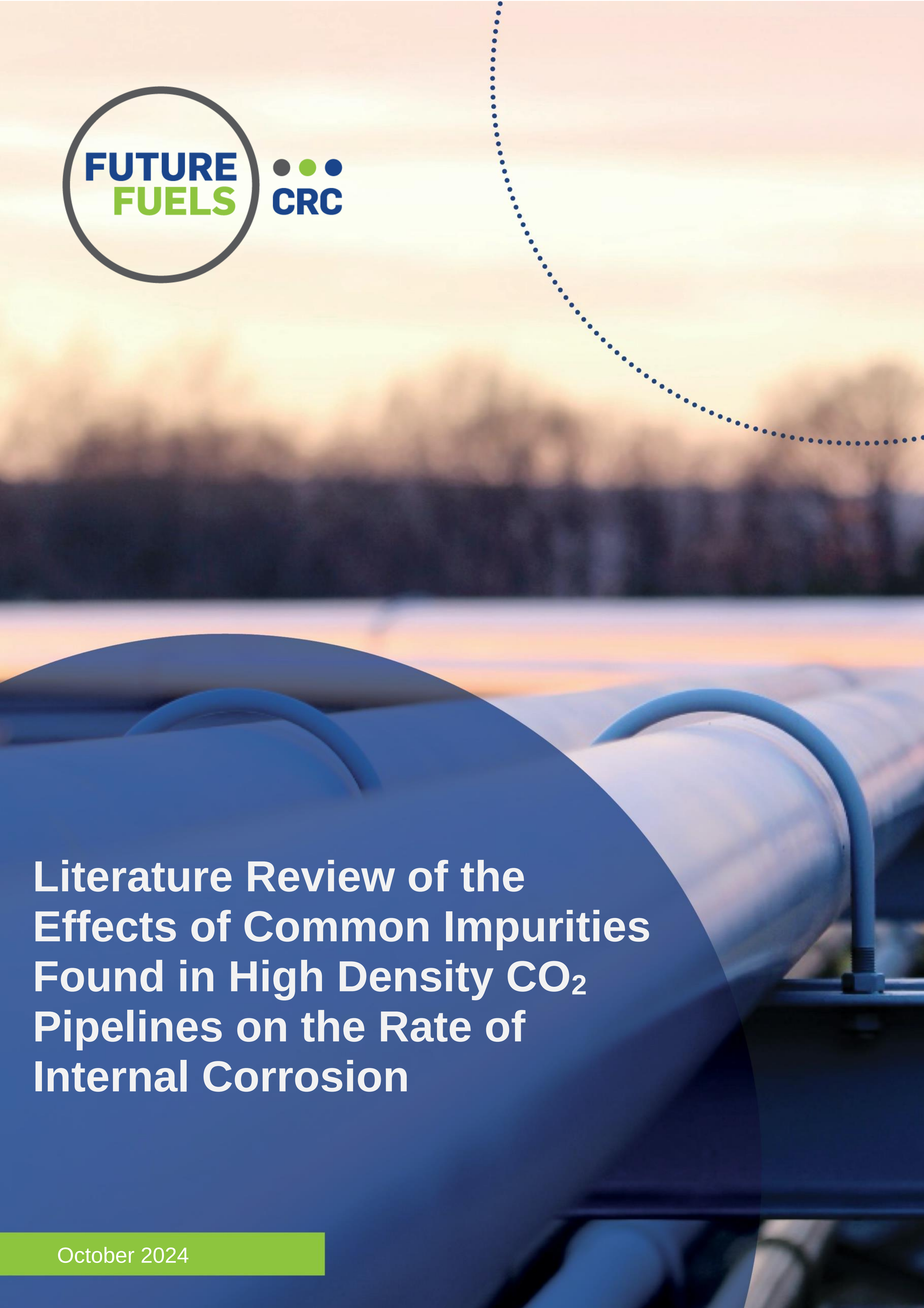

Literature Review of the Effects of Common Impurities Found in High Density CO_2 Pipelines on the Rate of Internal Corrosion

October 2024

Project number: RP3.4-10

Project title: Literature Review of the Effects of Common Impurities Found in High Density CO_2 Pipelines on the Rate of Internal Corrosion

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PROJECT INFORMATION	
Project number	RP3.4-10
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Research Program	RP3 – Network Lifecycle Management
Milestone Report Number	2
Description	Submission of a report, 1. Reviewing the current knowledge and recommended practices to manage internal corrosion of carbon steel pipelines transporting dense phase CO_2 2. Providing recommendations covering but not limited to: 3. Best current practices to avoid high corrosion rates looking at the synergistic effects of impurities 4. Possible conditions where knowledge of corrosion rates is limited that require further investigation 5. Knowledge expansion in terms of corrosion mechanisms and the development of new corrosion models
Research Provider	Deakin University
Project Leader and Team	Deakin University: Mike Tan, Research Director Deakin University: Ying Huo Atteris: Tom Seeber, Evelyn Xu, Jason Hemetsberger
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Related Commonwealth Schedule	Research Coordinator to advise
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Approved by	Thomas Seeber
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Summary of Report

This Report provides a comprehensive review of the current knowledge and recommended practices for managing internal corrosion in carbon steel pipelines transporting dense phase CO_2. The focus is on understanding the synergistic effects of impurities and providing recommendations to avoid high corrosion rates. Additionally, areas where knowledge of corrosion rates is limited and requires further investigation are identified, along with the need for expanding knowledge on corrosion mechanisms and the development of new corrosion models.

The Report highlights the importance of considering the combined presence of impurities, such as O_2, H_2S, SO_2, and NO_x, as they can significantly accelerate the corrosion of carbon steel pipelines. Synergistic effects among these impurities have been observed, resulting in corrosion rates higher than the sum of those associated with individual impurities. Therefore, best current practices are recommended to address these synergistic effects and mitigate the risk of high corrosion rates.

Furthermore, the Report identifies certain conditions where knowledge of corrosion rates is limited and further investigation is needed. These conditions may include specific combinations of impurities, varying concentrations, and specific operating conditions. It is crucial to expand the understanding of these conditions to enhance corrosion management strategies and develop targeted mitigation measures.

Additionally, the Report emphasizes the need for knowledge expansion in terms of corrosion mechanisms and the development of new corrosion models. Understanding the underlying mechanisms behind the synergistic effects of impurities and their interaction with the pipeline materials is essential for accurate corrosion prediction and effective corrosion management strategies. The development of new corrosion models will enable more reliable assessments and predictions of corrosion rates in dense phase CO_2 pipelines.

In conclusion, this Report provides valuable insights into managing internal corrosion in carbon steel pipelines transporting dense phase CO_2. By considering the synergistic effects of impurities, implementing best current practices, investigating conditions with limited knowledge, and expanding corrosion mechanisms and models, operators can enhance corrosion management strategies and ensure the integrity and reliability of CO_2 pipelines.

1. INTRODUCTION

The transportation of CO_2 (Carbon Dioxide) from the capture point to storage and utilisation sites is an integral component of CCUS (Carbon Capture, Utilisation and Storage) projects. Whilst ships, trucks and trains can be used to transport CO_2, pipelines are typically considered to be the most safe, reliable, and cost-effective method for transporting CO_2 [1], [2]. An understanding of the internal corrosion mechanisms present within CO_2 pipelines is required to manage and control internal corrosion and ensure that CO_2 pipelines can be safely operated.

Pipeline transportation of CO_2 over longer distances is typically regarded as most efficient and economical when the CO_2 is in either the compressible liquid or supercritical phases. This can be attributed to the larger density associated with these phases in comparison with gaseous phase CO_2 resulting in smaller frictional energy losses along the pipeline [3]. Whilst it has been acknowledged that supercritical CO_2 offers superior pipeline transportation properties in comparison with CO_2 in the gaseous phase, there is currently a poor understanding of internal corrosion mechanisms in supercritical CO_2 pipelines. Whilst it has been acknowledged by many operators that the formation of a free water phase in a supercritical CO_2 pipeline can result in severe corrosion rates, there is currently limited understanding of the effects that other impurities may have on internal corrosion rates. Given that many Australian Oil and Gas operators are interested in operating CO_2 pipelines, the information presented in this paper can be used by Australian Oil and Gas operators to carefully manage and control corrosion in their CO_2 pipelines.

The purpose of this paper is to review the available information in literature in relation to corrosion in supercritical CO_2 pipelines. This review will focus on the effect of impurities on supercritical CO_2 pipeline corrosion rates and discuss any potential synergistic effects between impurities that result in a significant increase in corrosion rates. Impurity specifications from CO_2 pipelines in the United States of America (USA) along with impurity level recommendations from literature and standards will also be presented. The effect of pressure, temperature, flow rate and localised corrosion on the overall corrosion rate will also be briefly reviewed. Industry interviews will also be conducted, so that an understanding of the impurities that Australian CO_2 pipeline operators are most concerned about can be developed.

By summarising the available information in literature in relation to supercritical CO_2 pipeline internal corrosion, this paper can be used by operators as a guide for managing and controlling corrosion. The literature review will also enable the current knowledge gaps associated with supercritical CO_2 pipeline transport to be identified. By identifying both the knowledge gaps in our current understanding of CO_2 pipeline corrosion and the impurities that Australian CO_2 pipeline operators are most concerned about, new research opportunities can be identified that will close the knowledge gaps that are of concern to industry.

2. CO_2 PHASE BEHAVIOUR

CO_2 is typically transported through pipelines as a dense phase fluid. For the purpose of this report, a dense phase fluid will be considered to be a fluid with a pressure that is larger than its critical pressure. A fluid in its dense phase can either be behaving as a compressible liquid, or a supercritical fluid. A supercritical fluid will be considered to be a fluid with a pressure and temperature that exceeds the critical pressure and temperature of the fluid. Figure 1 presents a phase diagram of pure CO_2. The critical pressure and temperature of CO_2 has been indicated on this phase diagram.

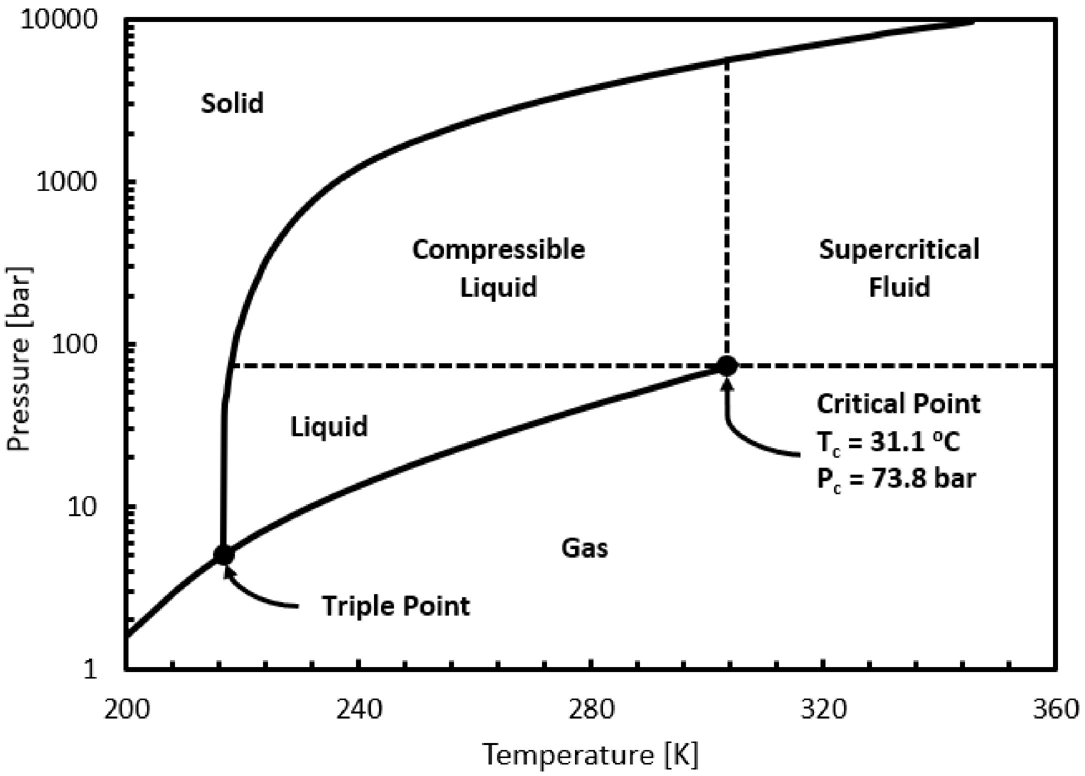

Figure 1. Phase diagram of pure CO_2. The data used to construct this phase diagram was extracted from Witkowski et al [4]. The critical properties of pure CO_2 were extracted from Peletiri et al [5].

It is important to note that the properties associated with CO_2 mixtures will vary as the mixture composition changes. This means that both the critical point and the phase diagram of the mixture will be dependent on its composition. Whilst the focus of this report is internal corrosion in supercritical CO_2, unplanned pipeline depressurisation and process upsets can result in phase changes associated with the pipeline fluid. The effect of phase changes associated with pipeline depressurisation and process upsets on corrosion rates will also be briefly discussed in this report.

3. IMPURITIES FROM COMMON CARBON CAPTURE SYSTEMS

The impurities that can result in corrosion in supercritical CO_2 pipelines are often introduced into the CO_2 stream during the carbon capture process. It is essential that CO_2 pipeline operators understand the impurities that may be present in their CO_2 pipelines so that they can carefully manage and control internal corrosion.

Post-combustion capture, pre-combustion capture and oxy-fuel are the three main process routes for capturing CO_2 from power plants [6]. The composition of a CO_2 pipeline will be directly dependent on the CO_2 source and carbon capture technology that has been employed. Table 1 provides a summary of the expected concentration of impurities in a dried CO_2 stream from post-combustion, pre-combustion and oxyfuel carbon capture processes on both coal-fired and gas-fired plants [7]. Table 1 can be used by operators to understand the impurities that may be present in CO_2 captured from power plants.

Table 1. Summary of the expected CO_2 impurity concentrations associated with the most common carbon capture processes on coal and gas-fired plants [7]. It has been assumed that the CO_2 streams produced from these carbon capture processes have been dehydrated.

Capture Process	SO_2 [vol%]	NO [vol%]	H_2S [vol%]	H_2 [vol%]	CO [vol%]	CH_4 [vol%]	N_2/Ar/ O_2 [vol%]	Total Amount of Impurities [vol%]
Coal-Fired Plants								
Post-Combustion Capture	<0.01	<0.01	0	0	0	0	0.01	0.01
Pre-Combustion Capture	0	0	0.01-0.6	0.8-2.0	0.03-0.4	0.01	0.03-0.6	2.1-2.7
Oxy-Fuel	0.5	0.01	0	0	0	0	3.7	4.2
Gas-Fired Plants								
Post-Combustion Capture	<0.01	<0.01	0	0	0	0	0.01	0.01
Pre-Combustion Capture	-	-	<0.01	1.0	0.04	2.0	1.3	4.4
Oxy-Fuel	<0.01	<0.01	0	0	0	0	4.1	4.1

The level of impurities that can be expected in CO_2 streams derived from other anthropogenic sources, such as the steam methane reforming (SMR) process, are likely to be significantly different [8]. It is essential that strict impurity level requirements are developed for CO_2 pipelines regardless of the source of CO_2. Table 2 summarises the CO_2 stream composition expected for CO_2 that has been produced from the SMR process and subsequently captured. The DYNAMIS CO_2 composition values presented in Table 2 correspond to the CO_2 mixture impurity levels expected for CO_2 that has been produced through the SMR process, captured using the activated methyl diethanolamine (MDEA) process, and then dehydrated and compressed [9]. The Port Arthur CO_2 composition values correspond to the composition of CO_2 produced in an industrial scale SMR and carbon capture process that is operated by Air Products at Port Arthur [8], [10]. It should be noted that both water and hydrogen sulphide (H_2S) have not been included in the Port Arthur CO_2 composition data, even though both of these components are expected to be responsible for major integrity threats at typical CO_2 pipeline transportation pressures, and it is expected that some H_2S will leak into the CO_2 mixture [8].

The impurity levels presented in Tables 1 and 2 should only be used as a guideline. The CO_2 mixtures produced from each carbon capture process can be purified further than the impurity levels presented in Tables 1 and 2, although larger capture costs would be incurred. Table 3 presents maximum impurity levels recommended in the literature for CO_2 pipelines, whilst Table 4 presents a summary of the maximum impurity levels used for existing CO_2 pipelines in the USA. Furthermore, Table 5 presents the planned CO_2 pipeline specifications for the ARAMIS project, which is a project that revolves around transporting CO_2 captured from hard-to-abate industries and storing it in depleted offshore gas fields under the Dutch North Sea.

Table 2. Summary of CO_2 mixture composition data for CO_2 that has been produced by the SMR process and subsequently captured. The DYNAMIS CO_2 composition values represent the expected impurity levels in a CO_2 stream produced by capturing and purifying the CO_2 produced in the SMR process using an activated MDEA process and dehydration [9]. The Port Arthur CO_2 composition values correspond to the composition of the CO_2 stream produced by the SMR process at Port Arthur [10].

Component	DYNAMIS Project Expected Composition of CO_2 Stream Produced by SMR Process [9]	Port Arthur CO_2 Stream [10]
H_2O [ppm Unless Stated]	400	-
CO_2 [vol% Unless Stated]	99.75	98.11 mol%
MDEA [ppm]	0	-
MEA (Monoethanolamine) [ppm]	0.1	-
CH_4 [ppm Unless Stated]	130	10800
H_2 [ppm Unless Stated]	1950	1600
CO [ppm Unless Stated]	4.6	2000
N_2 [ppm Unless Stated]	2.4	4600
TEG (Triethylene glycol) [ppm]	0.2	-

Table 3. Summary of the maximum impurity levels recommended for CO_2 pipelines by a wide range of literature studies [11].

Impurity	DYNAMIS Project (1) [9]	NETL (2) [12]	Literature Review [13]	CarbonNet (3) [9], [14]
H_2O [ppmv]	500	500	20-650	100
H_2S [ppmv]	200	100	20-13000	100
CO [ppmv]	2000	35	10-5000	-
O_2 [ppmv]	< 40000	10	100-40000	-
NO_x [ppmv]	100	100	20-2500	-
SO_x [ppmv]	100	100	10-50000	-

Notes

1. DYNAMIS was an integrated European project that investigated the composition requirements for CO_2 pipeline transportation applications.
2. NETL (National Energy Technology Laboratory) issued a report that summarises the recommended impurity limits for CO_2 pipeline transportation streams.
3. CarbonNet is a project exploring the feasibility of a commercial scale CCS network in Victoria, and they have developed a preliminary CO_2 specification for its CCS hub-based network.

Table 4. Summary of the maximum impurity levels associated with existing CO_2 pipelines in the USA [11], [12].

Impurity	Canyon Reef Carriers	Central Basin Pipeline	Cortex Pipeline	Weyburn
H_2O [ppmv]	122	630	630	20
H_2S [ppmv]	< 260	< 26	20	9000
CO [ppmv]	-	-	-	1000
O_2 [ppmv]	-	< 14	-	< 70
NO_x [ppmv]	-	-	-	-
SO_x [ppmv]	-	-	-	-

Table 5. Summary of the CO_2 composition specification selected for the proposed ARAMIS project [15].

Component	Constraint	Unit	Specification
CO_2	Larger Than	mol%	95
H_2O	Less Than	ppm mole	70
N_2	Less Than	mol%	2.4
O_2	Less Than	ppm mole	40
H_2	Less Than	ppm mole	7500
Ar	Less Than	mol%	0.4
CH_4	Less Than	mol%	1
CO	Less Than	ppm mole	750
$O_2 + N_2 + H_2 + Ar + CH_4 + CO$	Sum Less Than	ppm mole	40000
NO_x	Sum Less Than	ppm mole	2.5
H_2S	Less Than	ppm mole	5
H_2S + COS (Carbonyl Sulphide) + SO_x + DMS (Dimethyl Sulphide)	Sum Less Than	ppm mole	20
Amine	Less Than	ppm mole	1
Aldehydes	Sum Less Than	ppm mole	10
Carboxylic Acids and Amides	Sum Less Than	ppm mole	1

Phosphorous-Containing Compounds	Sum Less Than	ppm mole	1
NH_3	Less Than	ppm mole	3
HCN (Hydrogen Cyanide)	Less Than	ppm mole	2
Total Volatile Organic Compounds (Excluding Methanol, Ethanol and Aldehydes)	Sum Less Than	ppm mole	10
Methanol	Less Than	ppm mole	620
Ethanol	Less Than	ppm mole	20
C_{2+} (Aliphatic Hydrocarbons)	Sum Less Than	ppm mole	1200
Aromatic Hydrocarbons	Sum Less Than	ppm mole	0.1
Glycols (TEG)	Sum Less Than	-	Glycol specification will be selected by following a dew point specification (1)

Notes

6. The maximum tolerable mole fraction of glycols has been selected to be the mole fraction where the mixture dew point is -10 °C at 20 bar (As measured or predicted using the Cubic Plus Association equation of state).

The impurities reported in Tables 1 to 5 will be used as a basis for the impurities considered in this paper. Other impurities that have been established to increase corrosion rates in supercritical CO_2 pipelines will also be discussed.

4. PIPELINE CORROSION IN CO_2-H_2O SYSTEMS

DNV-RP-F104 (Design and operation of carbon dioxide pipelines) and ISO 27913 (Carbon dioxide capture, transportation and geological storage) have been identified as the main two standards for the design of CO_2 pipelines [3], [16]. ISO/TR 27921 is a technical report released by the International Organization for Standardization (ISO) that discusses dense phase internal corrosion [11]. Internal corrosion in CO_2-H_2O systems have been discussed in all of these standards and reports.

DNV-RP-F104 has indicated that internal corrosion represents a significant risk to the integrity of CO_2 pipelines if there is insufficient dewatering of the pipeline fluid [3]. This standard indicates that a combination of the formation of a free water phase and a high CO_2 partial pressure can result in severe corrosion rates due to the formation of carbonic acid. DNV-RP-F104 recommends that the water content level of the CO_2 is carefully monitored and controlled to ensure that a free water phase cannot form at any location along carbon steel pipelines during both steady state operation and pipeline depressurisation and process upset events. Whilst this standard has suggested that careful material selection can be used to significantly decrease internal corrosion rates in CO_2 pipelines with a free water phase, this is not a feasible design strategy for projects where existing subsea hydrocarbon pipelines are being repurposed into subsea CO_2 pipelines.

ISO 27913 has recommended that the maximum water concentration associated with the CO_2 pipeline mixture is determined such that corrosion rates are within the design margins [16]. This standard has suggested that the maximum water concentration will be dependent on the pipeline operating conditions, and that water specifications should be made on the basis of relevant operating experience, experimental data and reliable verified corrosion models [16]. Using existing onshore CO_2 pipelines in the USA as a basis, ISO 27913 has recommended that the maximum allowable water content of the pipeline mixture is specified to be between 20 and 630 ppmv. However, the CO_2 fluid that is typically transported through CO_2 pipelines in the USA tends to be relatively pure as it is captured from natural gas, which means that this recommendation is not necessarily applicable for CO_2 captured from other sources due to the presence of other impurities. The large range in the recommended pipeline allowable water content can be attributed to the synergistic effects between impurities, and due to a lack of data and current understanding in CO_2 pipeline corrosion mechanisms [16]. This means that the maximum allowable water content will be dependent on the concentration of the other impurities in the mixture. Both DNV-RP-F104 and ISO 27913 have indicated that there are currently not any reliable models for predicting corrosion rates in CO_2 pipelines that are being operated at both high pressure and with a free water phase [3], [16]. However, there is active research in this area.

ISO/TR 27921 has indicated that water dissolved in the dense phase CO_2 stream is not corrosive, and pipeline free water formation is required to produce a corrosive mixture [11]. This technical report has suggested that carbon steel can suffer general and pitting corrosion in wet CO_2 mixtures at rates of more than 1.0 mm/year, and that experimental studies show that corrosion rates in dense phase CO_2-H_2O mixtures increase with increasing temperature [11]. Under extreme conditions, ISO/TR 27921 has suggested that extremely large corrosion rates that exceed 30 mm/year can occur when steel is exposed to significant amounts of condensed water [11]. ISO/TR 27921 has also stated that the solubility of water in dense phase CO_2 decreases with decreasing pressure and temperature [11]. This result suggests that water drop out and significant corrosion rates could occur during process upset events that result in significant reductions in CO_2 mixture pressure and temperature. Whilst it has been acknowledged by ISO/TR 27921 that a protective Iron Carbonate ($FeCO_3$) corrosion product film can form when the concentration of dissolved corrosion products in the mixture become large, the technical report has indicated concerns about the failure in this film resulting in high localised corrosion rates [11].

A brief literature review of corrosion in dense phase CO_2 systems has also been provided in Annex A of ISO/TR 27921. Annex A has suggested that both laboratory experiments and field experience have confirmed that very low corrosion rates have been detected in dense phase CO_2 pipelines that have been operated in the range 20 ppmv to 650 ppmv [11]. This water impurity range is consistent with the water specifications used for current operating onshore CO_2 pipelines in the USA that were discussed in ISO 27913 [16]. Whilst ISO/TR 27921 has identified that thermodynamic models for predicting the formation of a free water phase in dense phase CO_2 systems can be used, these models cannot be extended to more complicated mixtures that have other components [11].

