should be noted that the average corrosion rate is discussed here, thus, some periods of the experiments can have higher or lower rates.

In a CO₂ transport situation, where cooling or heating of the CO₂ in the pipeline comes from the outside, the water would precipitate on the carbon steel walls if saturation limits are exceeded. So as long as the water...
concentration in the CO₂ is lower than the solubility limit of the coldest spot in the pipeline, it would be safe from a corrosion point of view. These observations would only be valid for CO₂/H₂O systems, if other impurities are introduced the conditions could change.

5. Conclusion

The corrosion rate of carbon steel in dense phase CO₂ was < 1 μm/y as long as the water is dissolved. By increasing the water content slightly above the solubility limit, the average corrosion rate increased to 1-1.4 μm/y. No localised corrosion was observed on the carbon steel coupons. For all cases a thin non homogeneous layer of FeCO₃ corrosion products was identified by SEM/EDS.

It seems like the degree of water saturation in CO₂, or formation rate of free water phase is the determining factor for corrosion and formation of protective corrosion products on the surface, and not the dissolved water concentration.

The results obtained in the present study indicate that corrosion will not threaten the integrity of CO₂ transport pipelines as long as the water is kept below the solubility limit. However, water control and water analysis will be an important part of a CCS pipeline integrity system and operating procedures.

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Chapter 8

Acid reactions in hub systems consisting of separate non-reactive CO$_2$ transport lines

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Acid reactions in hub systems consisting of separate non-reactive CO₂ transport lines

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ABSTRACT

Corrosion in carbon steel pipelines is a major threat for safe CO₂ transport, and there have been several projects studying the corrosivity of impurities which could be found in captured CO₂. Often only two or three of these impurities have been present while performing the experiments. Although these experiments have delivered valuable knowledge, there are still questions of what happens when impurities are present together. Furthermore, several transport pipelines may deliver CO₂ to a main pipeline through a hub system for storage or utilization, and while these streams may be safe individually, the blend in the main pipeline could create components that are hazardous for carbon steel.

The present study used a novel experimental setup to realistically simulate a CO₂ hub. Three individual “pipelines” were joined inside a glass tube in a transparent autoclave. The three “pipelines” were connected to three different reservoir pumps, simulating different capturing sources with dissimilar types of impurities. This gave a mix of low (ppmv) levels of oxygen (O₂), sulphur dioxide (SO₂), hydrogen sulphide (H₂S), nitrogen dioxide (NO₂), and water (H₂O). Three different experiments were performed with concentrations ranging from 5 to 35 ppmv of the impurities and at a total pressure of 100 bar at 25°C. All impurities were measured before and after the streams were mixed in the autoclave.

The experiments revealed that reactions between certain species occurred even at concentrations as low as 5 ppmv, but the reaction products were not considered detrimental in terms of corrosion. If the impurity concentrations were increased to about 35 ppmv, acids and solids were produced, and the situation became unacceptable for carbon steel.

1. Introduction

Carbon capture and storage is needed to meet the goal set by the International Energy Agency (IEA) (Energy Technology Perspectives, 2010) and the Intergovernmental Panel on Climate Change (IPCC) (IPCC, 2019). This will involve CO₂ capture, transportation, and permanent storage, and it is essential that the cost of the overall processes is kept as low as practically possible. Carbon steel is the only material that is economically feasible for long transport pipelines. However, the captured CO₂ may contain small amounts of additional components (called impurities in the present paper), which may be corrosive to carbon steel or cause operational problems. A quality specification for the CO₂ to be transported is therefore crucial to ensure the integrity of the pipeline. Several CO₂ specifications have been suggested, but most of them have not been tested in realistic experiments. Consequently, the validity of these specifications is unclear. Some impurities (i.e. NO₂ and SO₂) have concentration limits based on health, safety, and environmental reasons, while possible chemical and corrosion reactions have not been considered. Reaction between many of these impurities is likely to occur (Dugstad et al., 2014), but the practical consequences have not been investigated in detail. Table 1 shows the large range of impurity limits that have been suggested in various literature sources (IEAGHG, 2019; NETL, 2013; Mohitpour et al., 2012).

Previous work from our research group (Dugstad et al., 2014; Dugstad and Morland, 2016; Halseid et al., 2014) has shown that strong acids and elemental sulphur may form in CO₂ blends that are within established quality specifications (NETL, 2013; de Visser et al., 2008). The COORAL-project did also find traces of sulfuric acid and elemental sulphur in both gas and supercritical CO₂ experiments (Ruhl and Kranzmann, 2013; Yevtushenko et al., 2013; Yevtushenko et al., 2014). If these impurities react in the capture process they can most likely be removed before they enter the transportation system. However, it has...
been suggested that future transport projects will consist of multiple
capturing sites which deliver CO₂ to a hub system with a main transport
line, either as pipeline or by ships. One example of this is the full-scale
CCS demonstration projects in Norway (OED, 2016), where the cap-
tured CO₂ will come from three different capturing sites: a concrete
factory, an ammonia plant, and a waste fuelled energy recovery plant. It
is likely that these three CO₂ sources will have different impurity
contents that may be unreactive within each individual stream, but
reactions could occur at a later stage when the streams are mixed in the
transportation network.

The aim of this study was to identify chemical reactions that are
likely to occur in a realistic mix of impurities in CO₂ and/or verify if
there is a safe operation window for transporting impure CO₂ in pipe-
lines without creating a corrosive environment for the pipeline mate-
rial. The impurities in Table 1 were split up in three different transport
streams so the impurities could not react before the reaction chamber.
In so, they represent three individual safe CO₂ streams without chemical
reaction and corrosion. Mixing in a hub system was simulated by in-
jecting these streams in an autoclave (reaction chamber). The present
work applied a novel transparent autoclave that was built in-house.
Reactions between impurities were studied visually and with high
performance gas analysers.

2. Materials and methods

The experimental setup consisted of three parts; the reaction
chamber (transparent autoclave) with camera, an impurity injection
system, and the analysing module.

2.1. The reaction chamber

A transparent autoclave (Fig. 1) was used as reaction chamber to
allow in-situ visual observation of the experiment. The autoclave body
was made of 316 stainless steel, and it had a volume of 330 ml with a
maximum working pressure of 200 bar. The transparent windows con-
sisted of soda lime glass (exposed to the CO₂ phase) and polycarbonate
plates (exposed to air) which acted as pressure support for the lime
glass. A magnetic stirrer was placed in the bottom of the autoclave to
promote mixing of the CO₂ streams.

A T-shaped glass tube was placed inside the autoclave to simulate a
CO₂ hub where three different streams were mixed. The first injection
line delivered CO₂ with small levels (see Tables 3–5) of O₂, SO₂, and
H₂O. The second stream contained CO₂ with H₂S and the third stream
contained CO₂ with NO₂. Fig. 2 shows the hub with the inlet tubes
marked.

A camera was used to take still-images inside the autoclave, and a
LED-lamp was used to achieve constant light conditions. Typically, one
still image was taken every 10 min. The images were used to create
videos showing the experimental development.

The temperature (25°C) and the pressure (100 bara) were kept
stable during all experiments.

2.2. Impurity injection system

The impurities were injected as pre-mixed solutions of CO₂ and the
respective impurities. Three high precision piston pumps (266 ml vo-

cume) from Teledyne was used for this purpose. All pumps were held at
a pressure slightly more than 100 bar. In addition, pure CO₂ (sometimes
with H₂O) from a booster pump was also injected to the autoclave. The
latter stream was controlled by a liquid pressure regulator that ensured
a constant pressure of 100 bar. All four streams were injected at the
same rates (about 25% each), but if one of the piston pumps was
stopped, the pure CO₂ flow would increase correspondingly to maintain
the pressure and the same total flow. The piston pumps needed to be
filled with four times higher concentration since each pump represent
one fourth of the flow. Thus, the concentration at the tip of the injection
tubes and inside the glass tee was higher since the stream had not yet

Table 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration (ppmv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>20 – 650</td>
</tr>
<tr>
<td>O₂</td>
<td>10 – 40000</td>
</tr>
<tr>
<td>SO₂</td>
<td>10 – 50,000</td>
</tr>
<tr>
<td>H₂S</td>
<td>20 – 13,000</td>
</tr>
<tr>
<td>NO₂</td>
<td>20 – 2500</td>
</tr>
</tbody>
</table>

* Often given as 100 ppmv for HSE concern.

Fig. 1. Transparent autoclave with camera and injection tubing.

Fig. 2. Glass tee tube (simulated CO₂ hub) with three individual injection lines. The glass tee was located inside the autoclave.
been mixed (diluted) with the other streams. With the applied settings the piston pumps lasted about 24 h before they had to be refilled.

The exhaust CO₂ was taken to a heated vaporizing regulator (to prevent hydrate formation and precipitation of impurities) where the pressure was reduced from 100 to 1 bar before the gas was sent to the analysing module. A mass flow controller from Bronkhorst was placed at the low-pressure side to regulate the exhaust flow rate. Normally this flow was about 0.85 g/min during the experiment.

The water content in the “pure” CO₂ stream could be adjusted at any concentration from nominally bottle dry to saturation by mixing dry CO₂ and CO₂ saturated with water at 25 °C at a desired ratio using a mini Cori-flow controller from Bronkhorst. Therefore, no liquid water was injected into the reaction chamber in these experiments, only water fully dissolved in CO₂.

2.3. Analysing module

The analysing module consisted of two multicomponent laser-based analysing systems (Emerson CT5400 and ap2e ProCeas) and one oxide-based analyser (Michell XZR400) that were set in series to analyse the same gas. The system was configured in such a manner that either the exhaust CO₂ from the autoclave, or one of the individual CO₂ streams could be sent directly to the analyser module. Thus, the consumption of impurities could be detected as a measured difference in inlet and outlet concentrations. The CT5400 is a Quantum Cascade Laser (QCL) that could continuously analyse SO₂, NO, NO₂, N₂O, CO, and CO₂. The ProCeas is an Optical Feedback Cavity Enhanced Absorption Spectroscopy (OFCEAS) that uses infrared laser to continuously measure H₂O, H₂S, and O₂. None of the analysers could handle a pressure of 100 bar so the pressure was reduced to about 1 bar prior to the analysis. The O₂ content was analysed with a XZR400 from Michell in the first two experiments (Hub01 and Hub02), while the laser based ProCeas was used for the last experiment (Hub03). The XZR400 has a zirconium oxide sensor with metallic sealed reference. The sensor could not be exposed to corrosive or flammable gases, so the sampling gas had to be scrubbed through a scavenger which removed SO₂, NO₂, and H₂S. The instrument was therefore located as the last analyser in the gas analysis line. It was sometimes observed that right after a new impurity injection was started, the O₂ signal was too low during a transient period, before it came back to the expected level. The exact reason for this not understood, but it could be related to remnants of impurities in the analysis system.

The accuracy of the analysers was about 1 percent of the full scale, which amount to about ± 1 ppmv for SO₂, NO₂, and H₂S. While H₂O and O₂ had an accuracy of ± 3 ppmv. Since the measurements was performed at ambient pressure, ppm volume equals ppm mole at 25 °C and 1 bar. The analysers report concentrations in ppmv, therefore ppmv was used in this paper. When analysing the impurities from a 100 bar experiment it is important to remember that the reported ppmv are equal to ppm mole and the volume in ppmv is not related to the volume of the liquid CO₂ or the autoclave.

The heated vaporizing regulator could in theory trigger some additional reactions or precipitation since phase transition occurred at somewhat elevated temperature (45 °C). The solubility limits for acid and solids would also change in this environment due to the pressure transient through the regulator. This might give some deviation between the measured concentration at 1 bar and the real concentration at 100 bar.