All of the standards and technical reports have indicated the importance of free water formation on corrosion in dense phase CO_2 systems. The solubility of H_2O in CO_2 refers to the maximum amount of H_2O that can dissolve into the CO_2-rich phase at a particular pressure and temperature. A free water phase will form in a CO_2-H_2O system when the global water concentration of the system exceeds the solubility of water in the CO_2-dominant phase. Since corrosion in supercritical CO_2 systems relies on the formation of a free water phase, an understanding of the solubility of water in supercritical CO_2 pipelines is important.

Choi and Nešić have completed extensive studies on the mutual solubilities of CO_2 and H_2O in the two co-existing phases, and they have used the results from these studies to predict the equilibrium concentration of corrosive species in the free water phase as a function of pressure and temperature [17]. Figure 2 presents both experimental data and the outputs from a thermodynamic model for the solubility of water in dense phase CO_2 [17]. The solubility of water in dense phase CO_2 was considered at temperatures of 20 °C, 25 °C, 50 °C and 75 °C in this Figure.

The thermodynamic model used in this paper was based on both the Nešić model [17], [18] (Which models the chemistry of the water-rich phase) and the Spycher model [17], [19] (Which enables modelling of the mutual solubilities of CO_2 and H_2O). The Nešić model uses pressure and temperature dependent equilibrium constant expressions for the carbonic acid formation and dissociation reactions to calculate the concentration of corrosive species in the free water phase [17], [18]. The Spycher model uses the Redlich-Kwong (RK) equation of state (EOS) in conjunction with chemical potential equality calculations to model the temperature and pressure dependence of the mutual solubility of CO_2 and H_2O [17], [19].

Figure 2 indicates that in the supercritical region, an increase in system pressure results in an increase in the solubility of H_2O in the supercritical CO_2 phase. This Figure also suggests that the solubility of water in supercritical CO_2 is larger in comparison with the compressible liquid and regular liquid phases. This result suggests that phase changes in a supercritical CO_2 pipeline could result in the formation of a corrosive free water phase. The data also indicates that the solubility of water in the supercritical CO_2 phase increases as the system temperature increases from 50 °C to 75 °C.

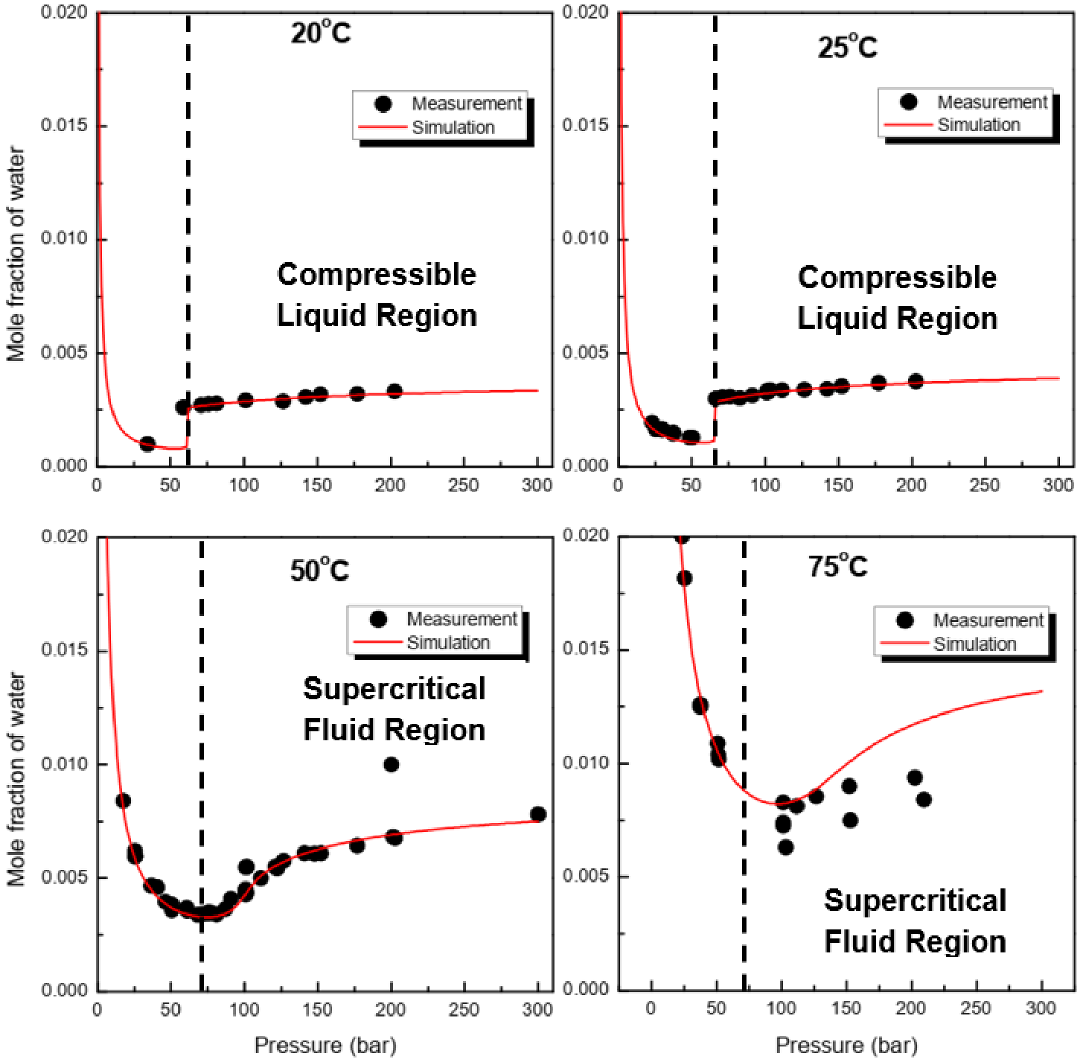

Figure 2. Experimental data and thermodynamic model outputs for the solubility of water in CO_2 [17]. The red curves correspond to the outputs from the thermodynamic model, whilst the black curves are experimental data points. The dense phase CO_2 region at each temperature condition lies to the right of the vertical dotted line.

Although there is strong agreement between the selected thermodynamic model and the experimental data for the solubility of water in supercritical CO_2 at relatively low temperatures, Figure 2 indicates that the thermodynamic model is diverging away from the experimental data above 75 °C.

The relationship between solubility of the solubility of water in CO_2 and pressure and temperature has also been explored using thermodynamic software. Figure 3 presents the relationship between the solubility of water in CO_2 in a H_2O-CO_2 mixture and pressure and temperature, as calculated by the OLI software. The outputs produced by the software appear to match the solubility behaviour depicted in Figure 2.

It should be noted that the solubility of water in CO_2 will be directly affected by the presence of other impurities in the mixture. The effect of other impurities on the solubility of water in CO_2 will be discussed later in this Report.

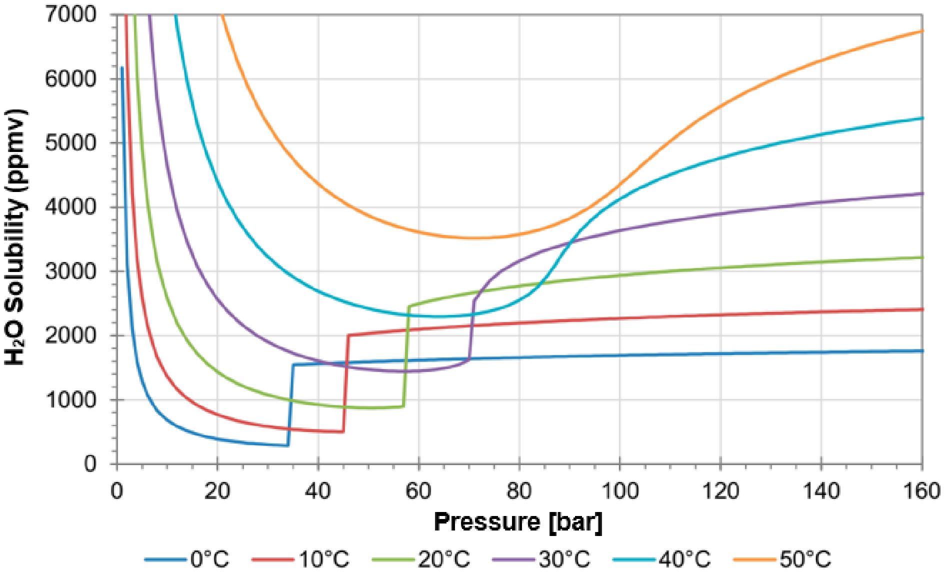

Figure 3. Presents a plot of the relationship between the solubility of water in CO_2 in a H_2O-CO_2 mixture, and the pressure and temperature of the mixture [20]. This plot was constructed using the thermodynamic software OLI.

Choi and Nešić have argued that the solubility of CO_2 in the aqueous phase is also important because this will have a direct impact on the corrosivity of any free water phase that has formed [17]. Carbonic acid will only form in the free water phase when both H_2O and CO_2 are present in that phase. The solubility of CO_2 in a free water phase has been studied by multiple authors. Figure 4 presents the solubility of CO_2 in water using the experimental data and thermodynamic model used by Choi and Nešić over a wide range of pressure and temperature values [17].

Figure 4 suggests that the thermodynamic model provided a good fit to the experimental data over the entire temperature and pressure range considered. It was noted by Choi and Nešić that the solubility of CO_2 in the aqueous phase was much larger in comparison with the solubility of water in the CO_2-rich phase [17]. Figure 4 also suggests that the solubility of CO_2 in water increases as the pressure of the system increases, and that the CO_2 solubility decreases as temperature increases.

Choi and Nešić used the outputs from their thermodynamic calculations in conjunction with aqueous chemistry models to generate curves for the equilibrium carbonic acid concentration and pH within the free water phase as a function of pressure and temperature. Figures 5 and 6 presents the effect of pressure and temperature on the equilibrium carbonic acid concentration and pH within the free water phase respectively. A larger solution pH is indicative of a more corrosive pipeline mixture.

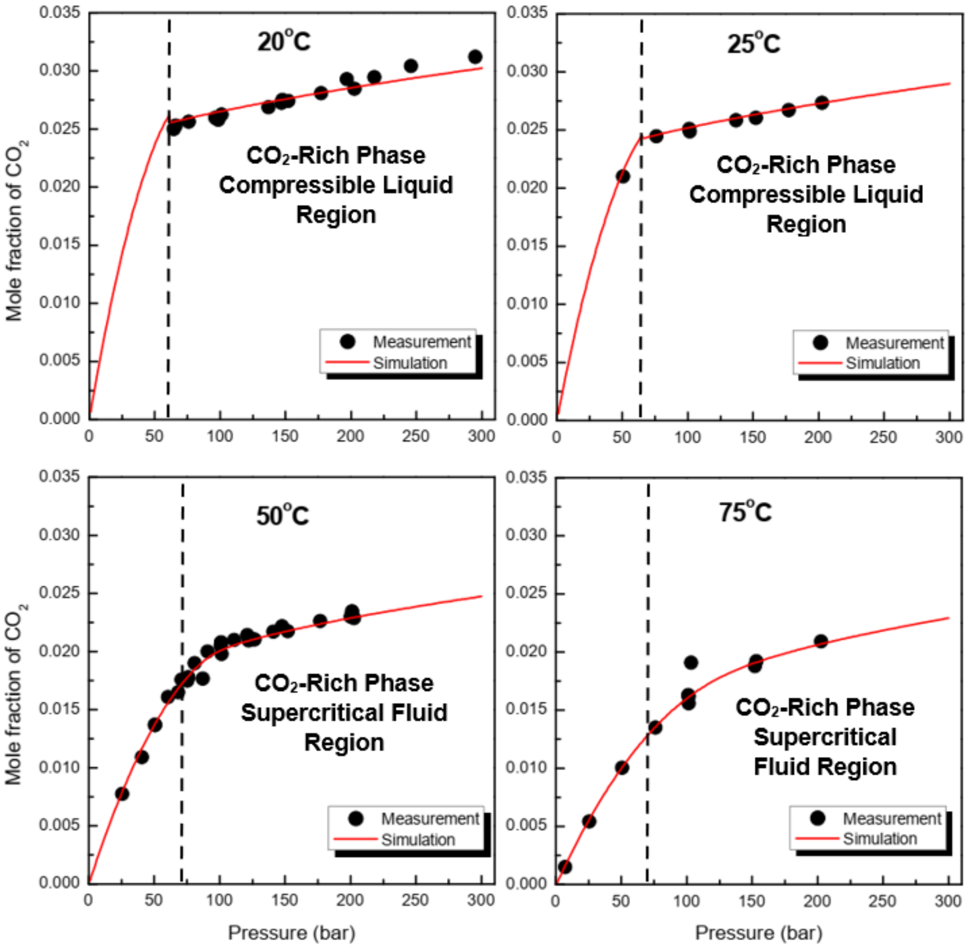

Figure 4. The solubility of CO_2 in the aqueous phase in a CO_2-H_2O system [17]. The red curve and the black dots correspond to the curve that was produced using the thermodynamic model and the experimental data respectively.

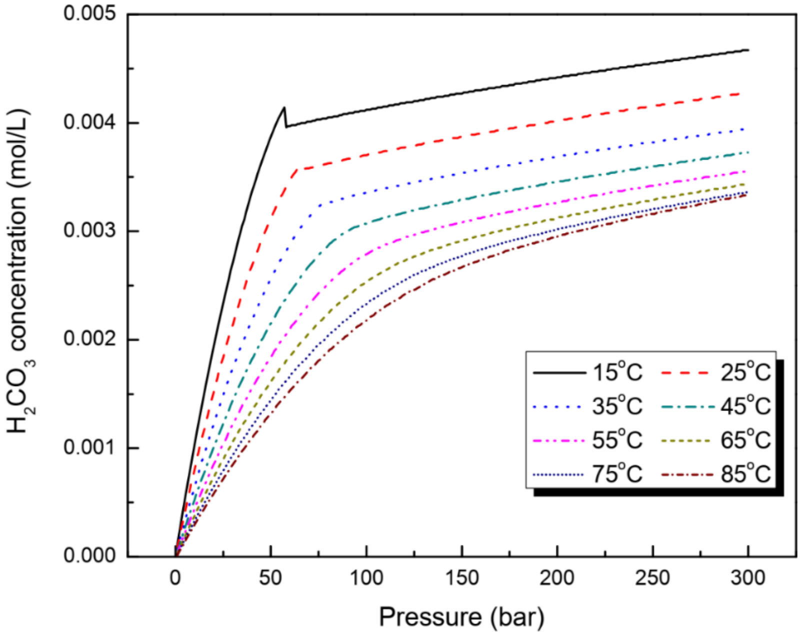

Figure 5. The effect of pressure and temperature on the equilibrium concentration of carbonic acid in the free water phase in a CO_2-H_2O system [17].

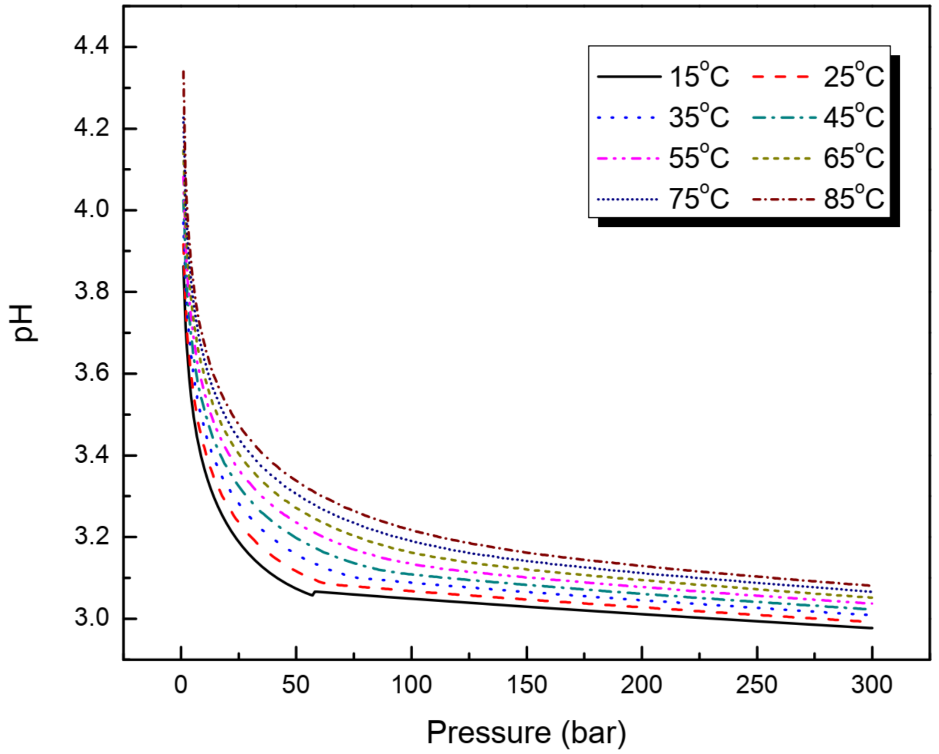

Figure 6. The effect of pressure and temperature on the equilibrium pH of the free water phase in a CO_2-H_2O system [17].

Figure 5 suggests that the equilibrium carbonic acid concentration in the aqueous phase increases as pressure increases, whilst this concentration value decreases as temperature increases [17]. Figure 6 shows that the solution pH decreased with an increase in pressure and increased as the system temperature increased [17]. This means that an increase in system pressure results in a more corrosive free water phase.

Halseid et al. has suggested that both field experience from the USA and lab experiments indicate that corrosion rates are insignificant when the water content is well below the solubility limit, which is consistent with the information provided in the CO_2 pipeline industry standards and technical reports [20]. The National Energy Technology Laboratory (NETL) has stated that corrosion does not occur in “rigorously dry CO_2” [12]. A study completed by Dugstad et al. suggested that corrosion does not take place in a dense phase CO_2-H_2O system with a water content of 500 ppmw (1221 ppm mole) [22], and this claim has been supported by other authors. Figure 7 presents the average corrosion rate of carbon steel in water-saturated supercritical CO_2 and under-saturated supercritical CO_2 at 50 °C and 80 bar for an experimental test that was run for 48 hrs [23]. Figure 8 presents the relationship between the average corrosion rate of carbon steel for supercritical CO_2 at 35 °C and 80 bar and the water content of the CO_2 mixture [23].

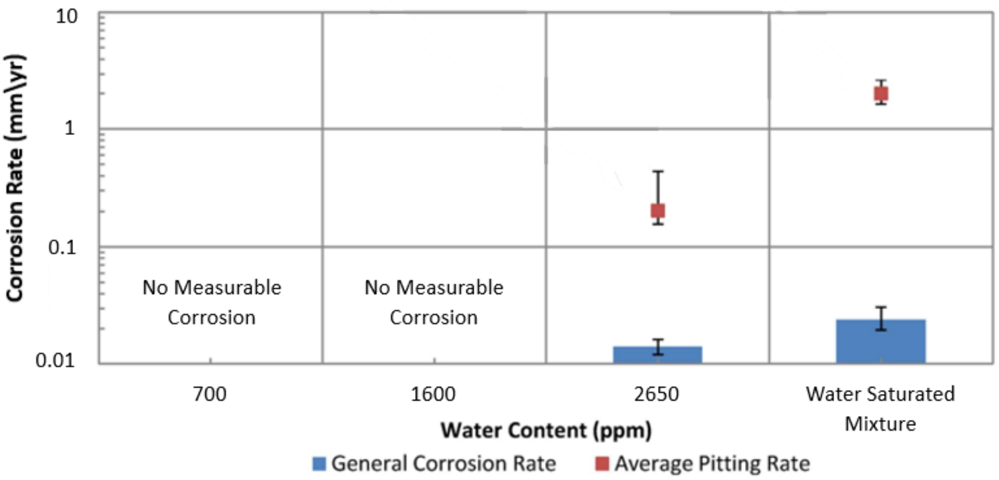

Figure 7. Average pitting and general corrosion rates of carbon steel in a supercritical CO_2-H_2O mixture at 50 °C and 80 bar [23]. The experimental tests used to collect the data in this plot were completed had a duration of 48 hrs. The water-saturated mixture experimental testing used a supercritical CO_2-H_2O mixture with a water concentration of 3400 ppm mole because the Spycher mutual solubility model indicates that 3400 ppm mole is the solubility of water in supercritical CO_2 at 50 °C and 80 bar [19], [23].

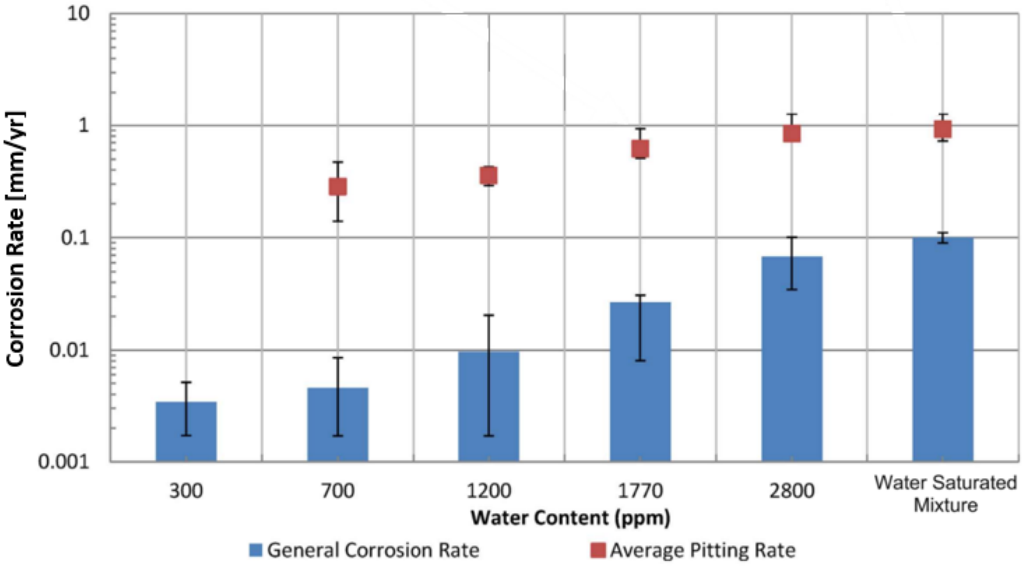

Figure 8. Average pitting and general corrosion rates of carbon steel in a supercritical CO_2-H_2O mixture at 35 °C and 80 bar [23]. The water-saturated mixture experimental testing used a mixture with a water concentration of 3437 ppm mole because the Spycher mutual solubility model indicates that this is the solubility of water in supercritical CO_2 at 35 °C and 80 bar [19], [23].

The key findings from the results presented in Figures 7 and 8 and the work completed by Hua et al. are as follows:

7. In water-saturated CO_2 at 50 °C, 90 % of the carbon steel surface did not show any signs of corrosion, and the dominant corrosion mechanism was pitting corrosion [23].
8. In water-saturated CO_2 at 35 °C, the entire carbon steel surface had suffered from corrosion and uniform corrosion rates were significantly larger in comparison with the 50 °C experimental testings [23].
9. Most importantly, the results suggest that a temperature reduction from 50 °C to 35 °C can result in pitting and uniform corrosion at lower water concentrations that lie well below the water saturation condition, and that localised corrosion rates can be over an order of magnitude larger in comparison with the average steel corrosion rate [23].

Many other authors have also investigated corrosion in saturated and undersaturated supercritical CO_2-H_2O systems. Table 6 provides a summary of the key experimental results when investigating localised corrosion in saturated and undersaturated supercritical CO_2-H_2O systems. Table 7 provides a summary of the key experimental results obtained by other authors when investigating the rate of uniform corrosion in saturated and undersaturated supercritical CO_2-H_2O systems. For comparison purposes, the results from the study completed by Hua et al. have also been added to both tables.

Table 6. Summary of the experimental results obtained by scholars who investigated the rate of localised corrosion in saturated and undersaturated supercritical CO_2-H_2O systems.

Authors and Reference	CO_2 Pressure [bar]	Temperature [°C]	Water Content [ppm mole]	Flow Rate [rpm Unless Stated]	Exposure Time [hrs]	Corrosion Test Method	Localised Corrosion Rate [mm/yr]
Sim et al. [25]	80	40	≈ 900 ≈ 1800 ≈ 2600 ≈ 3500 Water Saturated CO_2	Stagnant Conditions	168	Static Autoclave	Average ≈ 0.22 Maximum ≈ 0.65 Average ≈ 0.30 Maximum ≈ 0.64 Average ≈ 0.22 Maximum ≈ 0.55 Average ≈ 0.22 Maximum ≈ 0.65 Average ≈ 0.19 Maximum ≈ 0.50
Hua et al. [23]	80	35	300 700 1770 2800 Water Saturated CO_2 (3437 ppm mole)	Stagnant Conditions	48	Static Autoclave	0 ≈ 0.29 ≈ 0.62 ≈ 0.85 ≈ 0.92
Hua et al. [23]	80	50	700 1600 2650 Water Saturated CO_2 (3400 ppm mole)	Stagnant Conditions	48	Static Autoclave	No Attack No Attack 0.20 1.99

Table 7. Summary of the experimental results obtained by scholars who investigated uniform corrosion rates in saturated and undersaturated supercritical CO_2-H_2O systems.