Replacing the autoclave volume of liquid once took about 6.5 h with the applied settings, and about 18 h was needed to reach a stable impurity level (3 times volume replacement would give about 95% of the correct value). The sampling line from the autoclave to the analysers was made of 1/16” tubing, which gave a lag time of about 8 min.

2.4. Chemicals

Gas qualities used to make pre-mixed solutions of CO₂ are listed in Table 2.
was started consecutively one by one. For the latter case the order was somewhat different from experiment to experiment, but it was typically started by first injecting SO$_2$ and O$_2$ (first stream). Once the concentrations in the autoclave had stabilized, indicated by stable measurements of the exhaust gas, injection of the next impurity stream was started (often this was NO$_2$). After the values had stabilized, injection of the last impurity stream with H$_2$S was started. The order of impurity injection varied in order to detect any reactions that might occur with only two or three streams.

3. Results

Three experiments were conducted with three different concentration levels (5, 10 and 35 ppmv) of the key impurities. The concentration levels were given as what the concentration would be when mixed in the autoclave if no reactions occurred. The concentrations in the stock solutions were higher. These data are listed in the tables (Tables 3–5).

3.1. Hub01 (5 ppmv)

This experiment was carried out with stock solutions in the 22–110 ppmv range. The target concentration inside the hub was 5 ppmv for SO$_2$, NO$_2$, and H$_2$S (see Table 3). The H$_2$S stock solution was unfortunately contaminated with water, resulting in much higher water levels than what was initially intended.

The experiment was divided in two injection periods, the first was at 0–46 h (Fig. 3) and the second was at 115–164 h (Fig. 4). At 0 h all impurities (all four streams) were injected at the same time (Fig. 3). If no reactions occurred, then the concentrations should stabilize at the values given in Table 3 after some time (about 18 h). This was not the case, based on the analysis results, suggesting that one or more reactions were occurring.

The water content, mainly originating from the H$_2$S stock solution, increased as expected, but the rest of the impurities did not reach their target levels. H$_2$S was not detected at all. NO$_2$ was almost zero (about 0.2 ppmv) until the H$_2$S injection was stopped at 26 h, after which NO$_2$ increased up to the target value. SO$_2$ was measured at higher concentrations than the target level and O$_2$ was much lower than the target level. SO$_2$ and O$_2$ impurities were injected from the same piston pump in a ratio of 1:3. NO was detected even if it was not injected. At 26 h the H$_2$S injection was stopped and the system changed considerably, with a trend of all other impurities slowly changing towards the target (i.e. inlet) levels. The H$_2$S injection was started again at 41 h, resulting in mostly the same situation as when H$_2$S was injected for the first time. One difference, however, was that the oxygen content was lower and continued to decrease towards zero. At 46 h, injection of all impurities was stopped, and only pure CO$_2$ was injected.

The second injection period started at 116 h (Fig. 4). This time the impurity injections were not started at the same time. Injection of SO$_2$/O$_2$ was started first and when they stabilized, the H$_2$S injection was started (136 h). To reduce the stabilization time for H$_2$S, it was injected at a higher rate for the first three hours, and then decreased to the correct set-point. At 143 h the NO$_2$ injection was started, and the system changed character: SO$_2$ and NO increased while H$_2$S and O$_2$ decreased. NO$_2$ was not detected and at 154 h O$_2$ and H$_2$S reached the lower detection limit. At 163 h, injection of all impurities was stopped.

Still-pictures were taken repeatedly during the experiment (Fig. 5). Some colour changes inside the chamber were observed, but no separate liquid phases or solids could be identified.

3.2. Hub02 (10 ppmv)

The target values for this experiment were 10 ppmv for SO$_2$, NO$_2$, and H$_2$S. Table 4 shows the concentration injected (stock solutions) and the expected (theoretical) concentration after mixing, presuming that no reactions took place. The water content was initially high (about 250 ppmv) in this experiment, due to remnants of water in the impurity injection lines from a previous experiment.

The experiment was started with injection of SO$_2$/O$_2$ (0 h), and O$_2$ and SO$_2$ increased in the following period, see Fig. 6. At 12 h the injection rate of SO$_2$/O$_2$ was temporarily increased (to reach the target faster), which caused an increase in the SO$_2$/O$_2$ content. At the same time (12 h) injection of H$_2$S was also started, and H$_2$S was detected shortly after. Injection of NO$_2$ was started at 19 h, and this caused an increase of the SO$_2$ content to a stable plateau of about 20 ppmv while the H$_2$S content decreased to zero. The O$_2$ content increased intermittently before it decreased rapidly and after some time stabilised around 8 ppmv. This is not an expected behaviour and the reason for it is not quite understood. It could be caused by reactions in the wet scavenger compartment. In a test experiment (not shown) we confirmed that reactions involving oxygen can take place here. The oxygen in this and the previous experiment was measured with a zirconia sensor. This type of sensor is sensitive to flammable and corrosive gases, therefore the gas needed to be scrubbed before analysis. NO was detected after the NO$_2$ injection was started, and it increased slowly until the abrupt drop of O$_2$ after which it slowly decreased toward zero. NO$_2$ was detected after the abrupt O$_2$ drop, and it increased slowly with time.

At 84 h the NO$_2$ injection was stopped and at 108 h the experiment stopped due to a failure of the analyser. Before this occurred, the concentration of the remaining injected impurities moved towards their target injection values.

Still pictures (Fig. 7) taken during the experiment show colour change inside the chamber and in the lower right end of the glass tube there is some colour change at 62 h (Fig. 8).

3.3. Hub03 (35 ppmv)

For the last experiment the target concentration for SO$_2$, NO$_2$, and H$_2$S was increased to about 35 ppmv. There was some water...
contamination in the injection system, resulting in a water content of about 120 ppmv. Table 5 sums up the stock and expected solution concentrations.

SO₂ and O₂ was injected first, see Fig. 9, and after about 20 h the injection of NO₂ was started. This led to a decrease in the O₂ concentration. To verify that this decrease was real, the SO₂/O₂ stock solution was routed directly to the analyser (shown as discontinuous lines in Fig. 9 between 41–45 h), and it proved that the oxygen consumption was real. H₂S was introduced to the system at 51 h, and an immediate change in impurity concentrations was observed. The water concentration increased together with SO₂. At the same time, O₂ decreased rapidly while, NO₂ decreased slowly. H₂S was not detected until 10 h after the NO₂ injection was stopped at 101 h. The system then slowly reverted back to the original target values. When H₂S was stopped at 134 h the system was not affected, except for the decrease in water because contaminant water was injected together with H₂S. Finally, injection of O₂/NO₂ was stopped after 145 h.

Still-pictures (Fig. 10) acquired during the experiment showed that both, colour change, and precipitation of liquids and solids occurred inside the autoclave. The glass went from clear to yellow, then some solids and later liquids formed, and in the end the glass tube turned opaque. The first sign of precipitation occurred at 52 h (Fig. 9) about 1 h after the H₂S injection started, observed as blackening of the bottom glass tee (Fig. 10). At 53 h the first sign of dew occurred on the centre
tube in the glass tee, and both the black deposits and the dew were clearly visible at 62 h (picture c in Fig. 10). At 65 h the first sign of droplet formation became visible, and after this the liquid accumulated fast. The view became impervious after NO2 was stopped. The liquid inside the autoclave was analysed using ion chromatography after the experiment. Both SO4^{2-} and NO3^- were detected, which most likely originated from sulfuric acid and nitric acid formed during the experiment. The molar ratio was about 10:1 of SO4^{2-} (sulfuric acid) to and NO3^- (nitric acid). At about 68 h the NO2 pump was refilled with a more dilute stock solution with a theoretical concentration of 20 ppmv NO2. This could explain some of the decrease occurring at this time.

4. Discussion

In summary, the present test campaign has demonstrated that chemical reactions occur for certain blends of impurities. However, not all blends caused reactions and not all reaction products formed corrosive species. When corrosive species did form, the amount increased with increasing impurity content.

4.1. Fully dissolved reaction products

The first experiment (Hub01) clearly showed (Fig. 3) that several reactions occurred when all impurities were introduced simultaneously,
since none of the impurities reached their target concentrations. However, because all impurities were introduced at the same time it was difficult to identify possible individual reactions. The impurities were therefore added sequentially for the rest of the work.

In the second injection period of Hub01 there were no reactions until NO2 was introduced, demonstrating that a mixture with H2S, H2O, SO2, and O2 was stable under these conditions. This contrasts with observations in other systems, where reaction of H2S and O2 have been reported (Craig, 2002; Song et al., 2010; Song et al., 2011; Song et al., 2012). When the NO2 injection was started the second time (143 h in Fig. 4), indication of reactions became clear. The H2S content decreased at the same amount as SO2 increased. Another interesting observation was that the O2 content was reduced and after some time fully consumed. The new species NO was detected, while the NO2 level was at the detection limit. These trends were also observed in the other experiments, except that O2 did not completely disappear in Hub02 and Hub03, and the measured NO2 concentration was then higher. There was not much difference if NO2 was injected before H2S or vice versa, both had to be present simultaneously for reactions to occur.

A more detailed study of the measured and theoretical impurity content is shown in Figs. 11 and 12. The theoretical concentration is the calculated concentration if no reactions occurred (injection and dilution). With exception of Hub03, where liquid acid precipitated, the SO2 analysis was close to the sum of SO2 and H2S that was injected, clearly proving that all H2S was converted to SO2 in the presence of NO2. It can also be observed that NO2 was present in the exhaust feed only if O2 was also present. Furthermore, if no liquid acids were formed, the sum of NO and NO2 was always the same as the injected NO2 level.

It was demonstrated multiple times that H2S, O2, and SO2 can coexist (at least up to about 35 ppmv) together with water without reactions taking place, suggesting that NO2 is a very important reactant under these conditions. These observations lead to the proposal of the following reaction:

H2S + NO2 + O2 → SO2 + H2O + NO

(1)

H2S, NO2, and O2 react to produce SO2, H2O and NO. This is very clear in the second period of Hub01. It should be stressed that this is assumed to be the overall reaction, not including possible intermediate reactions. However, there are several indications that reaction 1 is not occurring under all conditions. For example, in Hub02 after the NO2 injection was stopped, the SO2 level continues to remain high for many hours (green and blue lines in Fig. 11b) until NO/NO2 has been removed from the system, after which the other impurities go back to their injection levels. This could indicate that H2S does not react directly with O2, but rather with NO2. If H2S and O2 could react directly, the SO2 level should have remained high also after NO2 had been removed from the system. Apparently even low concentrations (ppb) of NO2 is enough to oxidise H2S. It is therefore suggested that the following reactions can occur either in parallel with, or instead of, reaction 1:

H2S + 3NO2 → SO2 + H2O + 3NO

(2)

NO2 + ½O2 → NO3

(3)

Thus, it is suggested that NO2 is acting as an oxidation agent for H2S to form NO, SO2 and H2O, while O2 reacts with NO to form NO2 that again can react with H2S. Clear indication of this is shown in Fig. 11b, where the SO2 level (green line) continues to remain high until NO/NO2 is completely removed from the system, after which H2S and SO2 return to their injection levels. If NO2 was not needed to oxidize H2S, the SO2 should have followed the dashed blue line, which would represent dilution of already reacted H2S. Further support for this is the fact that NO2 is not detected if also O2 is present in the exhaust gas. Since the SO2 concentration follows the injection levels of the reactants to an almost perfect fit of the theoretical values (Figs. 11 and 12), it must mean that the reactions (1) - (3) are fast compared to the residence time (approximately 18 h).

However, there is some discrepancy for the oxygen analysis. Apparently, more O2 is consumed than what can be accounted for with reactions (1) - (3). Some of this is most likely related to analytical challenges (see Section 2.3), but it could also be related to production of certain species that were not analysed for. When NO2 was introduced to the system there were always observed some irregularity with the oxygen analysis. This could indicate that some form of reaction between O2 and NO/NO2 is taking place and producing some unidentified species.

4.2. Precipitated reaction products

Even though most of the reactants and products could be accounted for in the experimental campaign (see the previous paragraph), additional precipitated products were visually observed in Hub02 and Hub03. In Hub02 there was just a slight blackening of the glass tee, and the small amount of product that formed was not enough to be analysed. However, in Hub03 (Fig. 9) there was clear formation of liquid products (Fig. 10) and ion chromatograph analysis showed that these contained SO42− and NO3−. Most likely this was sulfuric acid (H2SO4) and nitric acid (HNO3), as also observed in previous work (Dugstad et al., 2014; Yevtushenko et al., 2014), but it could in principle also be H2SO4 or HNO3 acids that were further oxidised by air during sampling or by the aqueous eluent in the IC column during analysis. However, H2SO4 cannot exist in solution (Süßerle et al., 1988) and HNO3 cannot exist in gas phase (Kameoka and Pigford, 1977). Thus, the observed
In the Hub03 experiment, the first indication of "dew" occurred shortly after the injection of H$_2$S started (53 h in Fig. 9). Interestingly, the first sign of larger brown droplets was just after both SO$_2$ and H$_2$O started to decline. In addition, the SO$_2$ concentration never reached the sum of SO$_2$ and H$_2$S injected (which was 79 ppmv, see Fig. 11c). Instead it peaked at 57 ppmv, indicating that after 60 h, reaction 1 or 2 were not the only reactions in this experiment. When both SO$_2$ and H$_2$O started to decrease (62 h in Fig. 9), the amount of produced liquid precipitation visually increased in the reaction chamber. By using the fact that both SO$_2$ and H$_2$O decreased significantly, and NO$_2$ also decreased significantly while NO increased slowly, the following reaction is suggested:

$$2\text{SO}_2 + \text{H}_2\text{O} + \text{NO}_2 \rightarrow \text{NO} + \text{H}_2\text{SO}_4$$  \hspace{1cm} (4)

In-house data, which will be included in a later publication, have shown that the solubility of sulfuric acid in dense phase CO$_2$ may be as low as 1 ppmv suggesting that the "dew" and the first liquid observed on the glass tee was H$_2$SO$_4$ that had precipitated since the solubility limit was exceeded. The formation of nitric acid could be through many different routes, such as:

$$3\text{NO}_2 + \text{H}_2\text{O} + 2\text{HNO}_3 \rightarrow \text{NO} + \text{NO}_2$$  \hspace{1cm} (5)

However, Eq. (5) is not favourable based on standard Gibbs energy, with a positive value of 15.3 kJ/mol for gas phase reaction and 9.4 kJ/mol for liquid phase reaction (data in dense phase CO$_2$ are not available). Instead it is proposed that NO$_2$ reacts to nitrous and nitric acid in an aqueous solution. Since sulfuric acid is highly hygroscopic, it will absorb water from the CO$_2$ phase and thus provide the aqueous solution needed for the disproportionation of NO$_2$. The reactions would then be:

$$2\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_2 + \text{HNO}_3$$  \hspace{1cm} (6)

$$3\text{HNO}_2 \rightarrow \text{HNO}_3 + 2 \text{NO} + \text{H}_2\text{O}$$  \hspace{1cm} (7)

As shown previously, NO can be re-oxidized by O$_2$ to NO$_2$, therefore the overall reaction suggested by our data, would be:

$$2\text{HNO}_2 + \text{O}_2 \rightarrow 2\text{HNO}_3$$  \hspace{1cm} (8)

The ratio of 10:1 between sulfurous acid and nitric acid could reflect the amount of water available through absorption for reaction 6, but in-house data (to be published) show that the solubility of HNO$_3$ in dense phase CO$_2$ is 3 orders of magnitude higher than H$_2$SO$_4$. Thus, the nitric acid could be dissolved in the CO$_2$ and transported out of the autoclave. In fact, HNO$_3$ was frequently detected inside the heated vaporizing regulator on the exhaust line. Consequently, the ratio between these acids cannot be used as measure of the production ratio of these acids.
The elemental balance for all injected and analyzed species are summarized in Fig. 14a. The calculations showed that formation of both acids was limited by the excess of N and S, most of the time (i.e. H and O excess concentrations were larger than the equivalent excess N and S content). Fig. 14b shows the balance for production of H$_2$SO$_4$ and the lower line was the limiting reactant. Fig. 14c shows the balance for production of HNO$_3$ after H$_2$SO$_4$ was produced first (b) and again the lowest line would be the limiting reactant. These calculations show that hydrogen was the limiting reactant in the period between 55 and 65 h, partly preventing formation of H$_2$SO$_4$ and HNO$_3$. The reason for the low amount of hydrogen was the production/emission of H$_2$O in this period (55–65 h in Fig. 9). Still there was a consumption of sulphur, and this could indicate the formation of elemental sulphur. Precipitates were observed in the bottom of the glass tee in Fig. 10 after 62 h. In Fig. 14 it was assumed that sulfuric acid was produced first and that nitric acid was produced from the excess compounds (after sulfuric acid). For simplicity it is assumed that these assumptions are valid throughout the whole set of calculations.

The estimated product produced during the experiment between 50 and 100h is shown in Fig. 15. There is some excess oxygen after the formation of the strong acids and elemental sulphur. There could be several reasons for this excess. First, the water contaminated impurity injection system would represent some uncertainty regarding the water feed. Analytical deviations could also contribute to less accurate calculations, especially regarding O$_2$, which decreased when the NO$_2$ in-feed. Analytical deviations could also contribute to less accurate calculations, especially regarding O$_2$, which decreased when the NO$_2$ in-feed.

The analyses of the precipitate after the experiment showed that sulfuric and nitric acid were formed, but exact quantification was not possible. The calculations show that sulfuric and nitric acid were produced at a maximum average concentration of 44 and 11 ppmv, respectively. The solubility limit of sulfuric acid was therefore exceeded according to in-house data, meaning that sulfuric acid would precipitate and form a liquid phase, which was indeed observed. Nitric acid, on the other hand, was always present well below its solubility limit in pure CO$_2$, meaning that most of it was transported away with the vented CO$_2$. However, HNO$_3$ was also present in the liquid precipitates, indicating that the reaction took place in the newly formed liquid phase.

### 4.4. CO$_2$ transport specification

The results presented in the present paper clearly show that, when present in more than 35 ppmv, these impurities do create corrosive reaction products (strong acids) which is not acceptable for carbon steel pipelines. Even though no corrosion coupons were exposed in the present work, it is well known that HNO$_3$ and H$_2$SO$_4$ are corrosive for carbon steel. Thus, a CO$_2$ specification should not allow for these impurities to be present at values as high as 35 ppmv. According to the present results, an acceptable impurity level should be somewhere between 10 and 35 ppmv if H$_2$S, NO$_2$, SO$_2$, and O$_2$ are present. Another approach could be to completely remove one of the reactants. Removal of NO$_2$ is probably the best solution, but it should be noted that the present results indicate that even small amounts of NO$_2$ could start reactions. The only reaction that actually removes NO$_2$ from the CO$_2$ bulk phase is the production of HNO$_3$. In the production of sulfuric acid, NO$_2$ acts somewhat like a catalyst and is not part of the overall reaction in Eq. (4). Thus, just slight NO$_2$ could trigger formation of H$_2$SO$_4$ which may cause severe corrosion. Interestingly, the major acid formation started when H$_2$O and SO$_2$ reached about 180 and 60 ppmv, respectively. This could indicate that there is a threshold level above which production of acid starts. Hub01 and Hub02 had much higher H$_2$O concentrations, but the SO$_2$ content was ≤ 20 ppmv and no acids were observed. This could indicate that the acceptable SO$_2$ level is somewhere between 20 and 60 ppmv. Since H$_2$S may react to form SO$_2$, it would probably be best to use the sum of H$_2$S + SO$_2$ as the limiting level for these impurities.

Reactions occurred also in the experiments with 5 and 10 ppmv, but since the reaction products remained fully dissolved in the CO$_2$ phase they are probably not corrosive for the carbon steel pipeline. If they precipitate later in the pipeline, e.g. at other temperatures or pressures,
corrosive phases could form and be a threat to the pipeline. Further work should be carried out to study the corrosiveness of the products of the reactions at 5 and 10 ppmv.

5. Conclusion

When separate CO₂ streams with water, O₂, SO₂, H₂S, and NO₂ were mixed to simulate a CO₂ transportation hub system, reactions were observed. The types of products that formed were concentration dependent, and no corrosive species were observed for the lowest impurity concentrations (5 and 10 ppmv). A separate liquid phase containing H₂SO₄ and HNO₃ formed when the impurity concentration was 35 ppmv of SO₂, NO₂, H₂S, and 95 ppmv O₂. An impurity concentration of 10 ppmv and lower resulted in reactions, but the products were not corrosive and did not form a separate liquid phase and are therefore not considered a threat for carbon steel. Thus, a safe operation limit for these impurities will be somewhere between 10 and 35 ppmv of SO₂, NO₂, and H₂S.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at https://doi.org/10.1016/j.ijggc.2019.05.017.

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Chapter 9
Discussion

9.1 The effect of water condition and experimental artefacts

The setup used in most of the experiments reported in the literature have serious shortcomings and an important part of the present PhD has been the development of an improved test approach. The main improvement was pre-dissolving the water in the CO$_2$ before entering the test system and introduction of continuous replenishment of impurities (including water) during the experiments [1]. The system also included analysers that monitored the impurity concentration before, during, and after the experiments. In addition, a transparent autoclave that allowed visual observations inside the autoclave during experiments was designed [2-5].

The literature review (Chapter 2) showed how important it is to distinguish between three different corrosion situations; corrosion coupons submerged in a free water phase in equilibrium with a CO$_2$ phase, corrosion coupons hanging in a water-saturated CO$_2$ phase, and corrosion coupons hanging in a CO$_2$ phase under-saturated with respect to water. The corrosion mechanism is probably the same, for the three conditions, but the corrosion rates are significantly different. The amount of water is a key component for the reactions, and the presence of a separate water phase will favour high corrosion rates. It is crucial to keep control of how much water that is present and especially if it is above or below the solubility limit. The phase properties of the system can easily change when the temperature or pressure is altered and controlling the water saturation of CO$_2$ is not straightforward for corrosion experiments. The differences between free water, under-saturated, and water-saturated conditions, and the consequences of the conditions are discussed in the following chapters.

9.1.1 Effect of water on corrosion in systems with dense phase CO$_2$

The experiments with a free water phase (Chapter 3) showed clearly that the corrosion rate of carbon steel exposed to a bulk water phase in equilibrium with dense phase CO$_2$ is very high. Rates in the range of 10 - 20 mm/y were measured in the present work, but 5 - 50 mm/y have also been reported, depending on pH, flow, pressure and temperature. Even with a corrosion allowance of several mm, a pipeline would last for less than a year if exposed to such conditions. The parallel experiments in chapter 3, which exposed carbon steel to liquid water, had corrosion rates with a
standard deviation of about 30%, indicating that the results were relatively reproducible and well within the same order of magnitude. Although there are some spread in the reported corrosion rates in liquid water with CO₂, it is clear that the rates are too high to be acceptable from a pipeline integrity point of view. Thus, it can be concluded that liquid water must be avoided in CO₂ transportation systems of carbon steel, even for shorter periods.