Authors and Reference	CO_2 Pressure [bar]	Temperature [°C]	Water Content [ppm mole]	Flow Rate [rpm Unless Stated]	Exposure Time [hrs]	Corrosion Test Method	Uniform Corrosion Rate [mm/yr]
Choi and Nešić [24]	80	50	Water Saturated CO_2 (Approximately 3400 ppm mole)	Stagnant Conditions	24	Static Autoclave	≈ 0.4
Sim et al. [25]	80	40	244	Stagnant Conditions	168	Static Autoclave	0.08
			488				0.07
			732				0.06
			976				0.08
			1220				0.08
			3660				0.08
Hua et al. [23]	80	35	300	Stagnant Conditions	48	Static Autoclave	0.004
			700				0.005
			1200				0.012
			1770				0.028
			2800				0.068
			Water Saturated CO_2 (3437 ppm mole)				≈ 0.1
Hua et al. [23]	80	50	700	Stagnant Conditions	48	Static Autoclave	No corrosion
			1600				No corrosion
			2650				0.014
			Water Saturated CO_2 (3400 ppm mole)				≈ 0.024
Ayello et al. [26]	75.8	40	244	Stagnant Conditions	5	Using Electrochemical Impedance Spectroscopy in	1.2
			2440				2.3

						conjunction with an autoclave.	
Zhang et al. [27]	95 – 182	50 – 130	Water Saturated CO_2	995 rpm (Which is equivalent to an outer coupon surface rotation speed of 4m/s, resulting in the CO_2 mixture experiencing turbulent flow).	96	Autoclave equipped with a magnetic stirrer and a coupon at the end of the shaft.	0.014 – 0.043
Cabrini et al. [28]	123 – 146	25 – 60	Water Saturated CO_2	180	48-400	Autoclave equipped with a mechanical stirrer rotating in the free water phase.	0.01 – 0.1

Most of the results in Table 7 indicate that uniform corrosion rates are relatively low (Less than 0.08 mm/yr) when the mixture water content lies below the solubility limit of a CO_2-H_2O mixture [28]. It should be noted that the results obtained by Ayello et al. are inconsistent with the results produced by other authors, as they measured a corrosion rate of 1.2 mm/yr in an undersaturated supercritical CO_2-H_2O system with only 244 ppm mole of water [26]. Given that CO_2 pipelines in the USA operate under strict water impurity specifications to prevent free water formation (CO_2 pipelines in the USA are typically operated with a water content of less than 600 ppm) and the corrosion rate has been measured to be between 0.00025 and 0.0025 mm/year in these pipelines, the experimental corrosion rate data produced by Ayello et al. is inconsistent with the corrosion rates measured in the field [30]. The experimental results obtained by the other scholars are more consistent with CO_2 pipeline operational experience in America, and the expected corrosion behaviour for CO_2 pipeline systems presented in DNV-RP-F104 and ISO 27913.

Whilst the results produced by Hua et al. indicate that uniform corrosion rates rapidly increase as the water content of a CO_2-H_2O mixture increases and the CO_2-rich phase becomes saturated [23], there was a minimal increase in uniform corrosion rates as the CO_2-rich phase became saturated [25]. Sim et al. argued that the minimal increase in uniform corrosion rate between 976 and 3660 ppm mole water can be attributed to a protective corrosion scale (In the form of iron carbonate, $FeCO_3$) being most effective over this composition range at decreasing corrosion rates [25]. The formation of a protective $FeCO_3$ layer has significant effects on the overall general corrosion rate of steel because it has been shown that a $FeCO_3$ layer can reduce the corrosion rate of steel by over two orders of magnitude [28], [31]. The significant impact that the formation of a $FeCO_3$ layer has on corrosion rates at the steel surface can be attributed to the $FeCO_3$ film acting as a diffusion barrier to electrochemically active species and a surface coverage effect that results in the $FeCO_3$ crystals adhering to the substrate [28]. Sun et al. have developed a unified model for predicting $FeCO_3$ precipitation that accounts for both temperature and ionic strength and correlates well with experimental data [32]. Their model suggests that the tendency for $FeCO_3$ precipitation increases as the system temperature increases. Since this model indicates that the $FeCO_3$ precipitation is a direct function of ionic strength [32], the tendency of $FeCO_3$ to precipitate out as a solid will be dependent on the presence of other impurities in the pipeline mixture.

By studying the corrosion behaviour of carbon steels in a supercritical CO_2-H_2O mixture over an exposure time of between 24 and 120 hrs, it has been shown that an increase in the sample exposure time results in a significant reduction in the average general corrosion rate [31]. A visual inspection of the morphology and composition of the corrosion products revealed that the surface of the sample was covered by a dense and crystalline layer of $FeCO_3$ [31]. Both Choi et al. and Wei et al. have argued that these results can be attributed to the gradual formation of the $FeCO_3$ layer resulting in a reduction in corrosion rates over time [30], [31]. This result indicates that the formation of a protective corrosion layer can result in a reduction in supercritical CO_2 pipeline corrosion rates over time.

Regardless of whether a supercritical CO_2-H_2O mixture is undersaturated or saturated with water, Tables 6 and 7 indicate that pitting corrosion rates were much higher in comparison with the general corrosion rates [30]. These results suggest that pitting corrosion is the most dominant corrosion mechanism in undersaturated and saturated CO_2-H_2O systems [30].

In supercritical CO_2-H_2O mixtures that contain a significant amount of water, the main phase present is the free water phase [30]. This free water phase will contain dissolved supercritical CO_2. Choi and Nešić investigated the corrosion rate of carbon steels in a supercritical CO_2 mixture with a free water phase, and they showed that corrosion rates as high as 20 mm/year can be expected in the CO_2 saturated water-rich phase at 50 °C and 80 bar [24]. This corrosion rate is far faster in comparison with their measured CO_2-phase corrosion rate presented in Table 7, which highlights the acceleration of corrosion rates induced by the formation of a free water phase.

The severe corrosion rates identified by Choi and Nešić for supercritical CO_2-H_2O mixtures that contain a free water phase has also been detected by many other scholars. Figure 9 presents a comparison of the corrosion rates experienced by carbon steels in water-saturated supercritical CO_2 and supercritical CO_2-saturated water phase systems that do not contain any other impurities [30]. Figure 9 clearly highlights the extreme corrosion rates than can be present in CO_2-H_2O mixtures that contain a free water phase that is saturated with water. These extreme corrosion rates highlight the importance of carefully controlling the water content of CO_2 pipeline mixtures.

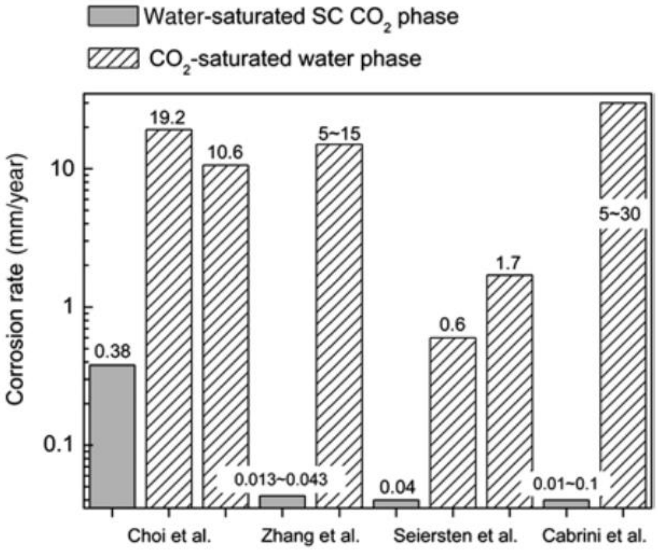

Figure 9. Comparison of the general corrosion rate in supercritical CO_2-H_2O systems that contain a water-saturated supercritical CO_2 phase, and systems that contain a free water phase that is saturated with supercritical CO_2 [30]. The graph was constructed by Wei et al. [30] and created using the experimental data produced by a wide range of scholars [27], [28], [31], [34], [35], [36].

Multiple authors have studied the effect of exposure time on the general corrosion rates in supercritical CO_2-H_2O water mixtures [30]. Zhang et al. investigated the effect of exposure time on the general corrosion rate of X65 pipeline steel in CO_2-saturated water at 80 °C and 95 bar [30], [38]. The results from their study have been presented in Figure 10. This Figure suggests that corrosion rates were extremely large (Approximately 28 mm/yr) after 2 hours of immersion, and Wei et al. have argued that the extreme corrosion rate at the beginning of the experimental testing can be attributed to no protective scale formation [30]. The Figure suggests that corrosion rates decreased rapidly over the 2 hr to 50 hr immersion time range [30], and Zhang et al. have indicated that this can be attributed to surface passivation by corrosion scales formed at the steel surface [38]. It should be noted that whilst a dense corrosion scale had formed after 96 hrs, corrosion rates in the CO_2-saturated water phase remained above 5 mm/yr [38].

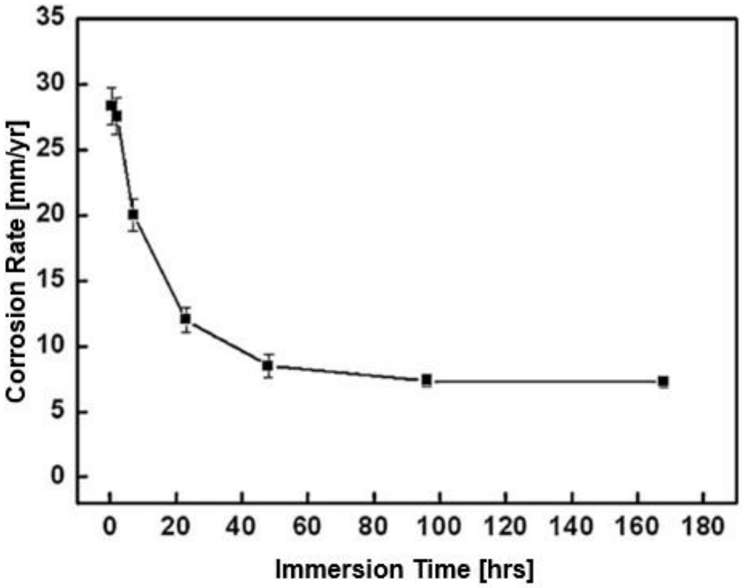

Figure 10. Presents the effect of immersion time on the corrosion rate of X65 pipeline steel in a supercritical CO_2-H_2O mixture at 80 °C with a CO_2-saturated free water phase [38].

The NORSOK [39] and KSC models [40] are often used to predict the corrosion rate of steel in CO_2 environments, but they do not provide accurate corrosion rate predictions in supercritical CO_2 pipelines [30]. The poor predictive capacity of the NORSOK and KSC models in water-saturated supercritical CO_2 mixtures was extensively studied by Seiersten [36]. Whilst the experimental work conducted by Seiersten indicated that the corrosion rates of X65 steel in water saturated with supercritical CO_2 at 75 to 90 bar and 40 °C ranged from between 1 mm/yr and 6 mm/yr, the NORSOK and KSC models predicted corrosion rates of 17 and 10 mm/yr, respectively [30], [36]. The significant discrepancy between the model outputs and the experimental results suggest that these models are not even capable of providing an indication of the potential corrosion rate in supercritical CO_2-H_2O mixtures [36].

5. PIPELINE CORROSION IN TERTIARY CO_2 MIXTURES THAT CONTAIN WATER

5.1 CO_2-H_2O-NO_X MIXTURES

It has been noted by many authors that the presence of NO_x in supercritical CO_2 pipelines can result in severe pipeline steel corrosion rates. The term "NO_x" is being used in this Report to refer to both nitric oxide (NO) and nitrogen dioxide (NO_2).

DNV-RP-F104 has identified NO_x as an impurity that can compromise the integrity of CO_2 pipelines. This standard has indicated that NO_x can participate in cross-chemical reactions that result in the formation of corrosive nitric acid (HNO_3) [3]. DNV-RP-F104 has also suggested that the presence of NO_x will result in the solubility of water in the supercritical CO_2 phase changing [3]. This means that the presence of NO_x will affect the pressure and temperature conditions that the formation of a corrosive free water phase can be expected.

DNV-RP-F104 has noted that laboratory experiments have shown that corrosion can occur in the presence of impurities such as NO_x in systems with low water content, including systems with a water content that lies below the solubility limit of water in supercritical CO_2-H_2O mixtures [3]. DNV-RP-F104 has suggested that the corrosion mechanisms in CO_2-H_2O-NO_x mixtures are not fully understood, although the standard has argued that NO_x is likely to form acids that can result in severe corrosion rates in combination with only a small fraction of free water [3].

ISO 27913 has also noted that the presence of NO_x as an impurity in a CO_2 pipeline can result in the formation of a free water phase containing strong acids that can significantly increase corrosion rates [16]. This standard has highlighted the experimental work completed by Dugstad et al. [41] as validation of the risks of nitric acid formation in CO_2-H_2O-NO_x mixtures. ISO 27913 has also noted that there is experimental evidence that nitric acid formation can occur at NO_x concentrations of less than 50 ppmv [16].

ISO/TR 27921 has highlighted similar concerns to DNV-RP-F104 and ISO 27913. ISO/TR 27921 has suggested that the extent of nitric acid formation and condensation will be strongly dependent on both the composition and the temperature of the CO_2 mixture [11]. ISO/TR 27921 has argued that an aqueous nitric acid phase can form at water contents of less than 100 ppmv, and it has flagged NO_x as one of the most aggressive impurities in CO_2 pipelines from a corrosion point of view [11]. ISO/TR 27921 has also noted that as of 2016, there was not any publicly available models that can accurately predict the formation of aqueous phases in CO_2-H_2O-NO_x mixtures [11].

Multiple studies in the literature have been dedicated to understanding the effect of NO_x on corrosion rates in CO_2-H_2O-NO_x mixtures. Table 8 provides a summary of the key experimental results presented in the literature for the uniform corrosion rates in supercritical CO_2-H_2O-NO_x mixtures. It should be noted that most literature studies do not focus on corrosion rates in CO_2-H_2O-NO_x mixtures; Rather they focus on corrosion rates in mixtures that contain additional impurities in addition to CO_2, H_2O and NO_x.

Table 8. Summary of the experimental results obtained by scholars who investigated uniform corrosion rates in supercritical CO_2-H_2O-NO_x systems.

Authors and Reference	**CO_2 Mixture Pressure [bar]**	**Temperature [°C]**	**Impurity Content [ppm mole Unless Stated]**			**Flow Rate [rpm Unless Stated]**	**Exposure Time [days Unless Stated]**	**Corrosion Test Method**	**Uniform Corrosion Rate [mm/yr]**
			NO_2	**NO**	**H_2O**				
Ayello et al. [26]	75.8	40	100 ppmv	0	2440 ppmv	Stagnant Conditions	5 hrs	Using Electrochemical Impedance Spectroscopy in conjunction with an autoclave	11.6
Brown et al. [42]	100	50	50 100 200 200 200 0	0 0 0 0 0 200	500	3 rpm, which corresponds to an average flow speed of 0.2 m/s.	1 7 1 3 7 7	Slim (Internal diameter 20-30 mm) autoclaves are rotated on a shaft inside a temperature controlled chamber. Test specimens were mounted on small cylindrical racks that slide from one end to the other as the autoclave rotates.	0.127 0.02 0.205 0.088 0.025 0.013

The differences in corrosion rates between Ayello et al. and Brown et al. are primarily influenced by water content and flow conditions. Ayello et al., operating under stagnant conditions with high water content (2440 ppmv), observed a significantly higher corrosion rate (11.6 mm/yr), suggesting that both stagnant flow and elevated H_2O levels accelerate corrosion. In contrast, Brown et al., with a rotational flow simulating 0.2 m/s and lower water content, recorded much lower corrosion rates (0.013 to 0.205 mm/yr), indicating that dynamic flow and reduced H_2O levels help mitigate corrosion.

Wei et al. have argued that the increase in corrosion rates caused by the presence of NO_2 in CO_2-H_2O-NO_2 mixtures can be attributed to the sharp decline in pH caused by the formation of nitric acid in the free water phase [30]. This assertion is consistent with the information provided by the CO_2 pipeline transportation standards. The mobility and reactivity of acids in supercritical CO_2 at 60 °C and 120 bar was also investigated by Ruhl and Kranzmann, and they found that nitric acid was extremely mobile and corrosive towards carbon steel [21], [47]. Wei et al. have also indicated that the corrosion product film formed during the nitric acid-induced corrosion of carbon steel is fluffy and has limited protectiveness, and that the severe corrosion rates seen in CO_2 mixtures that contain NO_x can be attributed to the poor protectiveness of this film [30].

Although Oxygen (O_2), sulphur dioxide (SO_2) and NO_2 all have the potential to accelerate corrosion rates in supercritical CO_2-H_2O environments, it has been established that NO_2 has the largest effect on the corrosion rate of carbon steel when all of these impurities are at the same concentration [27].

Whilst it is has been established that the dissolution of NO_2 into the free water phase of a supercritical CO_2 mixture will result in a reduction in pH, the exact mechanism is not fully understood. It is known that NO_2 will react with water to form nitric acid and NO under atmospheric conditions according to the following chemical reaction:

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$$

And this is the reaction that has also been proposed for dense phase CO_2 [21], [29]. Given that NO_x has the ability to promote extremely fast corrosion rates in supercritical pipelines, further study of the NO_x corrosion mechanism is required to define the safe stream compositions for CO_2 transportation [29].

5.2 CO_2-H_2O-SO_X MIXTURES

SO_x have been identified as another impurity that result in severe pipeline steel corrosion rates in supercritical CO_2 pipelines. The term “SO_x” is being used in this Report as a reference to sulphur dioxide (SO_2) and sulphur trioxide (SO_3). SO_x have been noted as one of the most aggressive impurities in CO_2 pipelines by ISO/TR 27921 [11].

The corrosion risks associated with the presence of SO_x as a CO_2 pipeline impurity, as described by DNV-RP-F104, ISO 27913 and ISO/TR 27921, appear to mirror the corrosion risks in CO_2 pipelines that contain NO_x. DNV-RP-F104 has suggested that SO_x have the ability to participate in cross-chemical reactions that result in the formation of a highly corrosive sulphuric acid (H_2SO_4) aqueous phase [3]. The potential for SO_x to accumulate in the free water phase of a CO_2 pipeline and forming sulphuric acid has also been highlighted by ISO 27913 [16]. Laboratory experiments have indicated that, like NO_x, corrosion may occur in CO_2-H_2O-SO_x mixtures with a low water content that lies well below the water solubility limit of water in supercritical CO_2 in H_2O-CO_2 mixtures [3]. Whilst it is understood that corrosion in CO_2-H_2O-SO_x mixtures can be aggressive even at low water content, the corrosion mechanisms in these mixtures are still not fully understood [3]. DNV-RP-F104 suggested that small scale laboratory testing has indicated that NO_x is more corrosive in comparison with SO_2 at very low water content [3]. DNV-RP-F104 has also indicated that the presence of SO_2 as an impurity could result in corrosion assisted fatigue in the presence of a free water phase [3].

DNV-RP-F104 has also flagged the potential for SO_x to affect the solubility of water in the CO_2-dominant supercritical phase [3]. This means that SO_x could possibly affect the pressure and temperature conditions that a corrosive free water phase could form in a CO_2 pipeline. ISO/TR 27921, however, has suggested that the presence of SO_2 in a CO_2 pipeline results in a negligible reduction in the solubility of water in the CO_2-rich supercritical phase [11].

ISO 27913 has also indicated that there is the potential for the deposition of solid sulphur (S) in CO_2 pipelines, in addition to the formation of sulphuric acid, when SO_x is present as an impurity [16]. This standard has also suggested that there is experimental evidence that sulfuric acid can be formed in CO_2 pipelines at SO_x concentrations of less than 50 ppmv [16]. ISO/TR 27921 has indicated that the extent of acid formation and condensation and the composition of the corrosive free water phase in CO_2 pipelines that contain SO_x will be strongly dependent on the pipeline operating conditions and the overall composition of the CO_2 mixture [11]. This technical report has also suggested that, as of 2020, there are no publicly available models that can be used to predict the formation of aqueous phases when reactive impurities such as SO_x are present [11].

The effect of SO_x on corrosion rates in supercritical CO_2 mixtures has received considerable attention in the literature. Table 9 provides a summary of the key experimental results that have been obtained from experimental studies on general corrosion rates in supercritical CO_2-H_2O-SO_2 systems.

Table 9. Summary of the experimental results obtained by scholars who investigated uniform corrosion rates in supercritical CO_2-H_2O-SO_2 systems.

Authors and Reference	**CO_2 Mixture Pressure [bar]**	**Temperature [°C]**	**SO_2 Partial Pressure [bar Unless Stated]**	**Water Content [ppm mole]**	**Flow Rate [rpm Unless Stated]**	**Exposure Time [hrs Unless Stated]**	**Corrosion Test Method**	**Uniform Corrosion Rate [mm/yr]**
Ayello et al. [26]	75.8	40	100 ppmv	2440 ppmv	Stagnant Conditions	5	Using Electrochemical Impedance Spectroscopy in conjunction with an autoclave.	4.6
Choi et al. [31]	80	50	0 0.8 (1 mole%)	Water Saturated CO_2	Stagnant Conditions	24	Static Autoclave	≈ 0.4 ≈ 5.6
Choi and Nešić [35]	80	50	0 0.08 (1 mole%)	650	Stagnant Conditions	24	Static Autoclave	< 0.01 3.48
Brown et al. [42]	100	50	100 200 100	500 500 50	3 rpm, which corresponds to an average flow speed of 0.2 m/s.	7 days	Slim (Internal diameter 20-30mm) autoclaves are rotated on a shaft inside a temperature controlled chamber. Test specimens were mounted on small cylindrical racks that slide from one end to the other as the autoclave rotates.	No Attack < 0.005 < 0.005
Farelas et al. [43]	80	50	0 0.08 (0.1 mole%) 0.04 (0.05 mole%)	650	Stagnant Conditions	24	Static Autoclave	0 0.03 0.05
Farelas et al. [44]	80	50	0.8 (1 mole%)	650	Stagnant Conditions	24	Static Autoclave	3.48

Ayello et al. reported a high corrosion rate (4.6 mm/yr) with stagnant conditions and a high water content of 2440 ppmv. Choi et al. observed corrosion rates ranging from 0.4 to 5.6 mm/yr under stagnant conditions with water-saturated CO_2, indicating that both water content and exposure duration influence corrosion. In contrast, Choi and Nesić, along with Farelas et al., tested with lower water content (650 ppm) and found reduced corrosion rates (<0.01 to 3.48 mm/yr), suggesting that lower water levels correlate with less corrosion. Brown et al., using a rotational flow rate (3 rpm) and moderate water content, observed minimal corrosion (<0.005 mm/yr), emphasising that dynamic flow helps reduce localised corrosion. Overall, higher water content and stagnant flow tend to increase corrosion rates, while lower impurity levels and dynamic conditions tend to mitigate corrosion.

5.3 CO_2-H_2O-H_2S MIXTURES

The corrosion of carbon steel in aqueous environments containing CO_2 and Hydrogen Sulphide (H_2S) is of significant concern in the oil and gas industry. Sour service can be expected in systems that contain both H_2S and a free water phase and it can result in a rapid increase in pipeline corrosion and cracking rates. This means that the impurity levels of H_2S need to be carefully controlled to ensure that the integrity of supercritical CO_2 pipelines are not compromised.

DNV-RP-F104 has suggested that an assessment of sour service material selection and qualification requirements is required for a CO_2 pipeline that contain H_2S as an impurity [3]. However, there are no sour service assessment standards that are currently available and directly applicable to CO_2 pipeline systems [3]. Whilst DNV-RP-F104 has indicated that the material selection recommendations and requirements for oil and gas production systems that contain H_2S provided by ISO 15156 [47] provides a good starting point for the design of CO_2 pipelines, these recommendations and requirements are not necessarily applicable to CO_2 pipelines [3]. The absence of a sour service assessment standard that is directly applicable to CO_2 pipelines is indicative of the lack of knowledge of the effect of H_2S on both corrosion and cracking rates in CO_2 pipelines. It should be noted that Det Norske Veritas (DNV) have recently launched a Joint Industry Project (JIP), CO_2 Safe and Sour, to investigate the levels of H_2S that are acceptable in CO_2 pipelines, and that the DNV recommended practice will be updated based off the findings from this project. This project is due for completion in 2024 [66].

The susceptibility of carbon steels to corrosion and cracking in the presence of H_2S is directly affected by the H_2S partial pressure, chloride concentration, temperature and solution pH of the CO_2 mixture. DNV-RP-F104 has indicated that the method used to determine the H_2S partial pressure and the free water phase pH in CO_2 pipelines that contain H_2S may need to be more elaborate than the methods discussed in Annexes C and D of ISO 15156-2 [65]. DNV-RP-F104 has also suggested that the pH of the free water phase in a CO_2 pipeline that contains H_2S is expected to be considerably lower in comparison with typical oil and gas pipelines [3], which highlights the corrosive potential of H_2S as an impurity in CCS pipelines.