However, when it comes to water that is fully dissolved in the CO₂ phase, there has been a large spread in the corrosion rates reported during the last decade, even for apparently similar conditions (chapter 2.1.2). Corrosion rates ranging over three orders of magnitude, from 0.003 to 2.5 mm/y, have been reported for water concentrations far below the solubility limit. Many of these reported rates are in complete contradiction with the present experimental results (Chapter 4), for which the corrosion rate was about 1 µm/y, even when the water concentration was close to the solubility limit. The discrepancy is very important for operation of CO₂ transport pipelines and will be discussed further in the next chapters.

In the literature review, it was observed that the corrosion experiments in dense phase CO₂ have been carried out using autoclaves or flow loops, and with many different approaches to reach the target conditions. Also, how the test systems were taken back to the ambient conditions after the experiments were finished varied and were often poorly described. Thus, it is most likely that the large difference in reported corrosion rates is caused by the different experimental approaches, rather than a fundamental different corrosion rate or corrosion mechanism. If the goal of one experiment is to investigate under-saturated water conditions, then it is important to be sure that the water is in fact fully dissolved in the CO₂ phase and that water precipitation does not occur on the corrosion coupons. One important difference in the way the present experiments and the experiments reported in the literature were carried out is how the water was introduced to the test chamber (autoclave). Many papers report that water was injected by weight or volume into the autoclave, meaning that the water was introduced as liquid water before the autoclave was filled with CO₂. Thus, water was present in the liquid state until it had completely dissolved in the CO₂ phase. The autoclave systems were usually closed during the whole experiment, and the concentration of the water during or after experiments was rarely measured. Ayello and Thodla [6-8] ran a series of experiments which has been frequently refereed in the literature, and they concluded that: “A very small amount of water (~100ppm) in supercritical CO₂ is sufficient for the formation of a second phase containing water. In consequence, the corrosion rate of carbon steel in the presence of a small quantity of water as a second phase in supercritical CO₂ is very high (1-2mm/year)”. This
Conclusion is in contradiction to the present work. It is not likely that an amount of water which is about 50 times lower than the solubility limit for the system, would form a second phase (liquid phase), at least not at equilibrium. All the injected water would dissolve if given enough time. However, the water was added as a droplet onto their corrosion coupon, and electrochemical measurements were used for monitoring the corrosion rates for 5 to 6 hours. They observed that the corrosion rate decreased during the experiments with both 100 and 1000 ppmw of added water, which probably was caused by the accumulation of alkaline corrosion products in the water droplet due to corrosion and loss of water to the CO₂. The experiments are therefore not representative for a situation with 100 or 1000 ppmw of under-saturated water, but for a transient period with liquid water dissolving in an under-saturated CO₂ phase. This could for example occur in a pipeline after accidental ingress of small amounts of water.

The method used in the present work was to dissolve the water in CO₂ first, and then inject the “moist” CO₂ into the autoclave. In this way no liquid water was introduced into the system, and the results were consequently not affected by the time required for the water to dissolve. The corrosion coupons were present from the start, the water concentration in the CO₂ inside the autoclave was always less than 5 ppmv in the beginning of each experiment (lowest practical achievable water content), and the water content was then gradually increased to the target by injection of “moist” CO₂. The water concentration was measured before, during, and after each experiment with an accuracy of 10 ppmv. Furthermore, all experiments were ended by 20 hours injection of dry CO₂ to get the water concentration below 20 ppmv before depressurization. This procedure prevented water precipitation during depressurisation. The water solubility is known to be reduced with pressure reduction, and particularly with phase change (CO₂ going from liquid/super critical to gas phase). Information about depressurisation procedures and possible water precipitation/condensation was usually not included in the reviewed corrosion papers. It is likely that this type of experimental artefact may have contributed, partly or fully, to the high corrosion rates that have been reported.

9.1.2 Experimental pitfalls with liquid water injection

When liquid water is introduced into an autoclave with corrosion coupons, different scenarios can be foreseen: (1) Micro droplets of water may accidentally hit the corrosion coupons during loading or depressurization of CO₂, resulting in artificially higher corrosion rates. (2) The time for water to dissolve in the bulk CO₂ phase has not been experimentally investigated. However, some experiments indicated that this process could take many hours [6,9] In-house data (to be published
1) showed that it took up to 20 hours for a droplet of water to fully dissolve in 0.3 dm² CO₂ at 25°C and 100 bar. The dissolution time will probably be affected by droplet size, temperature and convection, but anyway the consequence will be higher corrosion rates on the coupons exposed to water droplets, and lower corrosion rates on the coupons without droplets, since the expected water concentration in the CO₂ phase was never reached or reached later than expected. (3) During depressurization the solubility limits for certain impurities can be exceeded, and especially water precipitation may occur since the solubility limit is reduced with reducing pressure, as shown in Figure 9-1. The data is calculated by OLI studio version 9.6.3.[10-12]

![Figure 9-1: Water solubility in CO₂ (calculated with OLI studio, OLI systems).](image)

The Joule-Thomson effect will lower the temperature during depressurization, which in turn lowers the solubility limit (see different temperature lines in Figure 9-1). All dense phase CO₂ experiments have to go through depressurization to collect the exposed coupons, two examples of depressurizations are shown in Figure 9-2.¹ The fast depressurization took 19 minutes for which the temperature decrease inside the autoclave was 25 °C, while the slow depressurization took 308 minutes and had a temperature decrease of only 3 °C. The main temperature drop occurs when the system goes from one phase (liquid) to two phases (liquid-gas) and the temperature starts increasing when all liquid phase is vaporized and only the gas phase is left.

¹ To be presented at the CORROSION/2020 conference.
In sum these two effects (decrease of temperature and pressure) will increase the risk of liquid water precipitation, which obviously will enhance the corrosion since there will still be a significant amount of CO₂ present in the system. Scenario 1 and 3 will not only enhance the corrosion, but also increase the risk of localized attacks since micro droplet hitting the steel surface may sustain corrosion until completely consumed, thus leaving a pit behind. There is also a risk of oxygen corrosion (flash rust) if the wet coupons are exposed to air when the autoclave is opened after the experiment is finished. Present experiments with pre-dissolved water (Chapter 4) did not show any indications of localized attacks, even when the solubility limit was exceeded due to cooling of the system. Care was taken to make sure that no liquid water was present during loading or depressurisation. The exposed coupons were immediately submerged in isopropanol when the autoclave was opened as a precaution for avoiding corrosion by moist air and oxygen. Figure 9-3 shows coupons which have been exposed to essentially similar conditions, but the outcome is very different.
Sim et al. [13] exposed carbon steel coupons for seven days to supercritical CO$_2$ with 1220 ppmv H$_2$O at a pressure of 80 bar at 40 °C. The experiment was carried out in a closed autoclave and the water was injected as liquid. The carbon steel coupon had an even rusty brown surface (Figure 9-3A after the exposure. The reported water concentration was well below the solubility limit, so in principle no water precipitation should be expected. However, all the carbon steel coupons exposed to water concentrations from 240 ppmv to 3600 ppmv had similar attacks, which indicates that the results were affected by experimental artefacts. For example, there could have been more water present than the authors assumed, water may have precipitated during depressurization or possibly the coupons could have been subjected to corrosion in moist air (as indicated by the brown colour). Compared to the experiments of Hua et al. [14] (Figure 9-3B) and Morland et al. [1] (Figure 9-3C), the carbon steel coupons of Sim et al. had much more corrosion products even when the water content was reported to be lower. It might be due to liquid water hitting the coupons when the autoclave was loaded with CO$_2$, but it is more likely that water has precipitated onto the carbon steel surface during depressurization since the surface products was evenly distributed. Another possibility is water precipitation in the beginning of the experiment when the autoclave was heated up. During this period there is a temperature difference between the CO$_2$ phase and the carbon steel coupons hanging in the middle of the autoclave. This will be discussed further in chapter 9.1.2. Hua et al. (Figure 9-3B) found black spots on the coupons after 48 hours exposure to 80 bar CO$_2$ with 3400 ppmv water at 35 °C. They also used a closed autoclave with pre-injection of liquid water. The general corrosion rate was low, but underneath the black spots there were localized attacks. This occurred even when the water concentration was lower than the solubility limit at the test condition. There is no doubt that liquid water has been present on the steel surface, confirmed by black spots consisting of iron carbonate. The reason can be that the water was splattered on the coupons during loading of CO$_2$. The metal surface adjacent to the spots was unaffected and had
low/no corrosion. Most likely the splattered water was consumed by corrosion leaving behind localized attacks. For comparison, no attacks, general nor localized, were found on coupons exposed for 350 hours to 2500 ppmv water in 100 bar CO₂ at 35 °C (Figure 9-3C), using a flow loop with continuous injection of CO₂ with dissolved water.

9.1.3 Experiments in water-saturated CO₂ phase

Experiments with corrosion coupons exposed to water-saturated CO₂ are particularly vulnerable for temperature variations, since this may result in water precipitation on the corrosion coupons. The liquid water is quite often injected in excess of the solubility to ensure complete saturation. The amount of water that can precipitate depends on how much water that is available in the system. In Figure 9-4, a simplified mechanism of the water-saturation of CO₂ in a closed autoclave is shown, the principles of the autoclave are explained in Chapter 2.6.

Figure 9-4: Simplified sketch of the water-saturation / water transportation process inside a closed autoclave that is subjected to external heating. \( C_{H2O,S} \) is the water concentration at saturation, \( T_S \) is the saturation temperature, the temperature of the coupons is represented by \( T_{coupons} \). \( T_{fluctuation} \) indicates the influence from the temperature controller (heating jacket).

Although the experimental details often were poorly described, the following procedure was most likely used. The autoclave is loaded with water and CO₂ before the autoclave is heated to the designated temperature. When the temperature changes, there will be a water concentration/saturation-gradient that will be affected by water dissolution, diffusion and natural and thermal convection. Initially the CO₂ will be water-saturated \( (C_{H2O,S}) \) at the water-CO₂ interface, but it will take some time for the water-saturated CO₂ to distribute uniformly throughout the
autoclave, especially without mechanical convection. It is reasonable to assume that it will take many hours for the water content to reach saturation around the hanging coupons in the centre, since it took over 5 hours to fully dissolve a droplet of water, as discussed in chapter 9.1.1. This was actually reported by Tang et al. [9], who did in-situ electrochemical measurements in H_2O-saturated supercritical CO_2 environment, and they had to disregard the first 10 hours of measurements because the water film on the sample surface was not thick enough to run electrochemical measurements.