The presence of H_2S in a CO_2 pipeline can result in the formation of sulphuric/sulphurous acid, and the deposition of elemental sulphur. DNV-RP-F104 has suggested that the deposited elemental sulphur will be corrosive to carbon steel in the presence of a free water phase [3]. Furthermore, the accumulation of both sulphuric and sulphurous acid in the free water phase of a CO_2 pipeline can trigger severe pipeline corrosion rates. ISO 27913 has also suggested that the presence of H_2S in CO_2 pipelines can promote corrosion at lower water levels in comparison with pipelines that contain only CO_2 and H_2O [16]. Whilst DNV-RP-F104 and ISO 27913 have highlighted the corrosive potential of H_2S an impurity, ISO/TR 27921 has indicated that the impact of H_2S on corrosion rates can be considered to be negligible when the water content (Or the content of other impurities) is low [11].

It has been reported that even small amounts of H_2S can alter the absorbability of H_2O onto the steel surface, causing water to be adsorbed on the entire steel surface. This phenomenon accelerates both general and localised corrosion of carbon steel in the supercritical CO_2 phase [48].

Choi et al. demonstrated that the introduction of 200 ppmv H_2S in the supercritical CO_2 phase significantly increased the corrosion rate of various tested materials (carbon steel, 1Cr, and 3Cr steels) in CO_2 with saturated water [46]. However, reducing the water content to 100 ppm mole in supercritical and liquid CO_2, along with 200 ppmv H_2S, decreased the corrosion rate to less than 0.01 mm/year [46]. Table 10 provides a summary of the key experimental results that have been obtained from experimental studies on general corrosion rates in supercritical CO_2-H_2O-H_2S systems.

Table 10. Summary of the experimental results obtained by scholars who investigated uniform corrosion rates in supercritical CO_2-H_2O-H_2S systems.

Authors and Reference	CO_2 Mixture Pressure [bar]	Temperature [°C]	H_2S Content [ppmv Unless Stated]	Water Content [ppm mole]	Flow Rate [rpm Unless Stated]	Exposure Time [hrs Unless Stated]	Corrosion Test Method	Uniform Corrosion Rate [mm/yr]
Alami et al. [45]	150	80	3 vol%	Water Saturated CO_2	Stagnant Conditions	336	Unknown	>0.3
Choi et al. [46]	120	80	200	Water Saturated CO_2	Stagnant Conditions	48	Static Autoclave	0.41
	80			100		24	Static Autoclave	<0.01

The data suggests that the presence of H_2S and extended exposure time contribute to higher corrosion rates. Minimal corrosion (<0.01 mm/yr) was observed at a lower pressure of 80 bar with reduced water content (100 ppm) over 24 hours compared with the other test with water-saturated CO_2 and exposure time of 48 hours. This comparison highlights that higher H_2S levels, pressure, and prolonged exposure increase corrosion rate under stagnant conditions, especially with high water content.

5.4 CO_2-H_2O-H_2 MIXTURES

ISO/TR 27931 highlights that the low molecular weight of H_2 plays a significant role in reducing stream density and potentially necessitating larger pipeline diameters for its transportation [11].

Although concerns have been raised regarding the chemical effects of H_2, it is important to note that H_2 is neither toxic nor corrosive. However, H_2 can react with specific minerals. In terms of chemical impacts, H_2 is generally considered to be less significant compared to substances like SO_2, NO_x, and H_2S. These other compounds are typically regarded as having greater importance and potential effects [63].

5.5 CO_2-H_2O-N_2 MIXTURES

Foltran et al. discovered a decrease in the water solubility limit as a result of N_2. At a temperature of 40 °C and within the pressure range of 80 to 180 bar, the solubility of water (H_2O) in mixtures of CO_2 and N_2 was examined. The primary objective of this research was to enhance our comprehension of water solubility in complex CO_2-based mixtures, which is crucial for ensuring the safety of transporting anthropogenic CO_2 through pipelines in carbon capture and storage (CCS) technology [61].

The inclusion of N_2 in the mixtures led to a reduction of up to 42% in the mole concentration of water in CO_2 under the specified conditions. These findings hold significant value for the advancement of CCS pipeline development. Additionally, this study suggests that the temperature and overall density of the fluid mixture, rather than solely the applied pressure of the CCS mixture, are the key parameters influencing the solubility of H_2O in CO_2 + N_2 mixtures. This realisation could have implications for understanding the essential parameters that need to be monitored during the safe transportation of CO_2 mixtures through CCS pipelines [61].

5.6 CO_2-H_2O-O_2 MIXTURES

The presence of Oxygen (O_2) in CO_2 pipelines can result in the acceleration of pipeline corrosion rates. O_2 has been identified by ISO/TR 27921 as one of the most aggressive CO_2 pipeline impurities from a corrosion perspective [11], which highlights the importance of carefully controlling the O_2 content of CO_2 pipelines to ensure that the integrity of the pipeline can be maintained.

In DNV-RP-F104, laboratory experiments have demonstrated that corrosion can occur in systems with low water content, even below the solubility limit of water in pure CO_2, when by-products such as O_2 is present. The specific corrosion mechanisms are not fully understood, but these by-products have the potential to alter the solubility of water [3].

According to ISO 27913, O_2 content should be controlled to prevent the formation of acids, solids, and corrosion that could adversely affect the operational integrity of the pipeline throughout its intended lifespan. It should be noted that a much lower level of O_2 might be required to avoid undesirable downstream impacts [16].

In terms of the influence of O_2 on the extent of corrosion observed in dense-phase CO_2, there appears to be some contrasting observations in the literature. Table 11 provides a summary of the key experimental results that have been obtained from experimental studies on general corrosion rates in supercritical CO_2-H_2O-O_2 systems [29].

Some research indicates that the presence of O_2 up to a certain concentration can increase the general corrosion rate by delaying the formation of $FeCO_3$ film on the steel surface and providing an additional cathodic reaction. Choi et al. conducted research on the effect of O_2 content (0%, 2%, 4%, and 6%) on the corrosion of X65 steel in a water-saturated SC CO_2 environment at 80 bar and 50°C after 24 hours of exposure. They observed that the presence of O_2 increased the corrosion rate of X65 steel in an SC CO_2 environment, but the corrosion rate did not further increase with higher O_2 content. The maximum corrosion rate of X65 steel reached 1 mm/year with the addition of 4% O_2. In the absence of O_2, the steel surface was covered with a dense and protective $FeCO_3$ film [29].

However, the presence of O_2 inhibited the formation of a protective $FeCO_3$ film and induced the formation of porous iron oxides, resulting in an increased corrosion rate. However, the experimental results by Hua et al. revealed that increasing the O_2 concentration from 0 to 1000 ppmv caused a progressive decrease in the general corrosion rates of X65 steel in water-saturated supercritical CO_2 but tended to increase the extent of localised corrosion observed on both materials. The operating temperature and O_2 concentration in the system seem to play a significant role in determining the balance between the passivating effect of iron oxides and the enhancement of the cathodic reaction due to O_2 presence [29].

The corrosion rates of carbon steels in a water-saturated supercritical (SC) CO_2 environment were found to exceed 0.1 mm/year in the presence of O_2. However, when the water content was below the solubility limit in SC CO_2, and even with the presence of O_2, corrosion in steels was minimal or absent. Nevertheless, in a water-saturated SC CO_2 environment, the addition of O_2 could lead to severe corrosion [30].

Table 11. Summary of the experimental results obtained by scholars who investigated uniform corrosion rates in supercritical CO_2-H_2O-O_2 systems.

Authors and Reference	CO_2 Mixture Pressure [bar]	Temperature [°C]	O_2 Content [ppmv Unless Stated]	Water Content [ppm mole Unless Stated]	Flow Rate [rpm Unless Stated]	Exposure Time [hrs Unless Stated]	Corrosion Test Method	Uniform Corrosion Rate [mm/yr]
Choi & Nešić [34], [35]	80	50	0	Saturated (10 g)	Stagnant Conditions	24	Static Autoclave	0.38
			2 mol% (1.6 bar)					0.6
Choi, Nešić, & Young [33]			4 mol% (3.3 bar)					1
			6 mol% (5.1 bar)					0.9

Choi & Nešić [35]	80	50	4 mol% (3.3 bar)	650 ppmv	Stagnant Conditions	24	Static Autoclave	No Corrosion
				2000 ppmv				No Corrosion
				3000 ppmv				<0.01
Collier et al. [52]	94.8 – 103	49	30000	Saturated (100 g)	Stagnant Conditions	120	High pressure rotating cage	0.099 (X42)
								0.093 (X60)
Ruhl & Kranzmann [53]	100	60	≈ 1000	Saturated (1 ml 55.6 mmol)	Stagnant conditions	120	Static Autoclave	0.008
Dugstad et al. [54]	100	50	200	50v% (Saturated)	Stagnant Conditions	432	Static Autoclave	0.6 (pit corrosion rate 17)
Alami et al. [45]	150	80	1000	Saturated	Stagnant Conditions	288	Unknown	0.2 – 0.9
Hua et al. [49]	80	50	40000	400 ml Water phase	Stagnant conditions	24	Static Autoclave	19.3
			0					19.2
			40000			120		14.1
			0					10.6
Brown et al. [42]	100	50	500	500	3 rpm corresponding to average velocity of 0.2 m/s	168	Rotating Autoclave	0.006 (3 rpm)
Hua et al. [23]	80	35	0	Water-saturated CO2 (10 g water added to autoclave)	Stagnant Conditions	48	Static Autoclave	0.10
			20					0.09
			500					0.07
			1000					0.03
				300				0
				650				0
				1200				0.002
				1770				0.005
				2800				0.012

O_2 content appears to be the most significant factor affecting the corrosion rates across these studies, as seen in several cases where an increase in O_2 levels results in a notable rise in corrosion rate. Choi & Nesic report corrosion rates of 0.38 mm/yr at 0 mol% O_2, which increases to 1 mm/yr at 4 mol% O_2 under the same pressure and temperature conditions, indicating a strong correlation between O_2 content and corrosion severity. Similarly, Hua et al. observed an increase from 10.6 mm/yr at 0 ppm to 19.3 mm/yr at 40,000 ppm O_2. Water content also plays a role, with the presence of free water generally accelerating the corrosion process. Ruhl & Kranzmann reported lower rates (0.008 mm/yr) in a saturated environment (1 ml water), while other studies with larger water content reported higher rates.

5.7 CO_2-H_2O-CH_4 MIXTURES

The presence of water in dense CO2 can have different effects depending on whether the water content is below or above its solubility limit. When the water content is below the solubility limit, it dissolves in the bulk CO_2 stream. Conversely, when the water content exceeds the solubility limit, a condensed and segregated aqueous phase can form on the steel surface. These two forms of water, dissolved and condensed, have distinct impacts on the corrosion behaviour of steel in dense CO_2. Therefore, understanding the solubility of water in high-pressure CO_2 is crucial for assessing dense CO_2 corrosion [57].

Consideration should be given to the proportion of different chemical components, including CH_4, in the CO_2 stream, as highlighted in DNV RP-F104. This is important because it can significantly influence the CO_2 stream's ability to dissolve water [3]. ISO/TR 27921 states that CH_4, as an impurity, is water soluble and can have specific effects on the CO_2 stream. These effects include the formation of an aqueous phase and a reduction in the concentration of H_2O. One potential consequence of these effects is the increased risk of corrosion [11].

Previous research has explored this topic through experimental and modelling studies, with some researchers investigating the influence CH_4 on the water solubility limit in dense CO_2.

Thermodynamic models have been developed to determine the solubility of H_2O in mixtures of CO_2 and 5.31% CH_4, along with the solubility of pure CH_4 and pure CO_2 at 50°C. These models take into account the composition of the liquid CO_2 mixture, which reduces the CO_2 content as pressure increases, subsequently affecting the solubility of H_2O [58].

In more complex mixtures, researchers Song and Kobayashi [59] conducted experiments involving CO_2, H_2O, and CH_4 (5.31% CH_4). Figure 11 illustrates the effect of CH_4 in lowering the water solubility limit in dense CO_2. The lines represent calculated results obtained using the Soave-Redlich-Kwong equation of state with the Huron-Vidal mixing rule (SRK-HV) model, while the data points correspond to experimental data from Song and Kobayashi [60].

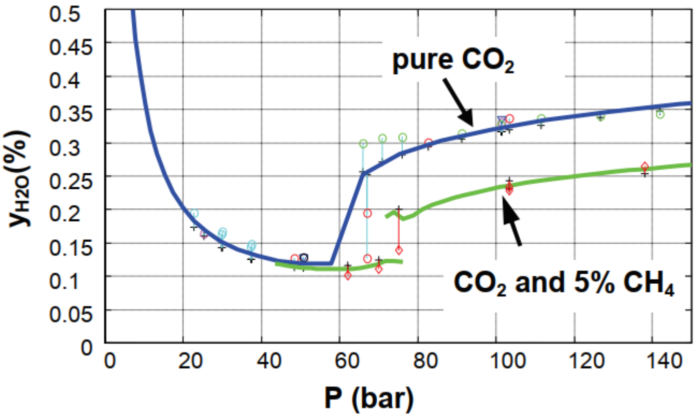

Figure 11. Water solubility in pure CO2 and in CO2-CH4 mixture [60].

5.8 CO_2-H_2O-CO MIXTURES

In pre-combustion technology, it is inevitable to have CO present in captured CO_2. CO is known for its strong reducing properties and can be readily oxidised to CO_2. Therefore, the concentration of CO should be low. While CO can react with certain minerals, in terms of chemical effects, it is generally considered to be less significant compared to other compounds such as SO_2, NO_x, and H_2S [63].

CO shares a similar characteristic to NO_x, as it can contribute to the occurrence of stress corrosion cracking (SCC) in CO_2-CO-H_2O environments, particularly when the partial pressure of CO_2 is below 20 bar. However, the investigation of this issue under high-pressure conditions in dense CO_2 is still an ongoing task. Presently, there is no evidence available to demonstrate whether CO can enhance or suppress general corrosion or induce localized corrosion in dense CO_2 environments [57].

5.9 CO_2-H_2O MIXTURES WITH MERCURY

Rohana et al. conducted a study that suggests the presence of both elemental and ionic Hg does not affect the corrosion activity of CO_2. The corrosion rates observed in glass cell and autoclave tests remained consistent with the simulated CO_2 corrosion rate, indicating that Hg has little to no impact [62].

This is likely because there is minimal or no reaction occurring between the ion carbonate (formed from the reaction between H_2O and dissolved CO_2 in the solution) and both the ionic and elemental forms of Hg. The stability of Hg species as compounds or elements prevents them from reacting with ion carbonate. Instead, ion carbonate is expected to release H+ ions, forming ion bicarbonate [62].

It should be noted, however, that the absence of fluid analysis for the solution limits the ability to draw conclusions about the interaction between ion carbonate and Hg species. The influence of Hg on CO_2 corrosion is solely based on the consistent corrosion rate values, regardless of the presence or absence of Hg [62].

6. PIPELINE CORROSION IN COMPLEX CO_2 MIXTURES

6.1 CO_2-H_2O-NO_X-O_2 MIXTURES

The available experimental data on impure dense-phase CO_2 systems, particularly those containing NO_x as an impurity, is limited. It is known that NO_2, being highly soluble in water, can react to form nitric acid and NO under atmospheric conditions. This reaction can lower the pH of the aqueous phase and accelerate the cathodic hydrogen evolution reaction rate [29].

According to DNV-RP-F104, O_2 will enhance the formation of elemental sulphur and sulphuric/nitric acid if SO_x/NO_x are present. Small-scale laboratory tests have shown that in CO_2 streams with very low water contents (50 ppmv), NO_x is more corrosive compared to SO_2. However, when the water content increases to 500 ppmv, both impurities lead to relatively high corrosion rates [3].

Recent research by Brown et al. has investigated the influence of NO and NO_2 on corrosion [42]. Their experiments involved different concentrations of O_2, NO, and NO_2 at a pressure of 100 bar and temperatures of 50°C. The corrosion rates were found to be highest in the presence of NO and NO_2. Specifically, tests conducted with 200 ppmv NO_2 and 500 ppmv O_2 showed a general corrosion rate of 0.275 mm/year, even with a water content of only 500 ppmv [29].

During the experiments, a notable trend was observed: corrosion rates decreased significantly with increasing test duration from 1 to 7 days. It is hypothesized that this reduction in corrosion rate is primarily due to the rapid consumption of impurities within the system, rather than the formation of a protective corrosion product. This hypothesis is supported by evidence indicating that the presence of NO_2 leads to the formation of a brown/orange-coloured dusty and porous film, which can be easily removed from the steel surface [29].

In the experiments conducted with a water content of 500 ppmv, all the specimens exhibited some degree of corrosion. The highest corrosion rate, exceeding 0.2 mm/year, was observed in the experiments involving NO_2 and NO. The corrosion rate was effectively reduced by reducing the water content from 500 to 50 ppmv, and minimal corrosion occurred only in the presence of NO_2 [42].

These findings support the principle of managing corrosion by controlling water content. However, it is premature to establish a definitive safe operational limit due to several factors. Firstly, only a limited number of impurity combinations were tested. Secondly, the experiments did not involve replenishing consumed impurities, and finally, the test duration was relatively short. Therefore, for designs expected to have impurities present even with water contents above 50 ppmv, it is advisable to conduct further experiments to ensure corrosion rates remain within acceptable limits [42].

Table 12 provides a summary of the key experimental results that have been obtained from experimental studies on general corrosion rates in supercritical CO_2-H_2O-NO_x-O_2 system.

Table 12. Summary of the experimental results obtained by scholars who investigated uniform corrosion rates in supercritical CO_2-H_2O-NO_x-O_2 systems.

Authors and Reference	CO_2 Mixture Pressure [bar]	O_2 Content [ppm mole Unless Stated]	NO_2 Content [ppm mole Unless Stated]	NO Content [ppm mole Unless Stated]	Water Content [ppm mole Unless Stated]	Temperature [°C]	Flow Rate [rpm Unless Stated]	Exposure Time [hrs Unless Stated]	Corrosion Test Method	Uniform Corrosion Rate [mm/yr]
Brown et al. [42]	100	0	50	0	500	50	3 rpm, which corresponds to an average flow speed of 0.2 m/s.	24	Rotating Autoclaves	0.127
		500	50	0						0.116
		0	100	0				168		0.020
		500	100	0				24		0.182
		0	200	0						0.205
		0	200	0				72		0.088
		0	200	0				168		0.025
		500	200	0				24		0.275
		500	200	0				168		0.090
		0	0	200						0.013
		500	0	200						0.030
		500	100	0	50					0.005
		10,000	100	0						No attack

The results show a significant impact of O_2 concentration, as an increase from 0 ppm to 500 ppm O_2, while keeping other factors constant, led to a rise in corrosion rates from 0.127 mm/yr to 0.182 mm/yr under similar exposure conditions (24 hours). Increasing O_2 to 200 ppm also results in higher corrosion rates, with values up to 0.205 mm/yr. This indicates that even low levels of O_2 can substantially accelerate corrosion.

Similarly, the presence of NO_2 shows a notable effect. In experiments with 200 ppm NO_2 at 500 ppm O_2, the corrosion rate increased to 0.275 mm/yr, demonstrating a synergistic effect between NO_2 and O_2 in accelerating corrosion. When only NO is present (200 ppm) without O_2 or NO_2, the rate remains relatively low (0.090 mm/yr), indicating that NO alone has a milder impact compared to O_2 and NO_2.

Exposure time also plays a role, with longer durations generally resulting in lower uniform corrosion rates, suggesting that corrosion rates may stabilise over time. The corrosion rate decreased from 0.205 mm/yr (24 hrs) to 0.088 mm/yr (72 hrs) for the same O_2 content (500 ppm). Flow conditions contribute as well, as seen in the significant drop-in corrosion rate (0.013 mm/yr) under flowing conditions compared to stagnant scenarios.

6.2 CO_2-H_2O-SO_2-O_2 MIXTURES

As per DNV-RP-F104, the presence of O_2 in the CO_2 system can contribute to the formation of elemental sulphur and sulfuric/nitric acid when SO_x are present. Laboratory tests conducted on a small scale have indicated that at very low water contents (50 ppmv), NO_x exhibits greater corrosiveness compared to SO_2 in CO_2 streams. However, when the water content rises to 500 ppmv, both NO_x and SO_2 result in relatively high corrosion rates [3].

In reference to the literature regarding the corrosion of carbon steel in supercritical CO_2–H_2O–SO_2–O_2 systems, Table 13 presents a consolidated summary of corrosion experiments conducted by several authors.

Multiple authors concur that exceeding a specific water content can compromise pipeline integrity due to the presence of SO_2 and SO_2/O_2 in dense-phase CO_2 systems. Some authors have observed a significant synergy between SO_2 and O_2, where the combined corrosion rate exceeds the sum of the individual corrosion rates caused by SO_2 and O_2 individually. This phenomenon is attributed to the ability of O_2 to react with SO_2 and H_2O, resulting in the formation of sulfuric acid (H_2SO_4) [29].

Choi and Nešić conducted a corrosion evaluation of X65 carbon steel in a supercritical CO_2 environment with a water content of 650 ppm mole. They varied the concentrations of SO_2 and O_2 in an 80 bar/50°C system. After 24 hours of exposure, the corrosion rate of X65 in the absence of O_2 and SO_2 at 650 ppm mole water was found to be less than 0.01 mm/year. However, when the SO_2 content was increased to 0.8 bar without the presence of O_2, the corrosion rate rose significantly to 3.48 mm/year. Furthermore, with the additional introduction of 3.3 bar O_2 alongside 0.8 bar SO_2, the general corrosion rate further increased to 3.70 mm/year. These findings demonstrate that corrosion can be significantly intensified in the presence of SO_2 and SO_2/O_2 combinations, even at low water contents that are typically recommended by pipeline operators. It should be noted, though, that concentrations of SO_2 and O_2 at the levels mentioned in the study are unlikely to be encountered in typical CO_2 service conditions [29].

Two studies in the literature have specifically examined the impact of SO_2 on the critical water content required to mitigate significant corrosion in CO_2 service. These studies aim to understand the relationship between impurity concentration, water content, and corrosion rates in order to develop effective corrosion control strategies.

Xiang et al. performed experiments on X70 steel at 100 bar and 50°C for 120 hours. They introduced a partial pressure of 2 bar SO_2 and an O_2 content of 1000 ppm to supercritical CO_2, considering relative humidity values ranging from 9% to 100% (equivalent to 414 to 4600 ppm mole). The results indicated that appreciable levels of corrosion (>0.1 mm/year) began when the humidity content exceeded 60% (2760 ppm mole).

According to the research conducted by Hua et al., it is noted that reducing the water content is a more favourable approach compared to reducing the SO_2 content in order to mitigate internal pipeline corrosion during transportation. The study observed that even in the absence of SO_2, significant levels of pitting corrosion were still observed when the water content was high enough. Therefore, the research highlights the importance of controlling and reducing the water content as an effective measure to minimize internal pipeline corrosion.

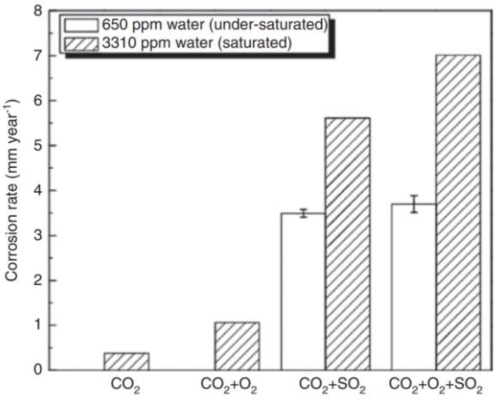

Figure 12. Effects of O_2, SO_2, and their mixtures on the corrosion rates of carbon steel in SC CO_2 phase with different amounts of water [30].

Table 13. Summary of the experimental results obtained by scholars who investigated uniform corrosion rates in supercritical CO_2-H_2O-SO_2-O_2 systems.

Authors and Reference	CO_2 Mixture Pressure [bar]	O_2 Content [bar Unless Stated]	SO_2 Content [bar Unless Stated]	Water Content [ppm mole Unless Stated]	Temperature [°C]	Flow Rate [rpm Unless States]	Exposure Time [hrs Unless Stated]	Corrosion Test Method	Uniform Corrosion Rate [mm/yr]
Choi, Nešić, & Young [33]	80	3.3	0.8	0	50	Stagnant Conditions	24	Static Autoclave	No attack
		0	0	Water-saturated CO_2 (10 g water added to autoclave)					~0.4
		3.3	0						~1.0
		0	0.8 (1 mol%)						~5.6
		3.3	0.8 (1 mol%)						~7.0
Choi & Nešić [35]	80	0	0	650	50	Stagnant Conditions	24	Static Autoclave	< 0.01
		0	0.8 (1 mol%)						3.48
		3.3	0.8 (1 mol%)						3.70
Xiang et al. [56]	100	1000 ppm	0.2 (0.2 mol%)	Water-saturated CO_2 (6 g water added to autoclave to ensure saturation)	50	120 rpm	288	Rotating Autoclaves	0.2
			0.7 (0.7 mol%)						0.7
			1.4 (1.4 mol%)						0.85
			2 (2 mol%)						0.9
			2 (2 mol%)	Water-saturated CO_2 (3 g water added to autoclave to ensure saturation)			24		2.0
							72		1.8
							120		1.4
							192		0.7
			2 (2 mol%)	414			120		~0
				2300					~0.04
				2760					~0.08
				3220					~0.35
				4048					~0.9
				Water-saturated CO_2 (≈4600 ppm mole)					~1.5
Hua et al. [49]	80	0	0	Water-saturated CO2 (3 g water added to autoclave to ensure	35	Stagnant Conditions	48	Static Autoclaves	0.10
		20 ppm mole	20 ppm mole						0.12
		20 ppm mole	50 ppm mole						0.37
		20 ppm mole	100 ppm mole						0.72

				saturation, approximately 3437 ppm mole)					
Hua et al. [37]	80	0	0	310	35	Stagnant Conditions	48	Static Autoclaves	0.003
				1185					0.005
				1770					0.009
				3400					0.027
				Water-saturated CO2 (3 g water added to autoclave					0.100
		20 ppm mole	50 ppm mole	310	35		48		0.003
				1185					0.006
				1770					0.009
				3400					0.028
				Water-saturated CO2 (3 g water added to autoclave					0.368
		20 ppm mole	50 ppm mole	310	35		48		0.003
				1185					0.004
				1770					0.039
				3400					0.067
				Water-saturated CO2 (3 g water added to autoclave					0.716

The most notable impact is observed with variations in O_2 concentration, as seen in the Choi & Nesic [33] data. When the O_2 content increases from 0 mol% to 3.3 mol%, the corrosion rate drastically shifts from -0.4 mm/yr (indicating no significant corrosion) to -7.0 mm/yr, suggesting a transition from passive protection to severe localised corrosion, likely due to the formation of a protective iron carbonate layer being disrupted by the presence of O_2.

SO_2 content also plays a significant role in increasing the corrosion rate. For the Choi & Nesic [35] dataset, the addition of 0.8 bar SO_2 to an environment with 0.8 mol% O_2 results in an increase in corrosion rate from <0.01 mm/yr to 3.70 mm/yr. This indicates that SO_2, even in relatively low concentrations, can significantly accelerate the corrosion process.

The influence of water content is evident in Xiang et al. [56], where corrosion rates in water-saturated CO_2 are much higher (e.g., 0.9 mm/yr at 72 hours) compared to cases with limited water (e.g., -0.04 mm/yr at 2300 ppm H_2O). This suggests that the presence of free water facilitates uniform corrosion, while lower water content promotes the formation of protective layers.

For lower impurity concentrations, as in the Hua et al. [49] and [37] datasets, corrosion rates generally remain low until a critical threshold is reached. At 20 ppm SO_2 and 50 ppm O_2, the rate is negligible (0.003 mm/yr), but increases sharply to 0.716 mm/yr with the addition of more H_2O, demonstrating the cumulative effect of these impurities and water.

6.3 CO_2-H_2O-SO_2-NO_2 MIXTURES

According to ISO/TR 27921, the presence of SO_2 in combination with NO_x can lead to the deposition of elemental sulphur as in the corrosion of components and pipes. This deposition can potentially alter the phase equilibria between the CO_2 stream and the newly formed phases. interaction between SO2, NOx, and the resulting phase changes is important to consider due to its potential impact on corrosion and the overall integrity of the system [11].

There is limited number of papers presenting data and discussing the effect of combined impurities on corrosion. When both, NO2 and SO2 are present, NO_2 catalyses the oxidation of SO_2 to form sulphuric acid. A synergistic corrosive effect of SO2 and NO2 dependent on relative humidity is observed in atmospheric corrosion. It is assumed that NO2 increases the rate of SO2 oxidation to sulphate and acts as oxygen carrying agent [21].

The available literature on the combined effect of impurities on corrosion is limited. However, it is recognized that when both NO_2 and SO_2 are present, NO_2 can act as a catalyst for the oxidation of SO_2, leading to the formation of sulfuric acid. This synergistic corrosive effect is known to be dependent on the relative humidity levels.

The effect of NO_2 is indirect given that nitrogen compounds have not been detected among the corrosion products and its influence is related with the increase in the rate of SO_2 oxidation to sulphate [51]. In atmospheric corrosion, it is believed that NO_2 facilitates the oxidation of SO_2 to sulphate and serves as an oxygen carrier in the process. Although further research is needed to fully understand the mechanisms involved, the presence of both NO_2 and SO_2 together has been shown to have a notable influence on corrosion behavior [21].

Corvo et al. have highlighted that the simultaneous presence of SO_2 and NO_2 can exhibit a synergistic effect on corrosion and material degradation, especially under atmospheric conditions. The extent of this effect depends on the relative humidity. It is worth noting that corrosion products containing nitrogen are rarely observed under atmospheric corrosion conditions. According to Corvo et al., the primary role of NO_2 is to catalyse degradation reactions. However, it has not been definitively demonstrated that this behaviour occurs under dense-phase CO_2 conditions. Further research is needed to establish the extent of these effects in CO_2 environments [29].

Table 14 provides a summary of the key experimental results that have been obtained from an experimental study on general corrosion rates in supercritical CO_2-H_2O-SO_2-NO_2 system.

Table 14. Summary of the experimental results obtained by scholars who investigated uniform corrosion rates in supercritical CO_2-H_2O-SO_2-NO_2 systems.

Authors and Reference	CO_2 Mixture Pressure [bar]	NO_2/NO Content [ppmv]	SO_2 Content [ppmv]	Water Content [ppm mole]	Temperature [°C]	Flow Rate [rpm Unless stated]	Exposure Time [hrs]	Corrosion Test Method	Uniform Corrosion Rate [mm/yr]
Paschke et al. [50]	110	100 ppmv NO	100	1000	60	Stagnant Conditions	168	Static Autoclaves	0.009

6.4 CO_2-H_2O-SO_2-H_2S-O_2 MIXTURES

According to DNV-RP-F104, when H_2S reacts with O_2, it can produce elemental sulphur, which has the potential to accumulate within the system and negatively impact the permeability of formations by clogging the pore system. Additionally, if elemental sulphur comes into contact with free water, it can lead to the corrosion of steel [3].

DNV-RP-F104 also highlights that the mechanisms underlying the H_2S-O2 reaction, including the minimum required concentrations of H_2S and O_2, the reaction rates, and the trigger mechanism, are still poorly understood. Additionally, there is a lack of literature data specifically for dense phase CO_2 systems. To define safe limits for H_2S and O_2 with confidence, it is crucial to gain a comprehensive understanding of the mechanisms that catalyse sulphur formation and quantify their effects under pipeline conditions [3].

The interactions among O_2, H_2S, and SO_2 in a water-saturated supercritical CO_2 system have been found to have significant effects on the corrosion behavior of X65 pipeline steel. The addition of multiple impurities, such as O_2, H_2S, or SO_2, accelerates the corrosion rate of X65 steel compared to systems with individual impurities. In particular, when multiple impurities are present, the corrosion impact factor is higher than the sum of the impact factors of corresponding single impurities, indicating a synergistic effect that intensifies the corrosion process [55].

The interaction between O_2 and H_2S leads to the precipitation of a water phase and the formation of elemental sulphur, providing additional electrolytes for corrosion and elemental sulphur corrosion. The interaction between O_2 and SO_2 promotes the formation of sulfuric acid, significantly increasing the corrosivity of water condensed on the steel surface. The interaction between H_2S and SO_2 leads to the formation of a water phase and elemental sulphur, which further results in the formation of sulfuric acid through the hydrolysis of elemental sulphur [55].

Overall, the complex synergistic effects among O_2, H_2S, and SO_2 contribute to the highest synergistic interaction impact factor, which corresponds to the highest corrosion rate observed in the system. These findings highlight the importance of considering the combined presence of multiple impurities when assessing the corrosion risk in water-saturated supercritical CO_2 environments [55].

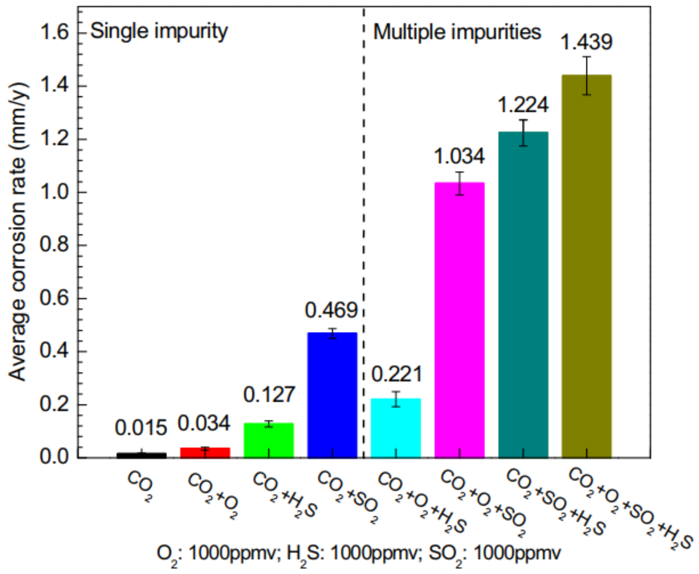

Figure 12. Corrosion rate of X65 steel exposed to water-saturated supercritical CO_2 containing various impurities for 120 h at 100 bar and 50°C.

Table 15. Summary of the experimental results obtained by Sun et al. who investigated uniform corrosion rates in supercritical CO_2-H_2O-SO_2-H_2S-O_2 systems.

Authors and Reference	CO_2 Mixture Pressure [bar]	O_2 Content [ppmv]	SO_2 Content [ppmv]	H_2S Content [ppmv]	Water Content [ppmv]	Temperature [°C]	Flow Rate [rpm Unless Stated]	Uniform Corrosion Rate [mm/yr]	Corrosion Test Method	Exposure Time [hrs]
Sun et al. [55]	100	0	0	0	Water-Saturated	50	Stagnant Conditions	0.015	Static Autoclaves	120
		1000	0	0				0.034		
		0	1000	0				0.127		
		0	0	1000				0.469		
		1000	1000	0				0.221		
		1000	0	1000				1.034		
		0	1000	1000				1.224		
		1000	1000	1000				1.439		

The results show a strong correlation between increasing impurity concentrations and the rise in corrosion rates. For instance, with no impurities present, the corrosion rate is minimal (0.015 mm/yr). However, the addition of 1000 ppmv O_2 alone raises the rate to 0.127 mm/yr, highlighting the significant effect of O_2 in accelerating the corrosion process. When SO_2 is introduced (1000 ppmv), the corrosion rate increases further to 0.469 mm/yr, even in the absence of O_2 and H_2S. This suggests that SO_2, due to its acidic nature, plays a more aggressive role in corrosion compared to O_2 alone. The combination of O_2 and SO_2 (both at 1000 ppmv) results in a synergistic effect, raising the rate to 1.034 mm/yr, which is much higher than the individual contributions of either impurity. The most severe corrosion is observed when all three impurities (O_2, SO_2, and H_2S) are present at 1000 ppmv each, where the rate escalates to 1.439 mm/yr. This indicates that H_2S, while having a relatively mild impact alone (0.034 mm/yr), exacerbates corrosion when combined with O_2 and SO_2.

6.5 CO_2-H_2O-SO_2-NO_2-H_2S-O_2 MIXTURES

As stated in ISO/TR 27921, the presence of multiple impurities such as H_2O, SO_x, NO_x, O_2, and H_2S in the CO_2 stream can lead to various cross-chemical reactions. These reactions have the potential to produce sulphuric/sulphurous acid, nitric acid, and elemental sulphur, which can form separate phases and contribute to corrosion. The formation and condensation of these acidic phases can occur even at low water contents, such as less than 100 ppmv. Therefore, the extent of acid formation and condensation, as well as the composition of the resulting condensates, strongly depend on the composition and temperature of the CO_2 stream. Consequently, the maximum acceptable concentration of any impurity is project-specific and influenced by the concentrations of other impurities, considering their potential interactions and chemical cross-reactions.

Limited investigations have been conducted on the possible corrosion and bulk phase reactions when CO_2 contains flue gas impurities such as SO_x, NO_x, O_2, in addition to H_2O and H_2S.

One study by Dugstad et al. examined dense phase CO_2 with 300 ppmv H_2O, 350 ppmv O_2, 100 ppmv SO_2, 100 ppmv NO_2, and 100 ppmv H_2S. The experiments revealed corrosion of carbon steel and the formation of elemental sulphur along with a liquid phase containing sulfuric and nitric acid. The corrosion rate of the carbon steel specimens was approximately 0.04 mm/year.

However, due to the limited number of experiments conducted by Dugstad et al., it is premature to draw definitive conclusions regarding the reaction mechanisms. Tentative mechanisms have been proposed based on observed changes in impurity concentrations when impurity injection was initiated or stopped in the experiments.

When H_2S, O_2, and SO_2 were simultaneously injected, no rapid cross chemical reactions were observed. However, the introduction of NO_2 resulted in an immediate increase in H_2O, SO_2, and NO concentrations for a short period, while NO_2 and H_2S concentrations decreased. A few hours after the start of NO_2 injection, a decrease in SO_2 and NO concentrations was measured. The presence of both sulfuric and nitric acid was confirmed through ion chromatography after the exposure, suggesting that acid formation commenced shortly after the introduction of NO_2.

Table 16 provides the key experimental results that have been obtained from the experimental study conducted by Dugstad et al. on general corrosion rates in supercritical CO_2-H_2O-SO_2-NO_2-H_2S-O_2 system.

Table 16. Summary of the experimental uniform corrosion rate results obtained for supercritical CO_2-H_2O-SO_2-NO_2-H_2S-O_2 systems [41].

CO_2 Mixture Pressure [bar]	O_2 Content [ppmv]	NO_2 Content [ppmv]	SO_2 Content [ppmv]	H_2S Content [ppmv]	Water Content [ppmv]	Temperature [°C]	Flow Rate [rpm Unless Stated]	Exposure Time [hrs]	Corrosion Test Method	Uniform Corrosion Rate [mm/yr]
100	350	100	100	100	300	45	3 rpm, which corresponds to an average flow speed of 0.2 m/s.	74	Rotating Autoclaves	<0.1
								133		0.04

7. EXISTING MODELS

7.1 THERMODYNAMIC MODELS

Having a strong comprehension of the thermodynamics of CO_2 fluids with impurities and selecting the appropriate equation of state (EoS) that aligns with the chemical properties of the impurities are crucial aspects [68]. When impurities are present in a CO_2 stream, the phase behavior of CO_2 is altered compared to pure CO_2.

Equations of state (EoSs) are utilized in the design and operation of CCS processes through process simulation software or other design programs. Typically, these EoSs incorporate binary interaction parameters that are fitted based on experimental data. Since no single EoS can adequately cover the wide range of components and conditions necessary for CCS, various types of EoSs have been proposed. Each EoS demonstrates satisfactory performance for certain systems but may exhibit limitations for others [67].

Modelling the phase behavior of mixtures containing CO_2 and associating/polar components can be challenging. Multiparameter equations of state, such as GERG-2008, demonstrate good predictive capabilities for calculating thermophysical properties, particularly in single-phase conditions. However, these equations of state have limitations and do not support polar and associating components. For such components, the Cubic-Plus-Association (CPA) equation of state appears to be the most suitable for modelling the complex interactions of polar and associating components [68].

The CPA equation of state is considered a reliable modelling tool in oil and gas applications when polar components are present. In the context of CCS applications involving CO_2-rich fluids, it has been demonstrated that the CPA equation of state performs well when compared to experimental data, even for mixtures containing water and other polar components [68].

While there is a considerable amount of experimental data available for CO_2–CH_4 and CO_2–N_2 binary systems, there is a scarcity of data for CO_2–SO_2, CO_2–NO, and CO_2–O_2 systems due to their toxic and explosive nature [67].

Austegard et al. [58] conducted research on mutual solubilities in H_2O-CO_2-CH_4 mixtures, employing three distinct models. They gathered experimental data for binary mixtures and assessed their quality and consistency before proceeding to evaluate binary interaction parameters through regression analysis. The study concluded that among the three models examined, the SRK-HV model proved to be the most valuable. This model yielded favourable outcomes and possessed a comparatively simpler structure when compared to the CPA model.

Nevertheless, ongoing efforts are being made to generate such experimental data. Recent reports have focused on CO_2 phase equilibria in binary and ternary systems containing impurities like SO_2, NO, O_2, and Ar. These studies have combined experimental observations with thermodynamic modelling to investigate the phase envelopes of CO_2-impurity mixtures, particularly in the CO_2-rich phase [67].

Deviations from the EoS models are represented by average absolute deviations (AAD). Complete comparisons of binary systems are summarized in Figure 13. Each coloured bar represents a type of deviation of calculated values from experimental data. For instance, in the case of the CO_2-N_2 system, the GERG-2008 EoS shows the most accurate results at the given range of temperatures, with AAD_{xAvg} of 2.98% and AAD_{yAvg} of 1.67%. The NLFHB EoS gives satisfactory results for liquid compositions, but vapor compositions near critical points are inaccurate [67].

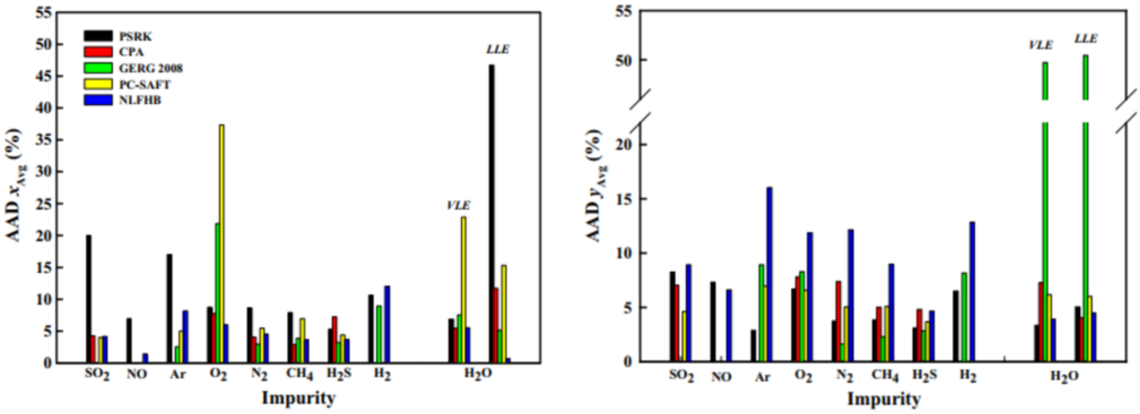

Figure 13. Comparisons of experimental data with calculated values using equation of state models for liquid (left) and vapor (right) compositions of CO_2-impurity binary mixture [67].

A study examines the corrosion of carbon steel in wet CO_2 under high pressure conditions. The results indicate that although corrosion rates are significant, they are considerably lower than what would be expected based on models developed for CO_2 corrosion at low pressure. Moreover, the corrosion rates decrease as the pressure exceeds 20 bar. At moderate pressures, the formation of carbonate films on the surface partially accounts for this phenomenon. However, at high pressure, it appears that another corrosion mechanism is at play. Further research is required to fully understand this corrosion mechanism. This preliminary investigation discusses the limitations of existing CO_2 corrosion models, which were primarily designed for gas production systems, and highlights their inapplicability to corrosion in supercritical CO_2 pipelines [69].

7.2 CORROSION RATE MODELS

Models for CO_2 corrosion have been developed in the past, taking the form of semi-empirical correlations or mechanistic models describing the different processes involved in CO_2 corrosion of carbon steel [70]. They would provide a deeper understanding of the complex corrosion processes occurring in these challenging conditions. Currently, the existing models in this area are limited in their scope and do not adequately capture the intricacies of corrosion in dense CO_2 with impurities.

The work conducted by Zheng et al. [70] presents a valuable mechanistic prediction model for CO_2/H_2S corrosion, serving as a useful reference for studying supercritical CO_2 corrosion in the presence of H_2S and other impurities.

The researchers investigated the electrochemistry of mild steel corrosion in a mixed H_2S/CO_2 aqueous environment and developed an electrochemical model to simulate the experimental findings. The experiments were designed to examine the impact of H_2S on CO_2 corrosion during short-term exposures before the occurrence of any interference from iron sulphide corrosion product layers.

An electrochemical model was formulated specifically for the mixed H_2S/CO_2 system, and it was calibrated using new experimental data. The model's predictions were compared to existing data from the open literature. The model exhibited good agreement with experimental data for short exposures lasting a few hours. However, it overestimated the experimental results for longer-term exposures spanning days and weeks. This discrepancy can be attributed to the formation of an iron sulphide corrosion product layer, which the current model does not account for.

Xiang et al. developed a mechanistic model that specifically addresses the prediction of carbon steel corrosion in dense CO_2 phase with SO_2–O_2–H_2O impurities. They integrate the traditional CO_2 corrosion models and the atmospheric corrosion model. The schematic diagram of the six-region model shows in Figure 14 [71].

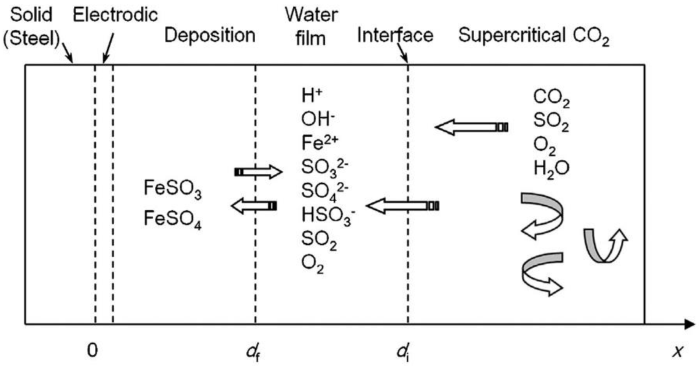

Figure 13. Schematic diagram of the SIWDES six-region model [71].

The accuracy of this model seems to be high, especially for cases with high SO_2 concentration and relative humidity (RH). However, for cases with extremely low SO2 concentration, the accuracy of this model seems to be low. These results suggested that the effect of dissolved CO_2 should be considered for conditions with low SO_2 concentrations. For low-RH conditions, the results of this model were also not satisfactory [57].

Further studies and research are necessary to enhance our understanding and develop more accurate mechanistic models that can effectively predict carbon steel corrosion in dense CO_2 environments with various impurities. This would greatly benefit industries dealing with supercritical CO_2 applications, enabling better corrosion control strategies and ensuring the integrity and longevity of carbon steel infrastructure.

8. RESEARCH GAPS

8.1 IMPURITY H_2O RESEARCH GAPS

The unique properties of supercritical CO_2, including its high solvency power, introduce significant uncertainties when extrapolating the current understanding of CO_2-water corrosion behaviour to pipelines that transport supercritical CO_2 [64].

To address these challenges, the ultimate objective should be to determine conditions where the formation of free water is unlikely. Achieving this goal will require a fundamental approach that involves understanding the thermodynamics of the corrosion mechanism between CO_2 and impurities, along with meticulous experimentation [64].

In the event of a water ingress into a pipeline carrying dry CO_2, the water is expected to dissolve quickly without significantly affecting pipeline integrity if CO_2 flow continues uninterrupted. However, continuous water entry or an extended shutdown after ingress has a greater risk. During shutdown, water removal is necessary, typically requiring pipeline depressurisation. The acceptable response time for addressing water contamination is dependent on system-specific factors such as the corrosion rate and the corrosion allowance.

8.2 IMPURITY O_2 RESEARCH GAPS

The presence of varying amounts of O_2 in dense CO_2 can result in different corrosion rates and corrosion patterns. It is important to note that when multiple impurities are present, the overall corrosion rate may not increase with an increase in O_2 concentration, as the localised corrosion rate may have been overlooked or disregarded. These contradictory findings suggest the need for further corrosion experiments that specifically investigate the effects of different O_2 concentrations in dense CO_2. Such research is necessary to uncover the complex influences of O_2 on corrosion behaviours [57].

Additionally, more extensive studies are required to elucidate the impact of different O_2 concentrations on the corrosion behaviour of steel in supercritical CO_2 environments containing water. It is crucial to identify the underlying mechanisms driving these effects to enhance our understanding of corrosion phenomena in these challenging conditions [57].

8.3 IMPURITY NO_X RESEARCH GAPS

Further research is necessary to explore the permissible concentrations of NO and NO_2 in CCS transportation systems and to develop effective strategies for mitigating their corrosive effects. This could involve investigating the concentrations of these gases in CO_2 emissions from various industrial processes and examining specific methods for monitoring and reducing their corrosion-inducing properties. By conducting such studies, it would be possible to gain a better understanding of the extent of their impact and implement appropriate measures to control and minimize corrosion risks.

8.4 IMPURITY SULPHUR RESEARCH GAPS

The studies available do not specifically address the behaviour of sulphur impurities under supercritical CO_2 conditions. Furthermore, they lack detailed information on the experimental techniques employed to investigate the sulphur impurities. Crucial aspects such as specimen preparation, exposure conditions, analytical methods for corrosion rate and sulphur impurity measurement, and result interpretation are not adequately discussed in the sources.

Therefore, further research is required to determine the most appropriate experimental techniques for studying the impact of sulphur impurities on CO_2 corrosion in the presence of flue gas impurities. This may involve developing novel experimental setups or modifying existing ones to simulate relevant conditions, including temperature, pressure, and gas composition, while accurately measuring the content of sulphur impurities and their corrosion effects. Additionally, advanced analytical techniques may be necessary to detect and quantify trace amounts of sulphur impurities in corrosion products and gain insights into their role in corrosion mechanisms.