During the heat-up period there will be a temporary temperature gradient from the wall, which is the warmest point, to the centre of the autoclave, which would be the coldest place, until the whole system has reached equilibrium. The corrosion coupons in the centre of the autoclave will then constitute the coldest spot inside the autoclave and water condensation could therefore occur in the transient period until the system has reached even temperature. When water-saturated CO_2 arrives at this point, water will precipitate/condense at the coupons surface due to this temperature difference. The significance of this hypothesis has not been established experimentally but is believed to lead to high corrosion rates and localized attacks since a free water phase is formed on the steel surface. Even in the most advanced temperature-controlled systems there will be small temperature fluctuations. These small temperature fluctuations will for a system which is fully water saturated act as a “water pump” to the surface of the coupons. Since the system is balancing on the saturation limit, an increase in temperature will trigger precipitation/condensation since the temperature difference between the saturated CO_2 and the steel surface increases, while a decrease in temperature would stop the condensation on the coupons but would probably not dissolve/remove water from the coupons since the solubility limit has been shifted due to lower temperature. However, the temperature decrease could lead to some fogging in the rest of the autoclave. The excess water in the bottom of the autoclave (which has a large contact surface to the CO_2) would continuously replace the water that condensate on to surfaces. The corrosion products/salt would probably also contribute to keeping water at the steel surface due to the salting-out effect. The condensation of water would probably be more pronounce at the autoclave top, since the lid usually is subjected to cooling from the outside, droplets may form underneath the lid and potentially hit the coupons when falling. Thus, care should be taken when comparing the results from water-saturated experiments to experiment with under-saturated water unless they are kept under very strict temperature and pressure control to avoid these artefacts. However, the water-saturated experiments contribute to increase the understanding of the corrosion mechanisms that comes into play during condensing conditions, for example during operation upsets with
accidental water condensation. This should be avoided since the corrosion is high and quite similar to a large free water phase, which would threaten the pipeline integrity.

Chapter 4 discuss an experiment where the water addition exceeded the solubility limit. To do so, the loop was cooled while injection of CO₂ with 2200 ppmv of water was maintained. When the temperature reached about 14 °C the solubility limit was exceeded, but the cooling continued until the temperature was 6 °C.

9.1.4 Mechanism for CO₂ – H₂O corrosion

The corrosion mechanism for the different types of water condition (free, saturated, and under-saturated) was not studied in detail. SEM analyses showed that the composition and morphology of the corrosion products were apparently the same indicating that the same CO₂ corrosion mechanism is involved. SEM and EDS indicated that iron carbonate (FeCO₃) was formed in all experiments, consistent with the CO₂ corrosion mechanism for gaseous CO₂ and water[15,16]. The typically reaction route will be that CO₂ dissolves in the water phase, some of the CO₂ forms carbonic acid which dissociates and reacts with iron to form iron ion (Fe²⁺), bicarbonate (HCO₃⁻), and H₂. When the concentration of these ions is high enough, iron carbonate will precipitate, and this might from a layer on the steel surface, as described in Chapter 2.1.1 and more thoroughly in the paper by Dugstad [16]. Very high corrosion rates have been reported with dense phase CO₂ when the water phase is large compared to the steel surface (5 to 50 mm/y is reported, Chapter 3). If the transport of species to and from the surface is high (high flow rates) and the water phase large enough to prevent super saturation of iron carbonate - no protective iron carbonate films can form and the corrosion will remain high. The situation will be different for experiments with water-saturated CO₂, since the amount of water is small and in many cases the availability of liquid water is limiting the corrosion process. However, there is still some water there and slight corrosion has been reported (>0.1 mm/y, Chapter 2). A limited water phase, which in this contest means very thin surface films, would be rapidly saturated by corrosion products, even with very low corrosion rates, which would create a partly protective layer of precipitated iron carbonate. The pH is a very important factor, even with very high CO₂ pressure, and as showed by Schmitt and Kriek-Defrain [17] the corrosion rate decreased with increasing pH in a water phase with 50 bar of CO₂. The experiment was carried out with injection of HCl to maintain a fixed pH during the whole experiment (i.e. counteract the effect of accumulated corrosion products). They also reported that the corrosion rate decreased when bicarbonate (Equation 2 and 4, Chapter 2.1.1) was allowed to accumulate in the water phase due to corrosion. For water completely dissolved in the CO₂ phase, the situation is different, the
water at the surface of the steel do not have the properties of bulk/free water phase until enough water molecules have adsorb to the surface. In atmospheric corrosion it is a rule of thumb that at least 60 to 80% relative humidity needs to be present before notable corrosion occurs [18,19]. If it is assumed that this principle also is valid for dense phase CO₂, then the water concentration should be about 60 to 80% of the solubility limits before corrosion is initiated. The reason for this limiting relative humidity is linked to monolayers of water adsorbed to the surface without actual having bulk water properties (less than three layers). A film thickness of 3 to 5 monolayers start to exhibit bulk water properties and species like CO₂ can absorb to form carbonic acid. The present work has shown that the water content could go up to the solubility limit and still the corrosion rate was very low, but traces of iron carbonate were found on the surface, which indicates that corrosion do occur but is slow. Even when the water monolayers transform to bulk/free water phase it would still be very little water available to corrode the steel surface, and amount of steel compared to water is enormous. So, it is reasonable to assume that the water phase would be quickly saturated with iron carbonate that may slow down the corrosion process further.

9.1.5 Exposure time and limiting corrosion rate

The duration of a corrosion experiments is an important parameter, particularly when corrosion rates are extrapolated, and extremely high corrosion rates could be reported especially if the exposure time is short. Normally, all experiment with liquid water injection and corrosion coupons in the CO₂ phase give an underestimation of the corrosion rate, since the water needs time to dissolve in the CO₂. Both literature [6,9] and unpublished work has shown that it may take 10 to 20 hours for one droplet to fully dissolve in the CO₂. If the experiment is performed in 24 hours, then the carbon steel coupons are only exposed for the correct conditions for a fraction of the exposure. Still many of these experiments reports relative high corrosion rates, if only the time when the experiment has correct water concentration is taken in account, the corrosion rates would be extremely high. The experiments performed in this thesis have the lowest corrosion reported of all, and all experiment was conducted with pre-dissolved water. The difference became even larger when other impurities were injected.

When a free water phase is present the corrosion rate will be between 5 to 50 mm/y, but this should not happen if the water concentration is below the solubility limit. However, when water is added by injection of liquid water (small amount to dissolve in the CO₂ phase), the coupons could be hit by droplets during loading of CO₂. As mention before, there might be a risk of condensation due to temperature difference inside the autoclave and during depressurization. It is also common practice
to cool the autoclave when the experiment is finalised for easy handling, and this will also change the solubility limit for water (see Figure 9-1). The only method to avoid condensation due to solubility changes is by removing the water before cooling and depressurization, as was routinely done in the present work. However, this is quite time consuming for water-saturated experiments which all has liquid water in excess. Experience from the laboratory work has shown that it may take about 4-5 days to remove 10 g of water from an autoclave if done gently, which is longer than the exposure time for most of the experiments in the literature. To theoretically investigate the impact of such an experimental artefact, it could be assumed that the coupon is exposed to a thin liquid water film in the end of an experiment during depressurizing and cooling. The corrosion rate in such a transient condition has not been studied in detail in the present work or by others, but if it is assumed “bulk water conditions” and at average 5 bar CO₂ and 25 °C, the NORSOK M-506 CO₂ corrosion model gives a corrosion rate of 15 mm/y for condensed water (pH 3.6) and 11 mm/y if the water is saturated with corrosion products (pH 4.8) and 2 mm/y for a pH of 6.5. Although the NORSOK model is not valid for thin water films; it indicates that the corrosion rate is significant, at least for a short period until the corrosion products builds up. If, for example, the whole process takes about 1 hour from onset of liquid precipitation until the autoclave is opened, the condensation artefact will then at maximum be 15 mm/y for 1 hour, which corresponds to about 2 µm corroded steel. If the experiment lasted for 24 hours this will contribute with an additional “corrosion rate” of 0.6 mm/y, while if the experiment lasted for 1 week it would correspond to 0.09 mm/y and for 1 year it would be 0.002 mm/y. The difference is huge if the 24 hours experiment is compared with a one-year experiment, and erroneous conclusions can be drawn due to this type of experimental artefacts. Since the difference between free water phase and under-saturated water corrosion is enormous it is strange that there has been so little focus on these experimental artefacts in the literature. Most likely these artefacts can explain a large fraction of the spread of the reported data for corrosion in CO₂ transport pipelines.

The over-estimation of corrosion rates in under-saturated water experiments can to a certain degree be estimated since water is the limiting factor for the corrosion rate. To corrode one mole of iron, one mole of water is needed (Equation (2-1) to (2-5), Chapter 2.1.1). If, for simplicity, it is assumed that all the dissolved water is converted to carbonic acid that corrodes the carbon steel coupons, the maximum possible corrosion can be calculated for a closed autoclave system. For example, a 1 L autoclave system with 1000 ppmv H₂O, 100 bar CO₂, 100 cm² carbon steel sample area, and 50 °C. The maximum achievable corrosion in this case is given by the following equations:

\[ n_{H_2O} = n_{Fe} \] (9-1)
\[ n_{H_2O} = \frac{C_{H_2O}}{1000000} \cdot n_{CO_2} \]  
\[ CR = \frac{n_{H_2O} \cdot MW_{Fe} \cdot 10}{\rho_{Fe} \cdot A_{Fe} \cdot \Delta t} \]

where \( n_{H_2O} \) is mole water present, calculated by the concentration of water, \( C_{H_2O} \), in ppmv and the mole of CO\(_2\) in the autoclave, \( n_{CO_2} \). MW\(_{Fe}\) is the molecular weight of iron (g/mol), \( \rho_{Fe} \) is the density of iron (g/cm\(^3\)), \( A_{Fe} \) is the total exposed area of the coupons (cm\(^2\)), and \( \Delta t \) is the exposure time in year.

At the case condition (100 bar and 50 °C), the density of CO\(_2\) is 384 g/l, so the autoclave contains 8.7 moles CO\(_2\), and the maximum achievable corrosion is 0.006 mm thickness loss (4.9 mg/cm\(^2\)) counted as average for the whole exposed surface. For an exposure time of one day this equals to 2.3 mm/y and for a week it equals 0.32 mm/y. A year of exposure gives a maximum corrosion rate of 0.006 mm/y. It is important to remember that for a closed autoclave this is the absolute maximum of corrosion possible when all the water is consumed, which of course is an overestimate since not all the water is likely to participate in the corrosion process. Still, this type of calculation will be a useful basis for evaluation of published results, which scatter a lot. Furthermore, this type of mass balance calculation also shows that if corrosion do occur, the initial water concentration will decrease, and gradually change from the target condition. In this case, if the measured corrosion rate from a one-day experiment is 1 mm/y then the final concentration of water would be 600 ppmv and not 1000 ppmv. So, if there is a water “threshold” where the corrosion sets on or starts to accelerate, the real corrosion rate at this point cannot be determined in a closed autoclave system since the water is consumed and the water concentration will decrease below the threshold value. One exception is for fully water-saturated conditions with a large liquid water reservoir in the autoclave, but this introduces other experimental challenges.

### 9.2 Impurity reactions and formation of liquid phases

The chemical reactions may occur in the dense phase CO\(_2\) (homogeneous reactions) or on surfaces (heterogeneous reactions). Both reaction types can in principle produce species that results in corrosion of carbon steel, but homogeneous formation will involve a transportation step and could therefore be slower. Some reaction can produce species that is not necessary more corrosive and might be tolerated, while other reaction products could create an aqueous phase which would increase the corrosiveness of the transported CO\(_2\).
9.2.1 Surface reactions

The literature on corrosion in CO2 transport systems is mainly focused on steel, especially carbon steel. Since the material choice is a very important factor for the transportation system (pipelines or ships), it is natural that the focus is on the reactions and corrosion products that could be found on the surface of the steel. The corrosion mechanism (Chapter 2.1.1) involves typically a bulk water phase on the metal surface in which the impurities are absorbed which results in formation of species such as carbonic, nitric, and sulphurous/sulfuric acid. However, the water layer on the steel surface needs to be above a critical thickness to obtain the “bulk properties” of liquid water, which is the case for water-saturated and condensing water experiments. The mechanism when this occurs is well documented by others [20] and has not been in focus in the present work. The additional presence of 75 ppmv SO2 and 220 ppmv O2 changes the situation, and the water concentration needed to be 1900 ppmv (60% of saturation) before the first sign of corrosion was observed (Chapter 7). The corrosion rate increased just slightly when the water content was increased further to 2400 ppmv. It appeared, however, that the corrosion stopped after relatively short time, either due to formation of protective surface film or because the water was consumed. Nevertheless, this suggests that the mechanism for corrosion can be linked to an increasing thickness of surface water, analogue to findings in atmospheric corrosion [19]. An EDS-analysis of the carbon steel coupon exposed in the SO2-O2-H2O experiment indicated that the corrosion product was FeSO4, which is the expected corrosion product in the presence of sulfuric acid. There are also some reports of hydrated iron sulphite (FeSO3·xH2O) as corrosion product in some water-saturated/free water experiments [20-22].

\[
\text{Fe} + \text{SO}_2 + \text{H}_2\text{O} \leftrightarrow \text{FeSO}_3 + \text{H}_2 \tag{9-4}
\]

Iron sulphate is usually found when also O2 is present and the reaction would be like this:

\[
2 \text{Fe} + 2\text{SO}_2 + 2\text{H}_2\text{O} + \text{O}_2 \leftrightarrow 2\text{FeSO}_4 + 2\text{H}_2 \tag{9-5}
\]

The limiting amount of liquid water is therefore the most likely reason for the low corrosion rate and the small amount of corrosion products found on the carbon steel.

However, in experiments with NO2 present, the first sign of corrosion was observed at a water content as low as 250 ppmv, and when the concentration was increased above 500 ppmv the corrosion rate became very high.
This calls for another explanation than just the thickness of the water film. The mechanisms involved are not understood, but it could start with monolayers of adsorbed water and co-adsorption of NO2 which triggers the first sign of corrosion. The products of these two might attract more water to the surface and at some point, even though the water concentration in the CO2 bulk is very low compared to the solubility limit, the water film gets thick enough to withhold properties as liquid water. Then absorption of NO2 into the water film is the driving force of the corrosion. It is also a point that HNO3 is known to be an oxidation agent and possibly it could oxidise iron (steel) even with limited amount of water present. There is no direct evidence for the details in this process, but the indications are strong. Firstly, the low water content needed to start the attack with NO2 present. Secondly, the published data on SO2 solubility in water films is about 10 times higher than for NO2 [23,24] meaning that, if the absorption of species in the water film is the only mechanism then corrosion in the SO2 and O2 experiment should have been observed at a lower water concentration. The rate of 3.6 µm/y with SO2/O2 versus 0.57 mm/y with NO2 indicate that other factors, like reactivity and protective layer, also affect the corrosion rate. There was no indication that the solubility limit of water was significantly affected by the presence of NO2 since there were no other phases observed e.g. nitric acids or other compounds. Low water content did not restrict the corrosion in the NO2-H2O experiment, the corrosion rate was high and large amount of corrosion products were formed. The products gave no protection as other corrosion film might do (e.g. FeCO3 and FeS), the EDS-analysis of the coupons showed mainly the present of iron and oxygen, but due to technical issues it was not possible to say if nitrogen also was present (i.e. if the corrosion products also contained iron nitrate). Very few papers report iron nitrate when NO2 is present [25], but it has been observed for atmospheric corrosion and may therefore not be directly comparable to CO2 environment. The reaction could be:

\[
Fe + 3NO_2 + 3H_2O \leftrightarrow Fe(NO_3)_3 + 3H_2
\] (9-6)

This could be a likely reaction when the amount of water was high as in water-saturated or free water experiments, but NO2 is a strong oxidizer and the reaction route of NO2 is complex so it cannot be ruled out that NO2 just delivers oxygen for reaction with iron to form iron oxide in some form.
(FeO, FeOOH, Fe₂O₃, or FeO·Fe₂O₃) in under-saturated water system, especially at the low water content in our experiment.

9.2.2 Homogenous reactions

Some of the reactions occur in the bulk CO₂ phase, while other reactions take place on (steel) surfaces. Chapter 5 [2] and Chapter 8 showed that H₂S and O₂ was consumed in reactions that produced SO₂ and H₂O (overall reactions). There was also measured an increase in NO when O₂ was low, and this observation led to the proposal of the following reactions:

\[ H_2S + NO_2 + O_2 \rightarrow SO_2 + H_2O + NO \] (9-7)

\[ 2NO + O_2 \rightarrow 2NO_2 \] (9-8)

Since the NO/NO₂ concentrations were in inverse ratio, depended on the O₂ content, it was suggested that O₂ is not directly involved in reaction 9-7, and instead the reaction could be written:

\[ H_2S + 3NO_2 \rightarrow SO_2 + H_2O + 3NO \] (9-9)

In summary this means that NO₂ is acting as an oxidation agent for H₂S to form SO₂, H₂O, and NO, while the amount of available O₂ determine how much NO that is oxidized back to NO₂. This fits well with the observation and these reactions are not necessarily harmful (i.e. corrosive) if the concentrations are low enough. The reactions occurred in all tested concentration levels (5, 10, 30, and 35 ppmv). It has been shown that SO₂-O₂-H₂O system is depending on high water concentrations to start the corrosion. Indirectly, H₂S-SO₂-O₂-H₂O system has also proven to be none-corrosive in the initial part of the Chapter 5 experiment, where these impurities were present for 70 hours at a concentration of about 35 ppmv without harming the carbon steel coupons. In other words, no reactions were observed as long as NO₂ was absent and the concentration of SO₂ and H₂S was ≤ 35 ppmv. Therefore, the uncertainty is if the presence of NO₂ (or NO) will initiate corrosion also for the low impurity concentrations that did not result in a formation of a separate liquid phase (5 and 10 ppmv). Since the hub experiments in Chapter 8 were performed without steel coupons to avoid catalysing effects of corroding steel surfaces, it cannot be concluded that no corrosion will occur at these low concentrations where no liquid is formed.

9.2.3 Formation of liquid phase

In Chapter 8, series of experiments with mixing of multiple CO₂ streams were carried out to simulate a hub where CO₂ streams from different sources was mixed. From these experiments, it became clear that the concentration of NO₂, SO₂, and H₂S should be kept below 30 ppmv to avoid formation of a separate liquid phase. The limiting factor for formation of liquids seemed to be the total
concentration of H$_2$S and SO$_2$, since the experiments show that all H$_2$S is converted to SO$_2$ when NO$_2$ is present. Figure 9-6 shows two different scenarios with the same outcome. In the Hub03 experiment, where NO$_2$ already was present when the H$_2$S injection started, the SO$_2$ concentration increased gradually to about 60 ppmv (the sum of injected concentrations of SO$_2$ + H$_2$S was 80), after which the concentration started to decline with time. In the other experiment (Chapter 5), H$_2$S was present when the NO$_2$ injection started, and also here the SO$_2$ concentration increased gradually to about 75 ppmv before the decline of SO$_2$ started in the same manner as for Hub03. The latter case had already H$_2$S present in the autoclave and all of it was converted to SO$_2$, which is probably the reason why the concentration of SO$_2$ got somewhat higher (75 instead of 60 ppmv). However, the SO$_2$ curve in the right diagram in Figure 9-6 has a change in slope at 60 ppmv which may indicate that liquid started to form at this point, which is in accordance with the visual observation.

Figure 9-6: The diagram to the left (hub03) shows conversion of H$_2$S to SO$_2$ when NO$_2$ is present and H$_2$S injection starts, while the diagram to the right (Chapter 5) shows conversion of H$_2$S to SO$_2$ when H$_2$S is present and NO$_2$ injection starts.

The liquid that formed in these experiments was analysed with ion chromatography (IC), and both nitric and sulfuric acid were detected. This fits well with other findings in the literature [26-28]. It is not possible to determine whether H$_2$SO$_4$ or HNO$_3$ was produced first. But since the decrease in the SO$_2$ and H$_2$O concentrations was so clear at the same time as the first sign of liquid was observed inside the autoclave, it is suggested that H$_2$SO$_4$ was formed first according to this reaction:

$$\text{SO}_2 + \text{H}_2\text{O} + \text{NO}_2 \rightarrow \text{NO} + \text{H}_2\text{SO}_4$$

Thus, the results indicate that this can occur in the CO$_2$ bulk phase first, and afterwards precipitate on surfaces. However, occurrence of such reactions in a thin surface film cannot be fully ruled out. In Chapter 6, the acid solubility of both sulfuric and nitric acid was found in a series of experiments. The
solubility of H$_2$SO$_4$ was typically in the range of 0.1 – 8 ppmv, while the solubility of HNO$_3$ was three orders of magnitude higher, 500 – 2500 ppmv. The calculation based on the consumption of impurities preformed in Chapter 8 with the hub03 experiment (left diagram, Figure 9-6), shown in Figure 9-7, gave us an estimate of the amount of acid produced. The concentration of produced H$_2$SO$_4$, as it would have been without accumulation inside the test chamber, is higher than the solubility of this acid, and therefore a liquid phase will be formed.

Figure 9-7: Estimate of the concentration produced species, Hub03 Chapter 8.

Sulfuric acid is known to be highly hygroscopic and could therefore absorb water from the CO$_2$ phase. This provides an aqueous solution for NO$_2$ to absorb into and form nitric acid. This reaction is more likely to happen in an aqueous solution, as described by [29]:

$$2\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_3 + \text{HONO}$$  \hspace{1cm} (9-11)

$$3\text{HONO} \rightarrow \text{HNO}_3 + 2\text{NO} + \text{H}_2\text{O}$$  \hspace{1cm} (9-12)

If there is O$_2$ in excess, the NO will react to NO$_2$ (reaction 9-8). There are numerous reaction routes for NO$_2$, and it is outside the scope of the present work to study the details of these reactions. However, Finlayson-Pitts et al. [30] suggested that N$_2$O$_4$ (a dimer of NO$_2$), could be an important precursor for reaction 9-11. An interesting observation is the difference in corrosion between the carbon steel coupon exposed in a specification testing experiment (SPEC-1) with all impurities present and the coupons which was only exposed to NO$_2$ and H$_2$O in Ramp04 (Figure 9-8). The corrosion rate was higher and more severe in Ramp04 when only NO$_2$ and H$_2$O was present, than in SPEC-1 with SO$_2$, O$_2$, and water. The carbon steel coupon in SPEC-1 was clearly wetted by acids, but the water concentration was lower in addition to be consumed by reactions to form acid. Therefore,
little water was available to corrode the coupons and to dissolve the corrosion products. Panossian et al.[31] showed that the corrosion rate in concentrated (>90%, mass) H₂SO₄ was lower than in 50% H₂SO₄, since the solubility of FeSO₄ is much lower in concentrated H₂SO₄. Therefore, a surface layer of FeSO₄ will be formed faster in concentrated than in 50% H₂SO₄. A surface layer of FeSO₄ can act as a mechanical barrier that protects carbon steel and slow down the corrosion process [32]. Another observation in the SPEC-1 experiment (right picture, Figure 9-8), was that the attacks started from the contact points between the coupon and the PEEK-holder. Even after 170 hours in the “acid cloud”, the carbon steel coupon had no significant corrosion attacks in the centre of the coupon. Apparently, the contact points acted as a flow path for either acid or water which enhanced the corrosion, possibly because liquid could form easier on the small contact point crevices. Note that liquid was observed at the centre of the coupon during the experiment.