8.5 IMPURITY MERCURY RESEARCH GAPS

The specific mechanisms and conditions that lead to mercury-induced corrosion remain insufficiently understood. Although it is recognized that mercury can react with steel surfaces and form amalgams, there may be variations in the properties of these amalgams depending on factors such as the concentration and chemical composition of the surrounding environment. Moreover, the interactions between mercury and other contaminants present in the environment, such as oxygen or sulphur compounds, may also influence the corrosion behavior of carbon steel.

To enhance the understanding of these mechanisms and their interactions, further research is necessary. This research could involve investigating the specific conditions under which mercury-induced corrosion occurs, exploring the properties of different types of amalgams formed, and examining the effects of environmental factors like the presence of oxygen or sulphur compounds. By gaining a better understanding of these complex interactions, more accurate models can be developed for predicting and mitigating mercury-induced corrosion in CO_2 and H_2S environments.

8.6 FLOW RATE RESEARCH GAPS

A limited number of existing studies have conducted supercritical CO_2 corrosion tests in flow loops, with these tests generally considered to provide more reliable results compared to tests performed in sealed autoclaves. It is widely acknowledged that further research is necessary to investigate corrosion under different flow conditions in flow loops, particularly for multiphase flow situations in CO_2 pipelines that encompass various flow regimes. These studies are crucial to understanding the corrosion behaviour in CO_2 pipelines, especially in worst-case scenarios involving gas-liquid flows [57]. By conducting experiments in flow loops that accurately simulate real-world conditions, we can gain valuable insights into corrosion mechanisms and develop effective corrosion mitigation strategies.

8.7 CO_2 CORROSION PREDICTION MODELS GAPS

The majority of CO_2 corrosion prediction models are typically applicable within a CO_2 partial pressure range of 0 – 20 bar. However, when these models are applied to higher CO_2 partial pressure conditions, the predicted corrosion rates often exceed the experimental values by nearly an order of magnitude. This discrepancy can be attributed to the distinct corrosion characteristics observed under high-pressure conditions [57].

The behavior of CO_2 corrosion under elevated pressures is more complex and can deviate from the assumptions and mechanisms accounted for in the existing models. Factors such as changes in the corrosion kinetics, alterations in the transport properties of the CO_2, and variations in the composition and morphology of the corrosion products may contribute to the disparity between predicted and observed corrosion rates. Consequently, additional research is needed to enhance our understanding of the corrosion mechanisms specific to high-pressure CO_2 environments and to develop more accurate prediction models that encompass these conditions.

8.8 IMPURITY H_2S CORROSION PREDICTION MODELS KNOWLEDGE GAPS

There are knowledge gaps regarding the specific conditions under which the electrochemical model of mild steel corrosion in a mixed H_2S/CO_2 aqueous environment is applicable. It is unclear whether this model can be applied to all concentrations or ratios of H_2S and CO_2, and whether other factors such as temperature, pressure, or the presence of additional contaminants can influence the corrosion process. Further research is necessary to clarify these conditions and refine the electrochemical model accordingly.

In addition to addressing the applicability of the electrochemical model, further studies could focus on evaluating the effectiveness of different corrosion mitigation strategies in this specific environment. Understanding how various mitigation techniques perform in the presence of mixed H_2S and CO_2, and identifying any potential synergistic or antagonistic effects, would be valuable for developing effective corrosion management strategies.

By conducting comprehensive research that considers various parameters and conditions, we can advance our understanding of the corrosion behavior in mixed H_2S/CO_2 aqueous environments and enhance the accuracy of prediction models, as well as develop targeted mitigation strategies for corrosion prevention and control.

9. CONCLUSIONS AND RECOMMENDATIONS

9.1 CONCLUSION

The handling of anthropogenic CO_2 presents challenges due to limited industry experience and the absence of a consensus on CO_2 stream composition. The presence of impurities, even at low concentrations, has been found to induce corrosion in carbon steel pipelines. The lack of corrosion data from laboratory experiments and field studies further impedes accurate corrosion rate predictions. To overcome these challenges, comprehensive research is necessary to study the reaction processes, formation of corrosive phases, and their impact on material degradation. Defining a safe operating window for CO_2 transport and developing effective corrosion management strategies are crucial for ensuring the integrity and reliability of carbon steel pipelines.

This Report has thoroughly reviewed the current knowledge and recommended practices for managing internal corrosion in carbon steel pipelines transporting dense phase CO_2. The findings highlight the importance of understanding the synergistic effects of impurities and their role in accelerating corrosion rates. By considering these synergistic effects and implementing best current practices, operators can mitigate the risk of high corrosion rates and safeguard the integrity of the pipelines.

However, there is a clear need for further research to enhance our understanding of corrosion in CO_2 pipelines. Additional laboratory experiments and field studies are essential to generate more data on corrosion rates and validate corrosion models. Standardisation of CO_2 stream composition and ongoing collaboration among researchers, pipeline operators, and stakeholders are vital for advancing our understanding of corrosion mechanisms and developing targeted corrosion management strategies.

Continuous improvement in corrosion management practices is also critical. Operators should regularly assess and update their corrosion management strategies based on evolving knowledge and advancements in materials science and corrosion engineering. By implementing best practices, continuously monitoring pipelines, and incorporating innovative technologies, operators can proactively address corrosion issues and ensure the safe and reliable transportation of CO_2.

In conclusion, by investing in research, collaboration, and ongoing improvement of corrosion management strategies, the industry can overcome the challenges associated with managing internal corrosion in carbon steel pipelines transporting dense phase CO_2. This will enable the industry to develop robust and effective corrosion mitigation measures, enhance the safety and reliability of CO_2 transportation, and contribute to the successful implementation of carbon capture, utilization, and storage initiatives.

9.2 RECOMMENDATIONS

Based on the findings of this report, the following recommendations are provided:

1. **Implement Best Current Practices**: Operators should adopt and adhere to the best current practices for managing internal corrosion in carbon steel pipelines transporting dense phase CO_2. These practices should take into account the combined presence of impurities, such as O_2, H_2S, SO_2, and NO_x, and their potential synergistic effects. From the collected data, it is clear that O_2 and SO_2 are critical impurities that significantly influence corrosion severity, especially in water-saturated environments. Therefore, best practices should focus on stringent impurity control to prevent high corrosion rates. Specifically, O_2 concentrations should be minimised. Moreover, management of water content should be emphasised, as free water presence significantly accelerates the uniform corrosion rate in most experiments. Operating conditions should be set to either avoid water phase formation or employ water-removal techniques. These findings imply that strict water content control and maintaining a dry pipeline environment are fundamental for minimising corrosion. Operators should also employ advanced monitoring and inhibitor injection techniques to counteract the potential effects of unavoidable water ingress. Continuous monitoring, regular inspection, and periodic maintenance should also be integrated into the overall corrosion management program to ensure the long-term integrity of the pipelines. By following these practices, operators can minimise the risk of corrosion and ensure the long-term integrity of the pipelines.
2. **Investigate Conditions with Limited Knowledge**: There are certain conditions, such as specific combinations of impurities, varying concentrations, and specific operating conditions, where knowledge of corrosion rates is limited. To effectively manage internal corrosion in carbon steel pipelines transporting dense phase CO_2, it is crucial to expand the understanding of corrosion mechanisms. Further research should focus on investigating the underlying mechanisms behind the synergistic effects of impurities and their interaction with the pipeline materials. It is recommended to conduct further investigation and research in these areas to enhance the understanding of corrosion mechanisms under such conditions. This knowledge will enable the development of targeted mitigation measures and more accurate corrosion predictions.
3. **Expand Corrosion Mechanisms and Models**: The development of new corrosion models will enable more reliable assessments and predictions of corrosion rates, leading to improved corrosion management strategies. Considering the observed scatter in corrosion rate data across multiple studies, it is unlikely that a single reliable predictive model can be developed without a detailed understanding of how multiple impurities interact under varying conditions. Corrosion rates are highly sensitive to not just individual impurity levels but also to their combinations. Developing a reliable model would require incorporating multi-phase flow dynamics, impurity interactions, and thermodynamic properties of the CO_2 mixture. Current industry initiatives should focus on refining these models by conducting long-term experimental studies under varying concentrations of impurities, exposure times, and operational conditions. Moreover, the corrosion rates observed in static conditions are significantly different from those in dynamic scenarios, indicating that models must account for varying flow regimes. The industry should also collaborate to establish standard testing protocols that replicate real-world conditions more accurately. Industry initiatives should therefore focus on bridging the gap between laboratory conditions and operational realities to develop realistic models.

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APPENDIX I: LITERATURE SEARCH DOCUMENT SUMMARY

Document	Document Type	Summary
A review of the basic safety requirements of emerging infrastructures for Green Transition [1]	Academic Paper	A general discussion about the effects of impurities on corrosion rates (E.g. Corrosion control through dehydration, carbonic acid formation) was provided.
Carbon Dioxide Capture and Storage [2]	Industry Report	Corrosion rates are negligible for dry CO_2 pipelines but can be rapid when free water is present. Methane reduces the solubility of water in CO_2, and H_2S, O_2 and N_2 may have a similar effect.
Identification and Selection of Major Carbon Dioxide Stream Compositions [3]	Industry Report	Impurity composition tables for Flue Gas, Combustion Stack from Coke Production, Cement Kilns, Natural Gas Combustion and Lime Production were provided.
Potential Dynamics of CO_2 Stream Composition and Mass Flow Rates in CCS Clusters [4]	Academic Paper	The presence of impurities such as O_2, SO_X and NO_X will produce more stringent restrictions on the allowable water content within the pipeline due to synergistic effects.
Corrosion and Bulk Phase Reactions in CO_2 Transport Pipelines with Impurities: Review of Recent Published Studies [5]	Academic Paper	$CO_2 – H_2O – H_2S$ System: Chevron did some experimental work in the 1970’s: No evidence of pitting or general corrosion attack with water content of 1000 ppmv, H_2S content of 800 ppmv and temperature between 3°C and 23°C. $CO_2 – H_2O – NO_2$ System: NO_2 increases the corrosiveness of a CO_2/H_2O mixture. NO_2 is highly soluble in water and will react with water to produce HNO_3. HNO_3 is approximately twice as corrosive in comparison with HCl and H_2SO_4. $CO_2 – H_2O – SO_2$ System: Sulphurous acid (H_2SO_3) and sulphuric acid (H_2SO_4) may form when H_2O, SO_2 and O_2 are present. It appears that corrosion is occurring below the water solubility limit of pure CO_2-water systems. $CO_2 – H_2O – SO_2$ - NO_2 and $CO_2 – H_2O – SO_2$ - $NO_2 – H_2S$ System:

		Synergistic corrosion effects have been observed for the CO_2 – H_2O – SO_2 - NO_2 system in dense phase CO_2. It has been proposed that the synergistic effects can be explained by the catalytic behaviour of nitrogen oxides increasing the rate of sulphuric acid production.
A thermodynamic model for predicting mineral reactivity in supercritical carbon dioxide: I. Phase behavior of carbon dioxide–water–chloride salt systems across the H_2O-rich to the CO_2-rich regions [6]	Academic Paper	CO_2–H_2O–NaCl System: Increasing NaCl concentration in a supercritical CO_2 – H_2O – NaCl system results in a small reduction in the solubility of water in CO_2. The water solubility of supercritical CO_2 increases as temperature increases. CO_2–H_2O–$CaCl_2$ System: Increasing the concentration of $CaCl_2$ in supercritical CO_2–H_2O–$CaCl_2$ results in a significant reduction in water solubility. Water solubility in supercritical CO_2 increases as temperature increases in this system.
Corrosion in dense phase CO_2 – the impact of depressurisation and accumulation of impurities [7]	Academic Paper	SO_2 and NO_2 are a significant concern if pipeline depressurisation occurs because these species will accumulate in the water phase, reduce the pH of the solution and increase the reactivity of this phase. There are concerns about other impurities accumulating during pipeline depressurisation events.
Corrosion of transport pipelines for CO_2 – effect of water ingress [8]	Academic Paper	Corrosion does not occur in dense phase CO_2 – H_2O and CO_2 – H_2O – O_2 systems when the water content is at 500 ppm. Corrosion however occurred at water concentration of 200 ppm when the system also contained SO_2. O_2 can also attack steel directly through an additional cathodic reaction that accelerates the overall corrosion rate.
Effect of SO_2 and NO_2 on corrosion and solid formation in dense phase CO_2 pipelines [9]	Academic Paper	Experiments showed that corrosion takes place at a water concentration far below the water solubility in the pure water-CO_2 system when NO_x and SO_x were present. Corrosion rates were very fast in the presence of NO_2.
Effect of Water Content on the Corrosion Behavior of Carbon Steel in Supercritical CO_2 Phase with Impurities [10]	Academic Paper	No significant corrosion attack was detected in the supercritical CO_2/O_2 phase with 650, 2000 and 3000 ppm of water. Trace amounts of SO_2 can result in an increase in corrosion rates. Significant corrosion was observed with 1% SO_2 under the current guideline for water in CO_2 pipelines (650 ppm).
Nitric and Sulfuric Acid Solubility in Dense Phase CO_2 [11]	Academic Paper	Sulphuric acid and nitric acid are both highly hydroscopic, which means that they can absorb water from the bulk CO_2 phase and create a highly acidic, concentrated aqueous phase that is corrosive to carbon steel. If the nitric and sulphuric acid remains dissolved in the bulk CO_2 phase, they can remain in the CO_2 stream without compromising the integrity of the transportation system.

Water Solubility in CO_2 Mixtures: Experimental and Modelling Investigation [12]	Academic Paper	For $CO_2 – H_2O$ mixtures with either NO_2 or SO_2, the solubility of water in dense phase CO_2 drops down to close to 500ppm.
Evaluation of Thermodynamic Models for Predicting Phase Equilibria of CO_2 + Impurity Binary Mixture [13]	Academic Paper	The typical concentrations of impurities in dried CO_2 were provided for different CCS sources.
Impact of CO_2 impurity on CO_2 compression, liquefaction and transportation [14]	Academic Paper	Maximum water content specifications for currently operating pipelines range between 20 ppmv and 640 ppmv. CH_4 and N_2 decrease the solubility of water in supercritical CO_2, whilst H_2S increases water solubility.
A systematic review of key challenges of CO_2 transport via pipelines [15]	Academic Paper	Amines were highlighted as an impurity that could affect the solubility of water in supercritical CO_2. O_2 corrosion of carbon steel, stress corrosion and hydrogen embrittlement and blistering were identified as other corrosion risks that need to be mitigated in supercritical CO_2 pipeline systems. $CO_2 – H_2O – SO_2 - NO_2 – O_2$ System: Corrosion rates increased as temperature decreased. Pipeline depressurisation events were identified as a significant concern, as the rapid cooling of the mixture could result in enhanced corrosion rates.
Carbon dioxide transport via pipelines: A systematic review [16]	Academic Paper	Paper has highlighted that there are conflicting opinions in literature regarding the effect of H_2S on corrosion rates. CO_2 quality regulations for CO_2 pipelines and a list of primary standards and specifications in relation to CO_2 pipeline design were also provided.
CASE STUDY ON CO_2 TRANSPORT PIPELINE NETWORK DESIGN FOR HUMBER REGION IN THE UK [17]	Academic Paper/Case Study	Corrosion rates of 10mm/year are usually quoted for CO_2 pipelines with free water. This paper indicates that corrosion rates increase as flow velocity and temperature increases.
CO_2 PIPELINES MATERIAL AND SAFETY CONSIDERATIONS [18]	Academic Paper	Expected CO_2 composition for different CCS technologies was provided. Post-combustion capture has the largest potential concentration for water in the CO_2 stream.

Corrosion Behavior of Carbon Steels in CCTS Environment [19]	Academic Paper	The reduction of carbonic acid to form H_2 and HCO_3^- may become important at pH > 5. Corrosion rates may not be as high as expected in supercritical CO_2 systems due to the formation of a protective $FeCO_3$ scale during carbonic acid corrosion. This protective scale may cover the metal surface and make the surface unavailable for further corrosion.
Determining the corrosive potential of CO_2 transport pipeline in high pCO_2-water environments [20]	Academic Paper	Corrosion rates are very slow in water-saturated CO_2 under high pressure conditions (Approximately 0.2mm/year) due to the formation of $FeCO_3$ on the steel surface. The solubility of water in supercritical CO_2 increases as temperature and pressure increases.
Development of a Guideline for Safe, Reliable and Cost Efficient Transmission of CO_2 in Pipelines [21]	Academic Paper	CO_2 pipeline operators in North America have had a significant focus on controlling the water content of their pipelines, which means that internal corrosion has not been a common failure mode.
IMPACTS: Framework for risk assessment of CO2 transport and storage infrastructure [22]	Academic Paper	Hydrosulphuric acid ($H_2S.H_2O$), nitrous acid (HONO), hydrogen fluoride (HF), ammonium nitrate (NH_4NO_3) and chlorine were identified as other chemical species that could contribute to internal pipeline corrosion if there is sufficient water in the pipeline.
Recommended Practice DNV-RP-J202 – Design and Operation of CO_2 Pipelines [23]	Standard	This Recommended Practice (RP) provides guidelines in relation to the design of CO_2 transportation systems. General information in relation to CO_2 pipeline corrosion and the prevention strategies that are available have been provided.
Towards a CO_2 Pipeline Specification: Defining Tolerance Limits for Impurities [24]	Academic Paper	The presence of H_2S appears to increase the solubility of H_2O in dense phase CO_2. Corrosion rates as high as 20 mm/year could be observed at high pressure and temperature when free water is present. It appears that a threshold water level does not exist for the onset of corrosion. Examples of CO_2 pipeline quality specifications and compositions have been provided.
Update of DNV recommended practice RP-J202 with focus on CO_2 Corrosion with Impurities [25]	Academic Paper	Experiments showed that dense phase CO_2 with 500 ppmv water resulted in corrosion under most circumstances when NO_2, SO_2, H_2S and O_2 were present in moderate amounts.

DYNAMIS CO_2 quality recommendations [26]	Industry Report	Provided recommendations on the impurity limits for CO_2 transportation pipeline systems. Even if no water is present in a CO_2 mixture, hydrogen sulphide will still corrode carbon steel pipelines and form iron sulphide. More stringent water control is required during CO_2 transport at lower pressure and temperature conditions.
Effect of Impurities on the Corrosion Behavior of CO_2 Transmission Pipeline Steel in Supercritical CO_2- Water Environments [27]	Academic Paper	One key reason why O_2 increases corrosion rates in a CO_2 – H_2O – O_2 system is because it inhibits the formation of a protective $FeCO_3$ layer.
Quality Guidelines for Energy System Studies – CO_2 Impurity Design Parameters [28]	Industry Report	CO_2 impurity guidelines were provided. O_2 can provide cathodic reaction paths that lead to the corrosion of carbon steel pipes, and it inhibits the formation of a protective $FeCO_3$ layer. This report indicates that in the absence of H_2O, SO_2 will not corrode carbon steel pipes.
State-of-the-Art Overview of CO_2 Pipeline Transport with Relevance to Offshore Pipelines [29]	Industry Report	At high partial pressures, existing models tend to overestimate corrosion rates. The paper indicates that corrosion attacks in CO_2 pipeline systems will often be localised at initial initiation sites, leading to high localised corrosion rates. MEG (mono-ethylene glycol) was identified as a potential corrosion inhibitor.
The upper limit of moisture content for supercritical CO_2 pipeline transport [30]	Academic Paper	The upper limit of moisture content in CO_2 pipelines is directly dependent on the temperature of the ambient surroundings, as well as the presence of thermal insulation.
Understanding dense phase CO_2 corrosion problems [31]	Academic Paper	Experimental Conditions: CO_2/SO_2/H_2O, SO_2 Concentration = 500ppm, H_2O = 3300ppm, supercritical conditions: Significant corrosion was detected under these conditions after 1100hr of exposure time. No pits or signs of localised corrosion was detected.
Recommended Practice DNV-RP-F104 – Design and operation of carbon dioxide pipelines [32]	Standard	This is the latest DNV standard in relation to the design of CO_2 pipelines. The standard provides a summary of the known corrosion mechanisms in CO_2 pipelines, and the strategies that can be used to mitigate against corrosion.
Carbon dioxide capture, transportation, and geological storage – Cross Cutting Issues – CO_2 stream composition [33]	Standard	Provides a general and succinct summary about CO_2 pipeline internal corrosion. The standard has also reported the impurity levels that have been used in existing pipelines, as well as published CO_2 recommended impurity levels.

CORROSION AND MATERIALS SELECTION IN CCS SYSTEMS [34]	Industry Report	Iron carbonates can form protective layers at above 60 °C (The formation of this film is dependent on CO_2 concentration). Iron sulphide can form protective layers when pCO_2/pH_2s ratios are less than 200:1. Chlorides in small quantities can promote breakdown of the passive film protecting stainless steel and nickel alloys. Both HCl and NaOH can promote the formation of a free water phase. Discussion of corrosion mechanisms, rates and material selection to mitigate against corrosion in this report is extensive.

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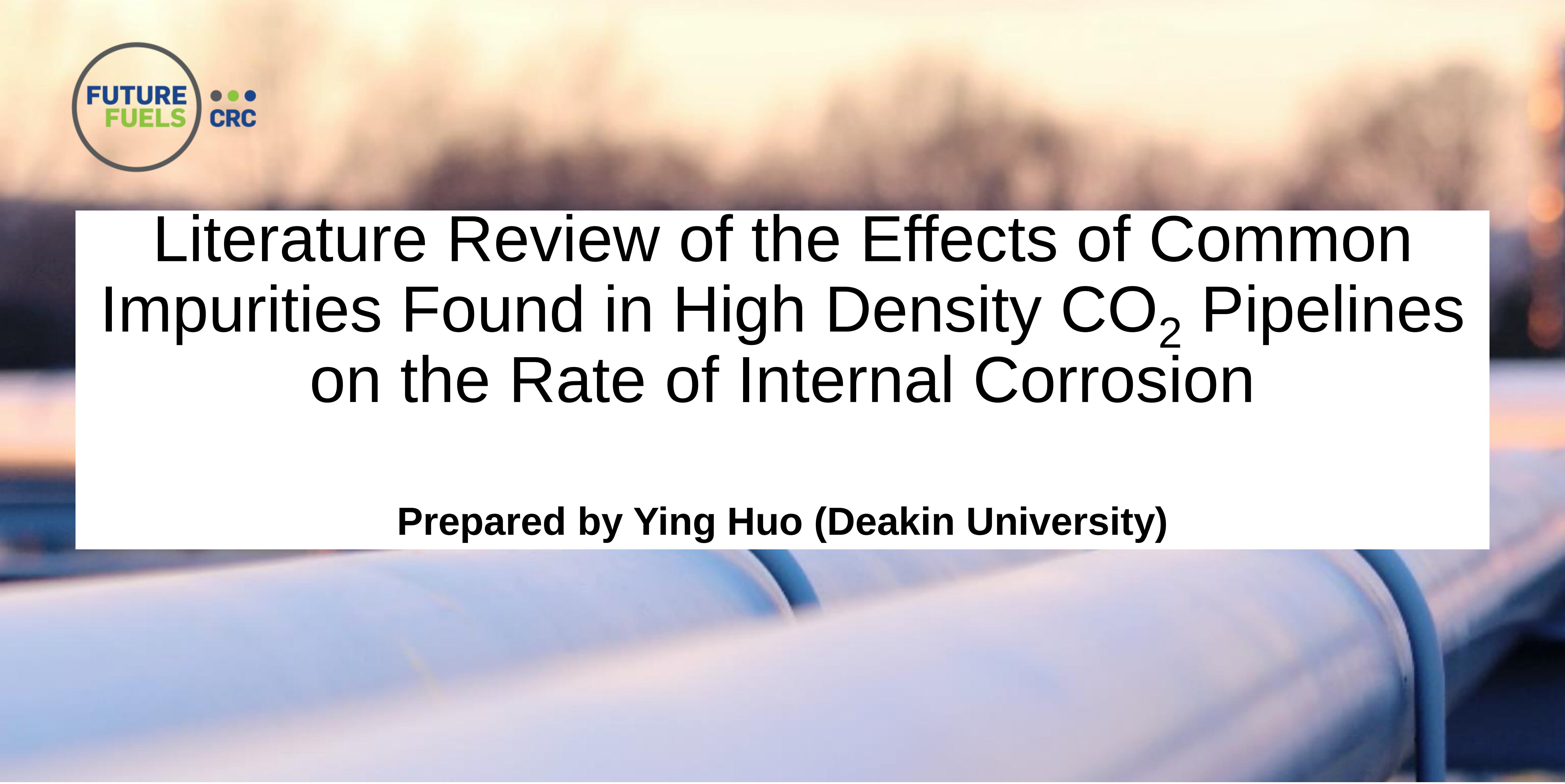
APPENDIX II: ACADEMIC DATABASE SUMMARY

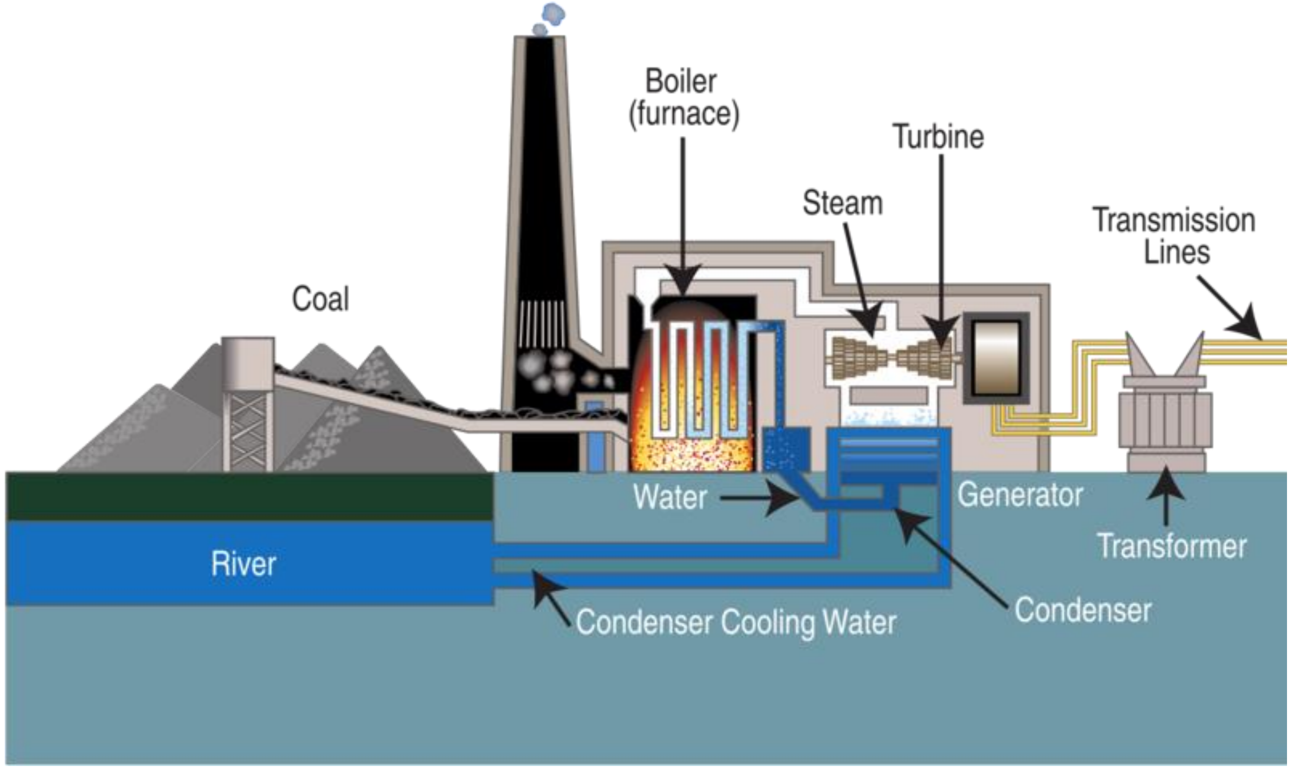


FUTURE FUELS CRC

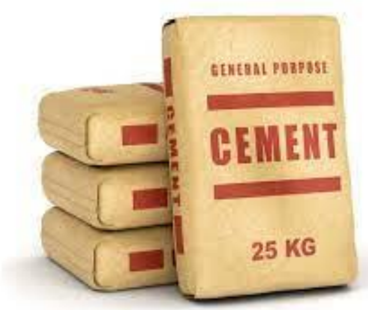
Literature Review of the Effects of Common Impurities Found in High Density CO_2 Pipelines on the Rate of Internal Corrosion

Prepared by Ying Huo (Deakin University)

Reduce Global Warming



Take actual steps in capturing CO_2 and store it or enhanced oil recovery (EOR) or other uses.