![Figure 9-8: The coupons in the left picture were exposed to NO₂ and H₂O in Exp04, and the picture to the right was taken during SPEC-1 with O₂, SO₂, H₂S, NO₂, and H₂O present.](image)

The ratio between sulfuric and nitric acid in the liquid phase analysed with IC was 10:1, nitric acid was a bit lower than compared with the ratio in Figure 9-7 which was 3:1. It is expected that more of the nitric acid is transported away with the CO₂ stream (exhaust CO₂) because of the higher solubility, but the consequence for the pipeline when running concentration levels shown in Hub03 and SPEC-1 with the products form as shown in Figure 9-7 would be severe. If the goal is to transport 1 Mt/y of CO₂ to storage, there could potentially precipitate about 30 tons of sulfuric acid and between 3 to 10 tons of nitric acid inside the pipeline every year when about 30 ppmv of NO₂, SO₂, and H₂S is present, according to Figure 9-7.
9.3 Limiting concentrations of impurities and making a CO₂ specification

The maximum allowed impurity concentration in a CO₂ specification should be set from one of two perspectives; either no chemical reactions should occur, or no corrosion of carbon steel should occur. In principle, some reactions could be allowed if the consequences are manageable from an operating perspective, meaning that no harmful reaction products should be formed, and that the corrosion rate should be very low. The latter would be a more realistic choice since cost is always in focus and unnecessary cleaning of the CO₂ will increase the overall price of the whole CCS chain. It is important to avoid precipitation of solid products since it may cause problems at the injection point and in the reservoir. The present work has clearly demonstrated that the number and types of impurities that are present is important for the maximum concentration for reactions and corrosion to occur. If the CO₂ contains fewer impurities, the acceptable maximum concentrations can be increased, sometimes significantly. Thus, it is clear that there must be a CO₂-specification for each combination of impurities, rather than one universal specification. This will be discussed further in the next sub-chapters.

9.3.1 CO₂ hub specification with H₂O, SO₂, H₂S, NO₂ and O₂ present

If the CO₂ specification should contain all impurities tested in this thesis, the impurity concentrations must be very low, including water, as summarised in Table 9-1. The CO₂ hub experiment showed that 5 and 10 ppmv of the SO₂, H₂S, and NO₂ (Hub01 and Hub02) did react but only to increase the SO₂ and H₂O concentration. While at an impurity content of 35 ppmv the acid precipitation started, and the liquid acid could be collected at the end of the experiment (Hub03 and SPEC-1).

<table>
<thead>
<tr>
<th>Maximum impurity content (ppmv)</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>SO₂</td>
</tr>
<tr>
<td>200</td>
<td>20</td>
</tr>
</tbody>
</table>

It should be noticed that the impurities in the proposed specification in Table 9-1 will react and therefore not be detected by analysis of the CO₂. Instead, the concentrations would be according to Equation 9-8 and 9-9, and the limiting reactant is oxygen. These reactions and products are perhaps most relevant when several individual CO₂ streams are mixed, for example in a CO₂ hub system. For a single CO₂ stream to the storage system, the reactions would have already occurred in the capturing plant or the compressor stage where it in principle could be removed.
The CO$_2$ specification (Table 9-1) is mainly based upon the Hub-experiments, where three individual CO$_2$ streams were mixed in a hub-system to follow the main flow out. Reactions did occur, and the critical point was when SO$_2$ and H$_2$S combined had a concentration above 60 ppmv, which led to formation of a liquid phase that contained acids. The presence of nitrogen dioxide acted as a catalyst that was back-produced as long as oxygen was in excess (Equation 9-8). Therefore, the sum of H$_2$S and SO$_2$ is set to maximum 40 ppmv in Table 9-1, to provide some safety margin. If nitrogen oxide is present, even at a concentration of a few ppm, it may catalyse the reaction with the help of oxygen. This was observed in the Hub-experiments, where NO$_2$ needed to be completely removed before the conversion of H$_2$S to SO$_2$ and H$_2$O stopped. The limit of 10 ppmv NO$_2$ in Table 9-1 was mostly set because of lack of experimental data, it might be that the concentration could have been higher based on the Ramp04-experiment as long as the water concentration is kept low (<250 ppmv). Water alone could threaten the pipeline integrity if precipitation is allowed and do accelerate surface reaction even below the solubility limit. This is the reason for the proposed low value of water in Table 9-1. For the Hub-experiments, water did not play an important role, except for when the acids already had precipitated. Then the water will absorb into the aqueous phase and increase the corrosion rate. The oxygen concentration was determined based on the restriction of NO$_2$, if oxygen is in excess there are no limits for which reactions NO$_2$ can “catalyse” since it is present in almost all proposed reactions (Equation 9-6, 9-7, 9-9, 9-10, and 9-11). By limiting oxygen, NO$_2$ will be limited to the conversion of H$_2$S to SO$_2$ and H$_2$O. It could be argued that the concentration of oxygen could have been set to 30 ppmv to achieve full conversion of H$_2$S, but instead a safe margin was used to ensure that no undesirable reaction occurs. It should be noted that much of the proposed specification in Table 9-1 is based on experiments carried out without carbon steel coupons.

9.3.2 Adapted CO$_2$ recommendation

There are several capture and purification methods for CO$_2$, and the impurities following the CO$_2$ stream will depend on the techniques used. Thus, using a CO$_2$ specification with all the impurities in Table 9-1 will impose unnecessary restrictions if one or several of the impurities are not present. Therefore, an adapted CO$_2$ recommendation is proposed in Table 9-2.
Table 9-2. Recommended maximum concentration based on experimental data with several different impurity systems at 25 °C and 100 bar. No safety margins are included.

<table>
<thead>
<tr>
<th>Maximum impurity content</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(ppmv)</td>
</tr>
<tr>
<td>H₂O</td>
<td>SO₂</td>
</tr>
<tr>
<td>2500*</td>
<td></td>
</tr>
<tr>
<td>2500*</td>
<td>80**</td>
</tr>
<tr>
<td>250</td>
<td></td>
</tr>
<tr>
<td>100 (300)</td>
<td>35</td>
</tr>
<tr>
<td>50</td>
<td>35</td>
</tr>
</tbody>
</table>

* Precipitation of liquid water must be avoided. The water solubility varies with temperature and pressure. Check the temperature and pressure profile for the transportation system to identify the point with lowest solubility. ** These impurities might be increased, since it was the water concentration that controlled/ramped up until corrosion occurred.

The three first recommendations in Table 9-2 are based on the findings in Chapter 3, Chapter 4, and Chapter 7. In the SO₂-O₂-H₂O recommendation, some corrosion would be expected at water concentration above 1600 ppmv but the corrosion rate found was low (4 µm/y). There should be done an assessment whether scale/products accumulating over several years of operation could detach from the steel surface and follow the CO₂ stream to the reservoir. As for the H₂S-SO₂-O₂-H₂O recommendation, no dedicated experiment was performed to confirm the safety in those values. However, several in-direct experiments have been performed. These in-direct experiments are the beginning of e.g. the acid formation experiment, SPEC-1, where the final goal of the experiment is to introduce NO₂ at the end. However, the injections in the beginning of the experiments were monitored with cameras and there were no visible attacks on the coupons even after 100 hours of stable impurity concentrations. No deviation between injection concentration and the concentration measured after the autoclave was detected. This was also the case for the numbers in the brackets in Table 9-2, but that experiment was not monitored by camera, so no visible conformation is available, and this should be confirmed in an additional experiment. The NO₂-SO₂-O₂-H₂O recommendation was confirmed in several in-direct experiments[33] with visual monitoring and impurity measurements, the longest exposure time was 330 hours without any sign of corrosion on the coupon surface [33]. There might be some reactions occurring which were not identified. In the Hub03 (Chapter 8), there was a sudden drop in the O₂ measurement in one of the laser-based analysers which measured in-situ, while another instrument using a different measuring technique did not detect this drop. This was thoroughly investigated and the drop in O₂ concentration was real but recovered when the vent-gas reach the second instrument. It was concluded that it might be intermediate/temporary species, the carbon steel coupon was not affected by the incident.
9.4 Implication of the proposed CO₂ specification

The proposed specification in Table 9-1 and Table 9-2 are solely made to identify maximum concentration of impurities in the transported CO₂ which do not harm carbon steel. It should be noted that there might be some type of carbon steel which reacts differently than the one used in this thesis (S355MC). The specifications/recommendations only apply for pipeline and ship and not for the injection point and the reservoir.

9.4.1 Oxy-fuel capturing vs. proposed specification

Three examples of the impurity content in the CO₂ from oxy-fuel capturing, are listed in Table 9-3.

<table>
<thead>
<tr>
<th>Compound (ppmv)</th>
<th>Example 1 [34]</th>
<th>Example 2 [35]</th>
<th>Example 3 [36]</th>
<th>Proposed specification (25 °C, 100 bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>100</td>
<td>0</td>
<td>&lt;20</td>
<td>200</td>
</tr>
<tr>
<td>SO₂</td>
<td>70</td>
<td>37</td>
<td>&lt;0.1</td>
<td>20</td>
</tr>
<tr>
<td>O₂</td>
<td>100</td>
<td>4000</td>
<td>&lt;30</td>
<td>20</td>
</tr>
<tr>
<td>NOₓ</td>
<td>100</td>
<td>33</td>
<td>&lt;5</td>
<td>10</td>
</tr>
<tr>
<td>H₂S</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>20</td>
</tr>
<tr>
<td>CO</td>
<td>50</td>
<td>-</td>
<td>&lt;10</td>
<td>N/A</td>
</tr>
<tr>
<td>Ar, N₂</td>
<td>100</td>
<td>1500</td>
<td>Trace</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Example 3 could most likely be transported without further cleaning, so might example 2 since there is not reported any water. But example 1 might be a problem because of the high SO₂ content. It was concluded that the total amount of SO₂ and H₂S should not be above 40 ppmv, and at 60 ppmv acid was produced in the experiment. The need for additional cleaning of the CO₂ depends on the oxy-fuel technique used.

9.4.2 Pre-combustion capturing vs proposed specification

In Pre-combustion, the CO₂ is captured before the combustion phase and solid fuel is converted to syngas. Some examples of the expected impurity concentrations are listed in Table 9-4.
Table 9-4. Expected impurities from pre-combustion CO2 capturing with pulverised coal.

<table>
<thead>
<tr>
<th>Compound (ppmv)</th>
<th>Example 1 [37]</th>
<th>Example 2 [38]</th>
<th>Example 3 [39]</th>
<th>Proposed specification (25 °C, 100 bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2O</td>
<td>600</td>
<td>378</td>
<td>10</td>
<td>200</td>
</tr>
<tr>
<td>SOx</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>20</td>
</tr>
<tr>
<td>O2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>20</td>
</tr>
<tr>
<td>NOx</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>H2S/COS</td>
<td>&lt;100</td>
<td>1700</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>CO</td>
<td>400</td>
<td>1300</td>
<td>400</td>
<td>N/A</td>
</tr>
<tr>
<td>Ar, N2, H2</td>
<td>10000</td>
<td>10000</td>
<td>10000</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Pre-combustion might work without further cleaning of the CO2, if adapted recommendation is used, but there are no data available for how COS and especially CO would affect the carbon steel pipeline, and this should be investigated before implementation. Blanco et al.[40] showed that CO had a negative effect on the storage process, but no corrosion related publications was found.

9.4.3 Post-combustion capturing vs proposed specification

Porter et al.[41] reviewed the range and concentration of impurities in the CO2 stream from post-combustion capturing plants and they are listed in Table 9-5.