Global warming

Carbon capture and storage (CCS)

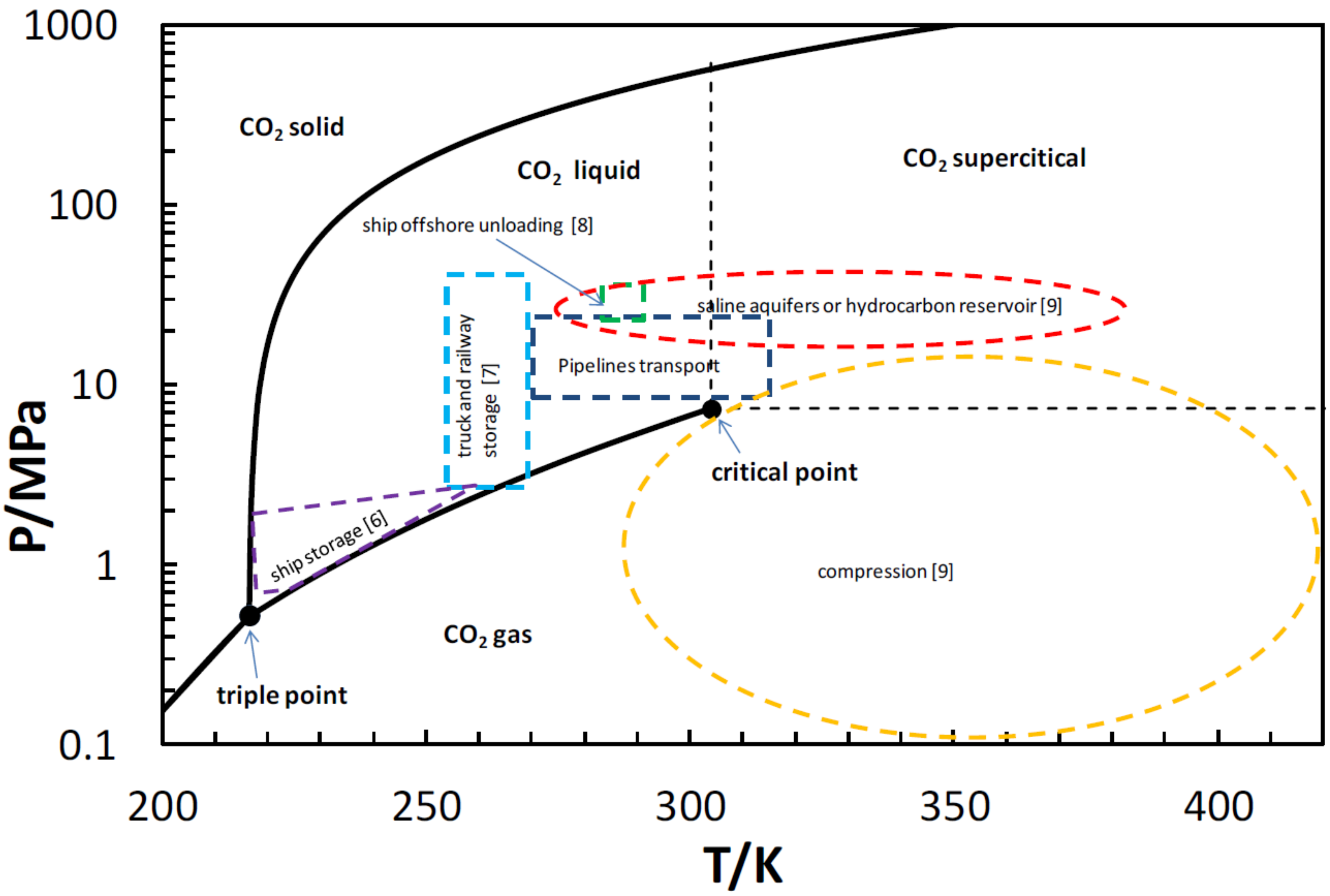
Gap

- The short- and long-term effects of impurities on corrosion in dense phase CO_2.
- The effects of pressure, temperature and flow on fluid corrosivity
- How impurities affect the H_2O solubility in a dense phase CO_2.
- Mechanisms of uniform and localised corrosion in dense phase CO2 with impurities.

Objectives of the Review

- Determine which impurities are most likely to be found within captured CO_2 in Australia.
- Identify existing research or corrosion models related to measuring or modelling the impact of these common impurities on corrosion rates and their limitations.
- Identify what is known about the level of impact these impurities have on corrosion rates, noting specifically any synergistic effects between impurities that significantly increase corrosion rates.
- Identify knowledge gaps and new research opportunities that could close these gaps.
- Develop/update general guidelines based on current knowledge that will ensure corrosion rates are minimal.

Various operations involved in the CO_2 transport (1)



CO_2 is transported in pipelines above the supercritical pressure of 73.8 bar and temperature of 31.1 °C to keep it in supercritical state. (2)

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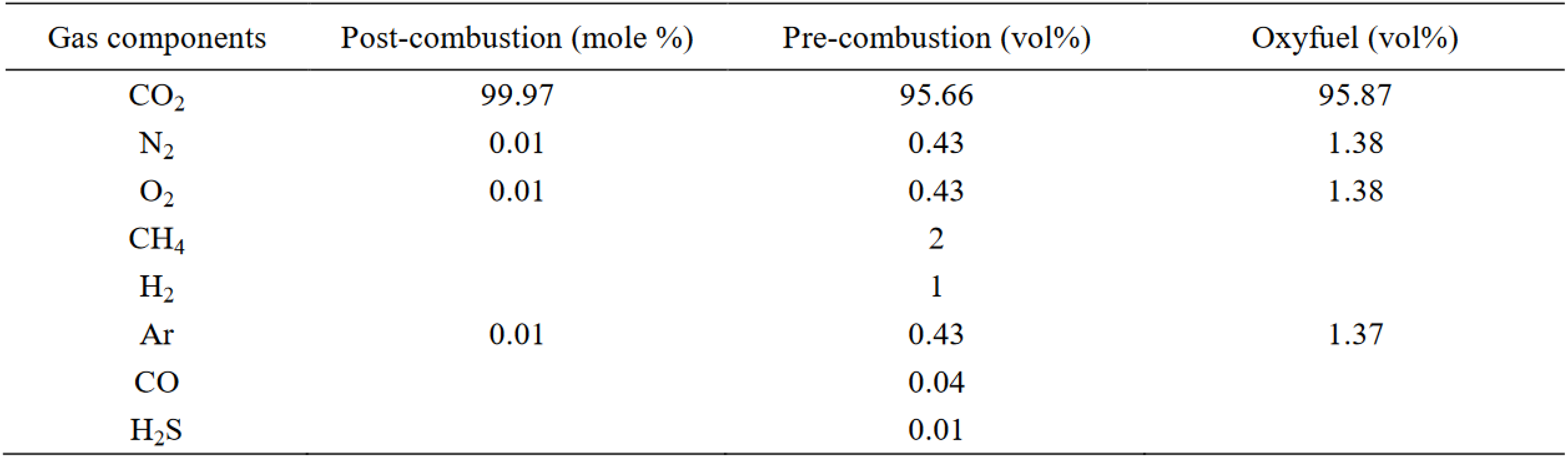
CO_2 impurities for Australian conditions (1)



Gas components	Post-combustion (mole %)	Pre-combustion (vol%)	Oxyfuel (vol%)
CO_2	99.97	95.66	95.87
N_2	0.01	0.43	1.38
O_2	0.01	0.43	1.38
CH_4		2	
H_2		1	
Ar	0.01	0.43	1.37
CO		0.04	
H_2S		0.01	

100% CO_2 is not corrosive. CO_2 corrosion refers to the carbonic acid corrosion is the issue. (2)

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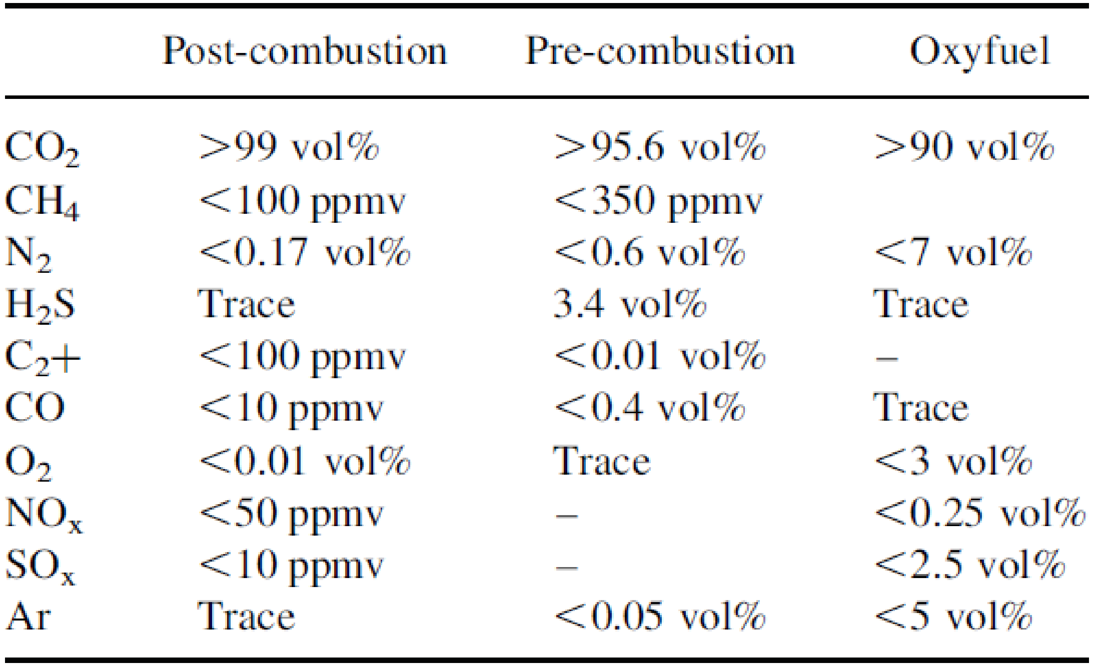
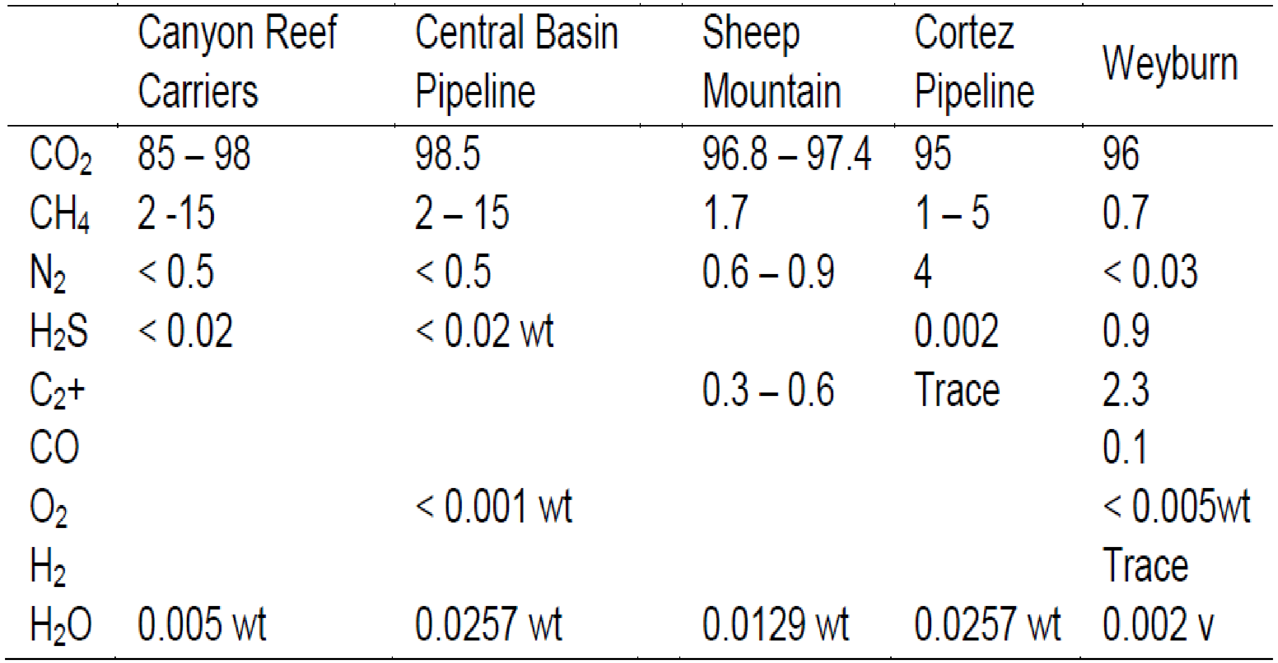
CO_2 impurities from other reports

Norway research report (1)



	Post-combustion	Pre-combustion	Oxyfuel
CO_2	>99 vol%	>95.6 vol%	>90 vol%
CH_4	<100 ppmv	<350 ppmv	
N_2	<0.17 vol%	<0.6 vol%	<7 vol%
H_2S	Trace	3.4 vol%	Trace
C_2+	<100 ppmv	<0.01 vol%	–
CO	<10 ppmv	<0.4 vol%	Trace
O_2	<0.01 vol%	Trace	<3 vol%
NO_x	<50 ppmv	–	<0.25 vol%
SO_x	<10 ppmv	–	<2.5 vol%
Ar	Trace	<0.05 vol%	<5 vol%

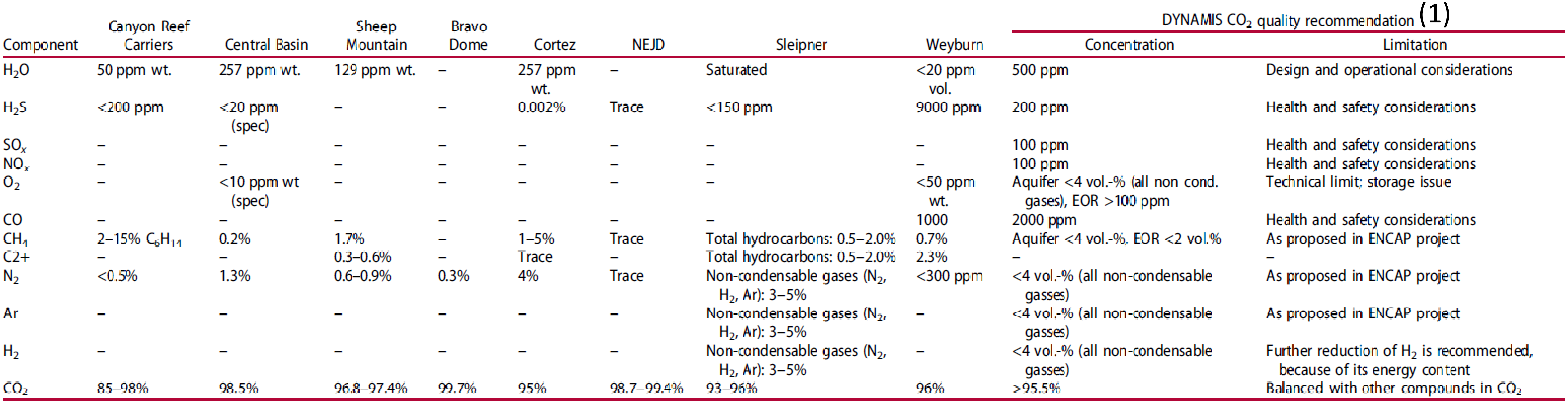
USA report (2)



	Canyon Reef Carriers	Central Basin Pipeline	Sheep Mountain	Cortez Pipeline	Weyburn
CO_2	85 – 98	98.5	96.8 – 97.4	95	96
CH_4	2 -15	2 – 15	1.7	1 – 5	0.7
N_2	< 0.5	< 0.5	0.6 – 0.9	4	< 0.03
H_2S	< 0.02	< 0.02 wt		0.002	0.9
C_2+			0.3 – 0.6	Trace	2.3
CO					0.1
O_2		< 0.001 wt			< 0.005wt
H_2					Trace
H_2O	0.005 wt	0.0257 wt	0.0129 wt	0.0257 wt	0.002 v

1. Oosterkamp, A. and Ramsen, J., 2008, State-of-the-art overview of CO2 pipeline transport with relevance to offshore pipelines, Research Council of Norway, Report number POL-O-2007-138-A.
2. Patchigolla, K. & Oakey, J. E. 2013. Design Overview of High Pressure Dense Phase CO2 Pipeline Transport in Flow Mode. Energy Procedia, 37, 3123-3130

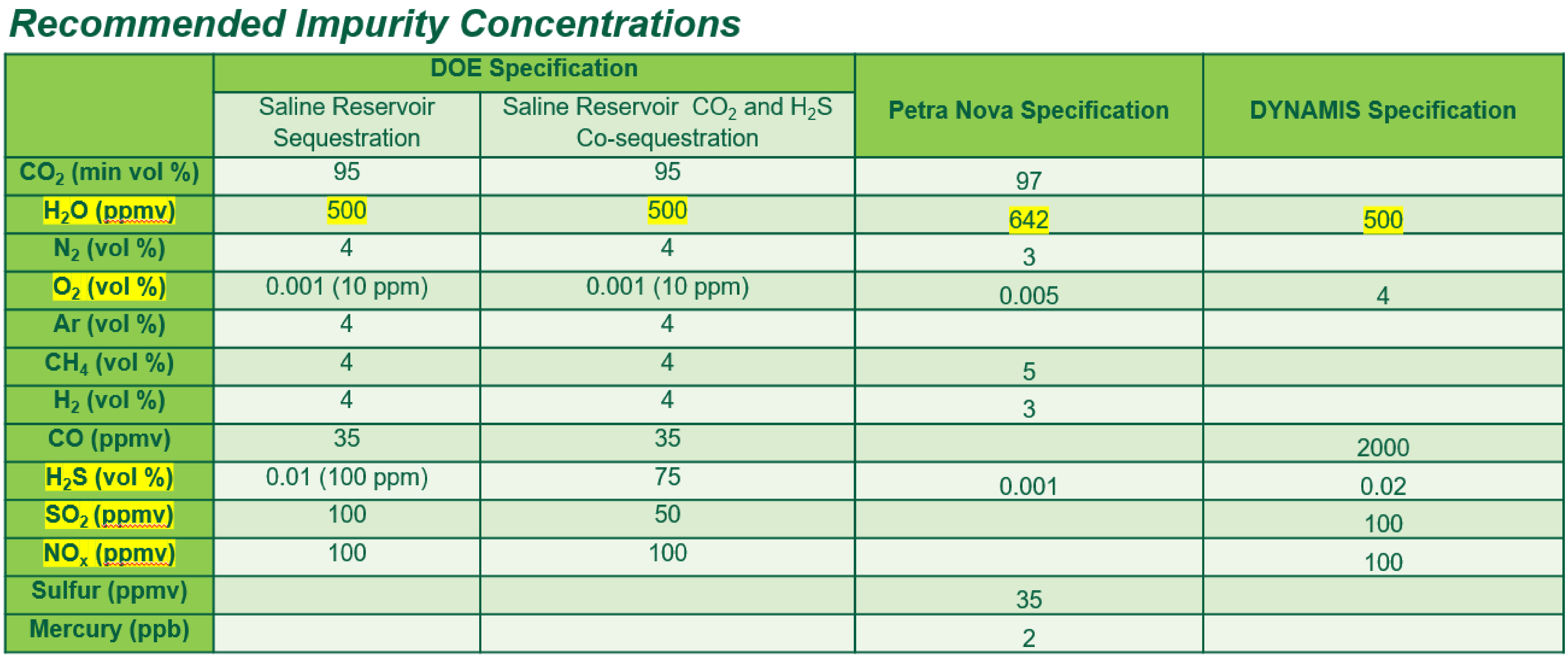
DYNAMIS CO2 quality recommendation compared to the existing CO2 qualities for EOR purpose



Component	Canyon Reef Carriers	Central Basin	Sheep Mountain	Bravo Dome	Cortez	NEJD	Sleipner	Weyburn	DYNAMIS CO_2 quality recommendation (1)	
									Concentration	Limitation
H_2O	50 ppm wt.	257 ppm wt.	129 ppm wt.	–	257 ppm wt.	–	Saturated	<20 ppm vol.	500 ppm	Design and operational considerations
H_2S	<200 ppm	<20 ppm (spec)	–	–	0.002%	Trace	<150 ppm	9000 ppm	200 ppm	Health and safety considerations
SO_x	–	–	–	–	–	–	–	–	100 ppm	Health and safety considerations
NO_x	–	–	–	–	–	–	–	–	100 ppm	Health and safety considerations
O_2	–	<10 ppm wt (spec)	–	–	–	–	–	<50 ppm wt.	Aquifer <4 vol.-% (all non cond. gases), EOR >100 ppm	Technical limit; storage issue
CO	–	–	–	–	–	–	–	1000	2000 ppm	Health and safety considerations
CH_4	2–15% C_6H_{14}	0.2%	1.7%	–	1–5%	Trace	Total hydrocarbons: 0.5–2.0%	0.7%	Aquifer <4 vol.-%, EOR <2 vol.%	As proposed in ENCAP project
C2+	–	–	0.3–0.6%	–	Trace	–	Total hydrocarbons: 0.5–2.0%	2.3%	–	–
N_2	<0.5%	1.3%	0.6–0.9%	0.3%	4%	Trace	Non-condensable gases (N_2, H_2, Ar): 3–5%	<300 ppm	<4 vol.-% (all non-condensable gasses)	As proposed in ENCAP project
Ar	–	–	–	–	–	–	Non-condensable gases (N_2, H_2, Ar): 3–5%	–	<4 vol.-% (all non-condensable gasses)	As proposed in ENCAP project
H_2	–	–	–	–	–	–	Non-condensable gases (N_2, H_2, Ar): 3–5%	–	<4 vol.-% (all non-condensable gasses)	Further reduction of H_2 is recommended, because of its energy content
CO_2	85–98%	98.5%	96.8–97.4%	99.7%	95%	98.7–99.4%	93–96%	96%	>95.5%	Balanced with other compounds in CO_2

1. de Visser E, Hendriks C, Barrio M, et al. Dynamis CO2 quality recommendations. Int J Greenh Gas Con. 2008;2(4):478–484.
2. Oosterkamp A, Ramsen J. State-of-the-art overview of CO2 pipeline transport with relevance to offshore pipelines. POL-O-2007- 138-A, POLYTEC, 2008.