Table 9-5. Expected impurities from post-combustion CO2 capturing with pulverised coal.

<table>
<thead>
<tr>
<th>Compound (ppmv)</th>
<th>Amine PC plant [41]</th>
<th>MEA PC plant [41]</th>
<th>Proposed specification (25 °C, 100 bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2O</td>
<td>100</td>
<td>640</td>
<td>200</td>
</tr>
<tr>
<td>SOx</td>
<td>10</td>
<td>1</td>
<td>20</td>
</tr>
<tr>
<td>O2</td>
<td>150</td>
<td>61</td>
<td>20</td>
</tr>
<tr>
<td>NOx</td>
<td>20</td>
<td>1.5</td>
<td>10</td>
</tr>
<tr>
<td>H2S/COS</td>
<td>0</td>
<td>0</td>
<td>20</td>
</tr>
<tr>
<td>CO</td>
<td>10</td>
<td>0</td>
<td>N/A</td>
</tr>
<tr>
<td>Ar, N2, H2</td>
<td>450</td>
<td>1800</td>
<td>N/A</td>
</tr>
</tbody>
</table>

The expected concentration of impurities from post-combustion is low, especially for SO2 and NO2. Since H2S is not present these CO2 streams could very well be transported in carbon steel pipelines or ships without additional cleaning of the CO2.

9.4.4 CO2 hub system vs proposed specification

It has been suggested that multiple capturing sites can be connected to one storage site through a CO2 transport network (pipelines). Such a network will result in mixing of CO2 streams from different sources with different impurity species and concentrations. The present work has clearly
demonstrated that certain impurity combinations can result in corrosion and formation of solid. Thus, testing or prequalification of the CO₂ streams to be mixed is recommended. Neither oxy-fuel or post-combustion capturing streams could be mixed with pre-combustion capturing streams with high H₂S content. H₂S and NO₂ will react to form SO₂ and acid will form when the amount of SO₂ exceeds 60 ppmv. Oxy-fuel and post-combustion streams contain enough O₂ to keep the reactions going. With the high O₂ concentration only traces of NO₂ is needed to produce sulfuric acid. Therefore, to make the hub system work with all these capturing methods, all traces of NO₂ need to be removed from the CO₂ streams before they are mixed.

9.5 References


Chapter 10

Conclusions

Prior to this study, there was some discrepancy about the corrosion rates for carbon steel exposed to dense phase CO$_2$ with fully dissolved water. By using a controlled method to dissolve the water in CO$_2$, it was experimentally demonstrated that the presence of dissolved water in the CO$_2$ phase will not give significant corrosion (less than 2 µm/y) for carbon steel. However, if the water is present as a free water phase, it will result in 3 to 4 orders of magnitude higher corrosion rates, in the range from 5 to 50 mm/y. This shows that the form of the water (fully dissolved in the CO$_2$ phase, saturated or present as a liquid phase) is critical for the integrity of carbon steel components. It is more than likely that the discrepancy of the corrosion rates reported in the literature is caused by a combination of the experimental procedure and the handling of the water, as several possible artefacts could occur during loading and depressurisation of the autoclave.

The most referred (Dynamis, NETL, CarbonNet, etc.) recommendation of impurities (100 ppmv of SO$_2$, NO$_2$, and H$_2$S) was tested in a novel test system that mimic the CO$_2$ transport conditions in a realistic manner. The test showed that a separate aqueous phase containing nitric and sulfuric acid was formed, which is corrosive to carbon steel. Thus, such impurity levels cannot be accepted for CO$_2$ transportation in carbon steel pipelines. This raised many interesting questions, like impurity concentration limits, solubility limits, corrosion and chemical reactions, and which could be used to make a safe operation specification for CO$_2$ transport in carbon steel. Since acids were formed by reactions of impurities, solubility data was needed to predict when the acids could precipitate and form a separate phase.

The solubility of nitric acid and sulfuric acid in dense phase CO$_2$ was determined through organises experimental work. The results showed that the solubility of nitric acid (~1000 ppmv) was about 3 order higher than sulfuric acid (~1 ppmv). The solubility increases slightly with increasing temperature, while pressure has a much larger effect, especially between 1 and 100 bar. The pioneer results from the acid solubility in CO$_2$ was used as the foundation of the CO$_2$ - acid model that has been implemented in the OLI thermodynamic model.

The experimental testing showed that sulfuric acid was formed by reaction of water, sulfur dioxide and nitrogen oxide. Although the details around formation of these acids is not fully understood, it is
assumed that sulfuric acid forms in the bulk CO₂ phase and, due to its low solubility, it will precipitate. Sulfuric acid is hygroscopic and will most likely absorb water from the CO₂ phase, thus creating an acid-rich aqueous phase. The results further indicate that nitric acid formation take place in an aqueous phase, not in the bulk CO₂ phase. Thus, nitric acid may start to form once enough water has been absorbed in the sulfuric acid phase.

Systematic studies showed that formation of corrosive phases was strongly affected by which impurities that were present together. Certain impurity combinations were essentially inert, while other combinations resulted in chemical reactions and corrosion. The concentration of water was critical and ramping of water experiment was conducted to establish water limits for several of the impurities. The experiments showed that CO₂ streams containing SO₂ and O₂ are not corrosive if the water concentration is less than 1600 ppmv at 100 bar and 25 °C. However, the situation is quite different for the NO₂-H₂O system. A corrosion rate of 0.57 mm/y was measured with 70 ppmv of NO₂ and only 670 ppmv of H₂O at 100 bar and 25 °C. The first sign of corrosion started already at 250 ppmv of H₂O. This indicates that the corrosion mechanism for SO₂/O₂ and NO₂ is different. Presence of SO₂ and O₂ and high concentrations of water did only result in negligible corrosion, while presence of NO₂ results in significant corrosion even when a relatively small amount of water is present. The reason for this significant difference has not been fully understood. It could be related to different surface adsorption/absorption processes or differences in the protectiveness of the corrosion products that form.

A future CO₂ transport network will most likely include CO₂ from different sources that will be mixed at some point (hub). Even if the individual CO₂ streams are non-reactive on their own, mixing of the streams may give certain impurity combinations that trigger chemical reactions. In this study, three different non-reactive CO₂ streams were mixed, and the reaction was studied through analysis of the exhaust gas and visual observation. The concentration level was set to approximately 5, 10 and 30 ppmv of SO₂, NO₂, and H₂S. Water and O₂ were also present, at a higher concentration. Acids were formed with 30 ppmv of impurities, while 5 and 10 ppmv of impurities gave reactions but no condensation of acids. These observations made it possible to identify two important reactions which produce reactants to the sulfuric acid reaction. The first was the reaction of H₂S and NO₂ to produce SO₂ and H₂O, and the second was the reaction between NO and O₂ to regain NO₂. Nitrogen dioxide acts like an oxidation agent and as long as O₂ is available, only trace amount of NO₂ is required to oxidise H₂S to SO₂. H₂S was always instantly fully consumed when NO₂ was injected to the autoclave.
The Hub-experiments gave also valuable inputs for cases with few impurities, since each impurity was introduced subsequently. Based on all the experimental testing, it was possible to establish limits for when corrosion and chemical reactions can be expected. Since the combination of impurities is so important, it was not possible to give a universal limit for each impurity, it had to be for a combination (Table 10-1). It should also be noted that the limits may change if other impurities (not yet tested) are present.

<table>
<thead>
<tr>
<th>Maximum impurity content (ppmv/ppm mole)</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O  SO₂  H₂S  NO₂  O₂</td>
<td></td>
</tr>
<tr>
<td>200  20   20   10    20</td>
<td>Formation of H₂SO₄ and HNO₃ if (SO₂+H₂S) &gt; 60 ppmv.</td>
</tr>
<tr>
<td>2500*</td>
<td>80**  240**</td>
</tr>
<tr>
<td>250</td>
<td>70**</td>
</tr>
<tr>
<td>100 (300)  60 (350)  35 (100)</td>
<td>Visual conformation and none reactive experiment. (None reactive experiment, but no visual conformation.)</td>
</tr>
<tr>
<td>50   35   80</td>
<td>Visual conformation and none reactive experiment.</td>
</tr>
</tbody>
</table>

* Precipitation of liquid water must be avoided. The water solubility varies with temperature and pressure. Check the temperature and pressure profile for the transportation system to identify the point with lowest solubility.
** These impurities might be increased, since it was the water concentration that controlled/ramped up until corrosion occurred.

The recommendation in Table 10-1 was compared with published impurity concentrations from capturing of various combustion sources, and it suggests that CO₂ captured from oxy-fuel, pre-combustion, and post-combustion processes can be transported in carbon steel pipelines without further cleaning. However, the streams must be kept apart, acid will be produced if they are mixed, and the integrity of the pipeline or ship will be threatened.
Chapter 11

Further work

This thesis has covered many topics but also revealed some gaps in the knowledge for proposing a safe operation specification. In this work it was observed that the first condensation of acid occurred when \( \text{SO}_2 \) exceeded a threshold of about 60 ppmv. In the experiments, however, such high \( \text{SO}_2 \) contents were only reached because \( \text{H}_2\text{S} \) was converted to \( \text{SO}_2 \) by reaction with \( \text{NO}_2 \), and it is not really known if the presence of \( \text{H}_2\text{S} \) is needed or if \( \text{SO}_2 \) alone above 60 ppmv would result in formation of acids. This should be investigated further.

Some of the proposed impurity limits in Table 9-1 was based on the observation that no aggressive reaction products (acids) was produced, but some of these experiments were carried out in the absence of corrosion coupons. These limits should be confirmed in dedicated experiments with carbon steel coupons present. The concentration limits in the \( \text{CO}_2 \) recommendation in Table 9-2 is based on the available experimental data from this thesis, and the maximum allowed concentration may in some cases might be increased but this needs to be verified by experiments. Such experiments may for example be; fixed water concentration at the maximum identified value and increasing single or multiple impurity until corrosion occurs.

The time for liquid water to dissolve in dense phase \( \text{CO}_2 \) has so far not been quantified experimentally, as discussed in connection with experimental artefacts in this work it, is very relevant for corrosion testing. The kinetics for liquid water to dissolve in dense phase \( \text{CO}_2 \) is important in several other part of the CCS chain, such as after hydro testing of pipelines to be used for \( \text{CO}_2 \) transport, or in the case of accidental water ingress. The time for dissolving the water will, to some extent, determine the amount of corrosion to be expected during this dry-up phase of the pipeline.

Carbon monoxide as impurity was not tested in the present work but it is present in most of the previously proposed specifications from the capturing process. However, no experimental data is available with respect to corrosion or chemical reactions between impurities. This should be included in future experiments.
The ramping experiments in chapter 7 revealed that CO₂ mixtures with SO₂-H₂O or NO₂-H₂O as impurities behaved very different with respect to corrosion. This can be related to adsorption/absorption effects – or the protectiveness of the corrosion products, but the details are not yet understood. It is important to understand the mechanisms that are involved, in order to be in the forefront in predicting unacceptable corrosion of CCS installations.

The sulphur chemistry is very complex and further research is needed to fully understand when elemental sulphur is produced in the system as it can lead to production of large quantities of solid matter, which again can result in clogging of pipelines and injection reservoirs.

The CO₂ quality specification in this study is a good starting point for ensuring the integrity for the carbon steel components (pipes, tanks, ...) involved in CCS, but it should be expanded to cover additional compounds like glycol and amines. Also, from a material aspect, the mechanism revolving phases, structures, and grain boundary in the metal could influence the initiation of corrosion and the amount of localised attacks.