Important information from Grahame provided presentation



Recommended Impurity Concentrations

	DOE Specification		Petra Nova Specification	DYNAMIS Specification
	Saline Reservoir Sequestration	Saline Reservoir CO_2 and H_2S Co-sequestration		
CO_2 (min vol %)	95	95	97	
H_2O (ppmv)	500	500	642	500
N_2 (vol %)	4	4	3	
O_2 (vol %)	0.001 (10 ppm)	0.001 (10 ppm)	0.005	4
Ar (vol %)	4	4		
CH_4 (vol %)	4	4	5	
H_2 (vol %)	4	4	3	
CO (ppmv)	35	35		2000
H_2S (vol %)	0.01 (100 ppm)	75	0.001	0.02
SO_2 (ppmv)	100	50		100
NO_x (ppmv)	100	100		100
Sulfur (ppmv)			35	
Mercury (ppb)			2	

Impurity impact summary table

No.	Impurity	Concise impact	Refer to page
1	**NO_x (ppmv)**	Severe corrosion issues by forming HNO_3	Impurity NO_X
2	**H_2O (ppmv)**	500→1000ppmv corrosion rate increase	Impurity: H_2O
		Corrosion rate not change when saturated	
3	**N_2 (vol %)**	Increase liquid density or viscosity and lead to higher compressor power capacity.	Impurity C_4, N_2, O_2
4	**O_2 (vol %)**	O_2 + H_2O + CO_2 lead to corrosion	Impurity O_2
5	**Ar (vol %)**	Not find yet	
6	**CH_4 (vol %)**	Lower the H_2O solubility	Impurities affect the H2O solubility
7	**H_2 (vol %)**	Hydrogen embrittlement	Impurity H_2
8	**CO (ppmv)**	CO_2-CO-H_2O lead to SCC problem (when pressure <2MPa)	Impurity CO

No.	Impurity	Concise impact	Refer to page
9	**H_2S**	Increase corrosion rate by reduce pH	Impurity H_2S
		Reduce corrosion by forming sulphate scale	
10	**SO_2**	SO_2 increase corrosion rate by reducing pH	Impurity SO_X
		SO_2 lower the tolerable water content	
11	**Sulphur**	Sulphur lead to pitting corrosion and react with H_2O to produce H_2S and sulphuric acid.	Impurity Sulphur
12	**Mercury**	Hg react with sulphide form HgS. This reaction reduce sulphide scale and increase corrosion rate.	Impurity Mercury
		Hg also react with NO to form NO_2 even without the presence of water.	
13	**Amines**	Monoethanolamine (MEA) reduce corrosion.	Impurity Amines
		Diethanolamine (DEA) increase corrosion.	

Synergistic impurities impact summary table

No.	Impurity	Concise impact	Refer to page
1	**NO_x+SO_2**	Increase atmospheric corrosion.	Impurities synergistic effect: NO_2 + SO_2
2	**O_2 +H_2S+SO_2**	Has remarkable corrosion behaviour on X65 steel.	Impurities synergistic effect: O2 +H2S+SO2
3	**SO_2+O_2+H_2O**	Produce sulphuric acid and iron oxyhydroxide. Lead to fast metal loss.	Impurities synergistic effect: SO2+O2+H2O and HIC
4	**H_2S + NO_x**	May lead to hydrogen-induced cracking (HIC)	Impurities synergistic effect: SO2+O2+H2O and HIC
5	**Factors influence H_2O solubility**	CH_4, N_2 and HCl lead to lower water solubility.	Impurities influence water solubility in CCS pipeline
6	**Other summary charts**	Synergistic impurities impact summary charts from literature review	Synergistic effects summary charts

Other factors impact summary table

No.	Factors	Concise impact	Refer to page
1	**Pressure**	Higher the pressure the higher corrosion rate.	Pressure
2	**Temperature**	Higher the temperature, the higher corrosion rate.	Temperature
3	**Flow rate**	Higher flow rate lead to higher corrosion rate.	Flow rate
4	**Localized corrosion**	Indicate the upper limit of water content.	Localised corrosion
5	**Steel chemistry**	Different pipe steel materials has different corrosion behaviours.	Steel chemistry
6	**CO_2 phase**	Different CO_2 phase has different corrosion behaviours.	Mechanism difference for different CO_2 phase conditions
7	**Corrosion product layer**	Reduce corrosion rate	Corrosion product layer
8	**Mechanistic prediction models**	CO_2 and H_2S models fit for short-term exposures conditions. CO_2 with SO_2-O_2-H_2O corrosion prediction models fit for high SO_2 concentration and RH.	CO_2 and H_2S corrosion prediction models
9	**Knowledge gap**		Knowledge gaps summary

Impurity NO_X

- NO_x stands for NO and NO_2, and NO can be oxidised to NO_2 by O_2.
- Both NO and NO_2 were found to cause very severe corrosion issues in pipeline steels (1, 2). $3NO_2 + H_2O \rightarrow 2HNO_3 + NO$
- HNO_3 has a similar accelerant effect on the corrosion behaviour of steel to HCl (3). However, the diffusion ability of HNO_3 is higher than for HCl and H_2SO_4, which means it may more easily induce severe corrosion problems on the internal surface of supercritical CO_2 pipelines (4, 5, 6). $Fe + 4HNO_3 \rightarrow Fe(NO_3)_2 + 2H_2O + 2NO_2$
- HNO_3 has a strong oxidation effect on Fe^{2+}, leading to the formation of a rust-like dusty product, which was always fluffy and exhibited poor protection on the substrate, without the ability to efficiently reduce the corrosion rate (7).
- A blackish/orange coloured dusty film was found forming on the X65 steel surface in wet supercritical CO_2 with NO_2 (8). The composition of the products formed in a continuous flow of CO_2 containing NO_2, SO_2 and CO was found to be very complex(9).
- HNO_3 was also found to increase the pitting potential in supercritical CO_2 (10)
- Sun et al. (2) found that localised corrosion commonly existed in water-saturated supercritical CO_2 systems containing NO_2 with and without other impurities. This is due to NO_2 can greatly accelerate the separation of water from dense CO_2 fluids causing localised corrosion of the steel underneath the water droplets.

1. Paschke B, Kather A. Corrosion of pipeline and compressor materials due to impurities in separated CO_2 from fossil-fuelled power plants. Energy Proc. 2012;23:207–215.

2. Sun C, Wang Y, Sun J, et al. Effect of impurity on the corrosion behaviour of X65 steel in water-saturated supercritical CO_2 system. J Supercrit Fluids. 2016;116:70–82.

3. Ayello F, Sridhar N, Evans K, et al. Effect of liquid impurities on corrosion of carbon steel in supercritical CO2. Proceedings of the 8th International Pipeline Conference (IPC2010), September 27– October 1, Calgary, Alberta, Canada; 2010.

4. Sim S, Cavanaugh MK, Corrigan P, et al. Aqueous corrosion testing and neural network modelling to simulate corrosion of supercritical CO_2 pipelines in the carbon capture and storage cycle. Corrosion. 2012;69(5):477–486.

5. Ruhl AS, Kranzmann A. Corrosion in supercritical CO2 by diffusion of flue gas acids and water. J Supercrit Fluids. 2012;68:81– 6.

6. Kolman DG, Ford DK, Butt DP, et al. Corrosion of 304 stainless steel exposed to nitric acid-chloride environments. Corrosion Sci. 1997;39(12):2067–2093.

7. Halseid M, Dugstad A, Morland B. Corrosion and bulk phase reactions in CO_2 transport pipelines with impurities: review of recent published studies. Energy Proc. 2014;63:2557–2569.

8. Dugstad A, Halseid M, Morland B. Effect of SO_2 and NO_2 on corrosion and solid formation in dense phase CO_2 pipelines. Energy Proc. 2013;37:2877–2887.

9. Ruhl AS, Kranzmann A. Corrosion behavior of various steels in a continuous flow of carbon dioxide containing impurities. Int J Greenh Gas Con. 2012;9(0):85–90.

10. Sim S, Cole IS, Bocher F, et al. Investigating the effect of salt and acid impurities in supercritical CO_2 as relevant to the corrosion of carbon capture and storage pipelines. Int J Greenh Gas Con. 2013;17:534–541.

NO_2 had a catalytic effect on corrosion reactions (1).
This procedures are electrochemical nature of hydrolysis of NOx. The following semi reactions are reported (2):
$NO + H_2O = HNO_2 + H+ 1e^-$
$NO + H_2O = NO_2^- + 2H^+ + 1e^-$
$NO_2 + H_2O = HNO_3 + H^+ + 1e^-$
$NO_2 + H_2O = NO_3^- + 2H^+ + 1e^-$
As can be observed, NOx reacts with water forming acids or nitrite/nitrate ions which are highly corrosive for steel materials.

1. Corvo F, Reyes J, Pérez T, et al. Role of NOx in materials corrosion and degradation. Rev Cenic Ciencias Químicas.2010;41:1–10.
2. M. Pourbaix, Atlas of Electrochemical Equilibria in Aqueous Solutions, NACECEBELCOR, Houston-Brussels, 1974

Impurity: H_2O

- With the water content increase, the general and localised corrosion rate increase.(1)
- Yevtushenko and Bäßler (2) found that the corrosion rate increased when increasing the water content from 500 to 1000 ppmv in the flow loop test. However, Thodla et al. [3], who showed that in auto-clave test, when the water content was reduced from 1000 to 100 ppm, the corrosion rate increased.
- Sim et al. [4] found that the corrosion rate did not change much with the addition of water, once the water content in the supercritical CO_2 reached saturation.
- The US Department of Energy per- formed some research related to supercritical CO_2 corrosion in 1979 [5] and 1996 [6], which also indicated a low corrosion rate of steel when the water concentration was low.

1 Hua Y, Barker R, Neville A. Effect of temperature on the critical water content for general and localised corrosion of X65 carbon steel in the transport of supercritical CO2. Int J Greenh Gas Con. 2014;31:48–60.

2 Yevtushenko O, Bäßler R. Water impact on corrosion resistance of pipeline steels in circulating supercritical CO2 with SO2- and NO2- impurities. CORROSION/2014, NACE International, San Antonio, TX, USA, Paper No. 3838, 2014.

3 Thodla R, Francois A, Sridhar N. Materials performance in supercritical CO2 environments. CORROSION/2009, Atlanta, GA, 03/22/2009, 2009, NACE International.

4 Sim S, Bocher F, Cole IS, et al. Investigating the effect of water content in supercritical CO2 as relevant to the corrosion of carbon capture and storage pipelines. Corrosion. 2014;70(2):185– 195.

5 DeBerry DW, Clark WS. Corrosion due to use of carbon dioxide for enhanced oil recovery. Austin (TX): DOE; 1979.

6 Propp WA, Carleson TE, Wai CM, et al. Corrosion in supercritical fluids. Idaho Falls: Idaho National Engineering Laboratory; 1996.

Impurity: H_2O

- Condensation of water in CO_2 system with carbon steel present will give corrosion (1, 2, 3) and must be avoided.
- When water is the only impurity, the water concentration limit for corrosion to occur can be set slightly below the saturation limit of the system (4)
- For systems that might experience local temperatures below 10 ◦C there is a risk for hydrate or ice formation (5) and the lowest acceptable water concentration for such systems can be lower than for corrosion and therefore determine the water limit.

1 Choi, Y.-S., Nesic, S., Young, D., 2010. Effect of impurities on the corrosion behaviour of CO_2 transmission pipeline steel in supercritical CO_2 Water environments. Environ. Sci. Technol. 44, 9233–9238.

2 Hua, Y., Barker, R., Neville, A., 2015. Understanding the influence of SO_2 and O_2 on the corrosion of carbon steel in water-saturated supercritical CO_2. Corrosion 71, 667–683. .

3Dugstad, A., Morland, B., Clausen, S., 2011. Corrosion of transport pipelines for CO_2 - Effect of water ingress. Energy Procedia 4, 3063–3070. .

4 Morland, B.H., Dugstad, A., Svenningsen, G., 2017. Corrosion of carbon steel in dense phase CO_2 with water above and below the solubility limit. Energy Procedia 114, 6752–6765.

5 Morland, B.H. Corrosion in CO_2 Transport Pipeline–The Effect Of Dissolved And Free Water In Dense Phase CO_2. Master thesis, University of Oslo, April 2015. .

6 Propp WA, Carleson TE, Wai CM, et al. Corrosion in supercritical fluids. Idaho Falls: Idaho National Engineering Laboratory; 1996.

Impurity O_2

- Oxygen will inevitably be encountered in the CO_2 stream in CCS systems that capture CO_2 from coal-fired plants, especially for the oxy-fuel capture technology.
- Dugstad et al.(1) and Choi et al. (2) preliminarily studied the effect of O_2 content on the corrosion rate of pipeline steel in supercritical CO_2. It was previously believed that the presence of O_2 generally increased the corrosion rate.
- However, the experimental results by Hua et al. (3)revealed that increasing the O_2 concentration from 0 to 1000 ppm caused a progressive decrease in the general corrosion rates of X65 and 5Cr steel in water-saturated supercritical CO_2 but tended to increase the extent of localised corrosion observed on both materials.
- Zeng et al. (4)concluded that the influence of oxygen on corrosion is related to the existence of water and the CO_2 stream pressure, and there is a threshold pressure (∼10 MPa) of a supercritical CO_2 stream containing water and oxygen, above which the corrosion rates of pipeline steels become noticeable.
- Ayello et al. (5) found that a small amount (100 ppm) of O_2 had essentially no impact on the corrosion rate of steel in supercritical CO_2.
- Xu et al. (6) found that high O_2 concentrations exerted no influence on uniform corrosion rates of X70 steel in supercritical CO_2 at a relative water content of 45%, enhanced the general corrosion at a relative water content of 50–60% and localised corrosion at a relative water content of 50–88%, but decreased the general corrosion at a relative water content of 75–100% and localised corrosion at a relative water content of 100%. They also found that the addition of O_2 decreased the tolerable water content of the transport system.

1 Dugstad A, Morland B, Clausen S. Corrosion of transport pipelines for CO_2-effect of water ingress. Energy Proc. 2011;4:3063– 3070.

2 Choi YS, Nesic S, Young D. Effect of impurities on the corrosion behavior of CO_2 transmission pipeline steel in supercritical CO_2- water environments. Environ Sci Technol. 2010;44(23):9233– 9238.

3 Hua Y, Barker R, Neville A. The effect of O_2 content on the corrosion behaviour of X65 and 5Cr in water-containing supercritical CO_2 environments. Appl Surf Sci. 2015;356:499–511.

4 Zeng Y, Pang X, Shi C, et al. Influence of impurities on corrosion performance of pipeline steels in supercritical carbon dioxide. CORROSION/2015, NACE International, Dallas, TX, USA, Paper No. 5755, 2015.

5 Ayello F, Evans K, Thodla R, et al. Effect of impurities on corrosion of steel in supercritical CO_2. CORROSION/2010, Houston, TX, USA, 2010, NACE International, Paper No. 10193.

6 Xu M, Zhang Q, Wang Z, et al. Effect of high-concentration O_2 on corrosion behavior of X70 steel in water-containing supercritical CO_2 with SO_2. Corrosion. 2017;73(3):290–302.

Impurity H_2

- Lead to pipe hydrogen embrittlement (1).
- Mikhailovski (2000) has developed a sensor technology, DH-1 hydrogen sensor for monitoring hydrogen embrittlement in carbon steel hydrocarbon conveying pipelines (2).

1. Irzhov, G. G., Golovanenko, S. A., and Sergeeva, T. K., 1982, Hydrogen embrittlement resistance of steels for main pipelines, Materials Science, 18: 266–270.
2. Mikhailovskii, Yu. N., Marshakov, A. I., Ignatenko, V. E., and Petrov, N. A., 2000, Estimation of the probability of hydrogen embrittlement of steel pipelines in the operation zones of cathodic stations, Protection of Metals, 36: 118–123.

Impurity CO

- For pre-combustion technology, CO will inevitably exist in the captured CO_2. The CO_2–CO–H_2O can lead to SCC problem with the partial pressure of CO_2 below 2.0MPa (1). Microscopic examination of the failures indicated fine trans-granular cracks initiated from the internal surface of the vessel containing the gas mixture. The investigations also showed that cracking initiated at sites subject to tensile stress typically generated from the high pressure of the contained gas.
- The current understanding for the occurrence of CO_2-CO-H_2O SCC is summarised: (2, 3)

✓ The presence of water is critical for the incidence of cracking.

✓ The presence of CO in CO_2-H_2O systems is critical for the occurrence of transgranular cracking in carbon steels.

✓ An increase of the CO activity in CO_2-H_2O systems increases the susceptibility to cracking the crack growth rate is greater, and the minimum initial stress to be applied for SCC occurrence is lower. At high CO activity, fine branched cracks are formed during crack propagation, whilst at low CO activities voids are created below the metal surface. It is possible to generate cracking under freely corroding conditions at high CO partial pressures.

✓ The additional presence of oxygen will increase the susceptibility to SCC in this system.

✓ Crack growth rates of 10^{-6} mm/s were reported.

✓ The mechanism of SCC for the CO_2-CO-H_2O system can be classed under the ‘strain-generated active path’ model. This is the result of the formation of a mono-molecular CO film on the surface of the carbon steel and its rupture under stress.

✓ Most of the experimental data are limited to low partial pressures of CO_2 (<20 bar (<2 MPa)).

1. Sandana D, Dale M, Charles EA, et al. Transport of gaseous and dense carbon dioxide in pipelines: is there an internal stress corrosion cracking risk? CORROSION/2013, Orlando, FL, USA, 2013, NACE International, Paper No. 2516.
2. Brown et al., “Electrochemical investigation of SCC of plain carbon steel in carbon dioxide-carbon monoxidewater system”, Corrosion-NACE, Vol. 5, pp 686-695, 1973
3. M. Kowaka et al., “SCC of mild and low steels in CO2-CO-H2O environments”,, Corrosion- NACE, Vol. 32, pp 395-401, October 1976

Impurity H_2S

- When H_2S exists in dense CO_2, it can dissolve in the water layers and promote corrosion by affecting both the anodic and cathodic processes. Aqueous H_2S is a mild acid that can partially dissociate in two steps (1):

$H_2S \rightarrow H^+ + HS^-$ and $HS^- \rightarrow H^+ + S^{2-}$

- H_2S can either enhance CO_2 corrosion by acting as a promoter of anodic dissolution through sulphide adsorption and lowering the pH or reduce CO_2 corrosion by forming a protective sulphide scale (2).

$Fe + H_2S(aq) \rightarrow FeS_{1-x} + xHS^- + (2 - x)H^+ + 2e^-$

- Usually, the H_2S-induced corrosion is always highly localised (pitting or mesa-type attack) (3, 4, 5).
- Choi et al.(6) showed that the addition of 200 ppm H_2S in the supercritical CO_2 phase dramatically increased the corrosion rate of all tested materials (carbon steel, 1Cr and 3Cr steels) in CO_2 with saturated water. However, lowering the water content to 100 ppm in supercritical and liquid CO_2 with 200 ppm H_2S reduced the corrosion rate to less than 0.01 mm/y.
- Small amount of H_2S was reported to change the absorbability of H_2O onto the steel surface (7), causing the adsorption of H_2O on the whole steel surface, thus accelerating the general and localised corrosion of carbon steel in the supercritical CO_2 phase.

1 Zheng Y, Brown B, Nešić S. Electrochemical study and modelling of H_2S corrosion of mild steel. Corrosion. 2014;70(4):351– 65.

2 Kermani MB, Morshed A. Carbon dioxide corrosion in oil and gas production – a compendium. Corrosion. 2003;59(8):659– 83.

3 Ning J, Zheng Y, Brown B, et al. A thermodynamic model for the prediction of mild steel corrosion products in an aqueous hydrogen sulfide environment. Corrosion. 2015;71(8):945–960.

4 Ning J, Zheng Y, Young D, et al. Thermodynamic study of hydrogen sulfide corrosion of mild steel. Corrosion. 2014;70(4):375– 389.

5 Pessu F, Barker R, Neville A. Early stages of pitting corrosion of UNS K03014 carbon steel in sour corrosion environments: the influence of CO_2, H_2S and temperature. CORROSION/2015, Dallas, TX, USA, 2015, NACE International.

6 Choi Y-S, Hassani S, Vu TN, et al. Effect of H_2S on the corrosion behavior of pipeline steels in supercritical and liquid CO_2 environments. CORROSION/2015, NACE International, Dallas, TX, USA, Paper No. 5927, 2015.

7 Wei L, Pang X, Gao K. Effect of small amount of H_2S on the corrosion behaviour of carbon steel in the dynamic supercritical CO_2 environments. Corros Sci. 2016;103:132–144.

Experiments have shown that O_2 and H_2S can react and form elemental sulphur and water (1). The reaction was kinetically slow, but in the presence of certain iron oxides the reactions went to almost full completion.

If the H_2S content is kept below a certain threshold that corresponds to the solubility of elemental sulphur (2), the risk of accumulation of solid elemental sulphur should be eliminated.

1. Dugstad, A., Halseid, M., Morland, B., 2014. Experimental techniques used for corrosion testing in dense phase CO_2 with flue gas impurities. In: Proceedings of CORROSION/ 2014, 2014/5/13/, NACE International. Houston, TX, p. 4383
2. Morland, B.H., Dugstad, A., Svenningsen, G., 2017. Corrosion of carbon steel in dense phase CO_2 with water above and below the solubility limit. Energy Procedia 114, 6752–6765.

Impurity SO_X

- SO_x stands for SO_2 and SO_3, and SO_2 can be oxidised to SO_3 by O_2. Dissolved SO_2 can ionise in two steps as follows
  (1): $H_2O + SO_2 \rightarrow H^+ + HSO_3^-$ and
  (2): $HSO_3^- \rightarrow H^+ + SO_3^{2-}$
- The general corrosion mechanism in dense CO_2 with SO_2 and H_2O has been reported by several authors (2 ,3, 4).
- When a relatively high concentration of SO_2 (for example, 2% mol) is present, the corrosion behaviour of steel in dense CO_2 is not dominated by CO_2 but by SO_2. Choi et al. (2) and Xiang et al. (5) found that when SO_2 was added to the supercritical CO_2 system, iron sulphite was the main corrosion product instead of $FeCO_3$.
- It was found that SO_2 concentration tends to lower the tolerable water content for avoiding pipeline corrosion in supercritical CO_2 transportation (6).

1. Jolly WL. Modern inorganic chemistry. New York (NY): McGraw-Hill, Inc; 1991.

2. Choi YS, Nesic S, Young D. Effect of impurities on the corrosion behavior of CO_2 transmission pipeline steel in supercritical CO_2- water environments. Environ Sci Technol. 2010;44(23):9233– 9238.

3. Hua Y, Barker R, Neville A. Effect of temperature on the critical water content for general and localised corrosion of X65 carbon steel in the transport of supercritical CO2. Int J Greenh Gas Con. 2014;31:48–60.

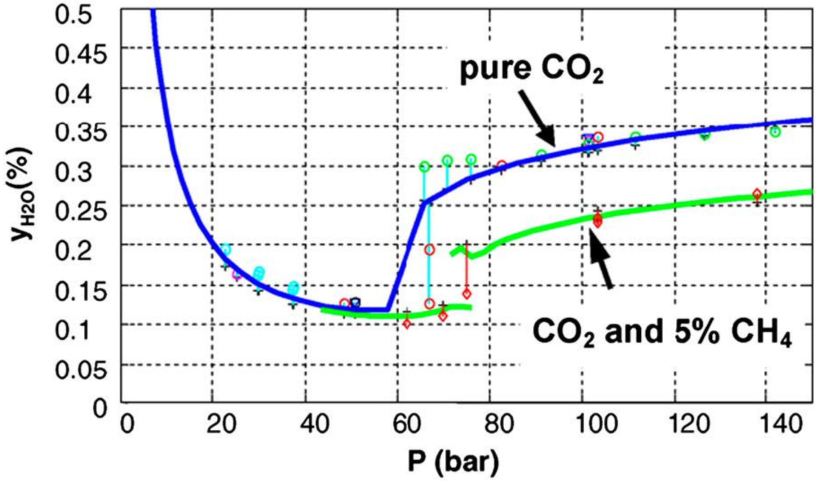
4. Xiang Y, Wang Z, Yang X, et al. The upper limit for moisture content in CO_2 pipeline transport. J Supercrit Fluids. 2012;67:14–21.

5. Y. Xiang, Z. Wang, C. Xu, C. Zhou, Z. Li, and W. Ni: 'Impact of SO_2 concentration on the corrosion rate of X70 steel and iron in water-saturated supercritical CO_2 mixed with SO_2', J Supercrit Fluids. 2011;58(2): 286–294.

6. Hua Y, Barker R, Neville A. The influence of SO_2 on the tolerable water content to avoid pipeline corrosion during the transportation of supercritical CO_2. Int J Greenh Gas Con. 2015;37:412–423.

Impurities affect the H_2O solubility

The impurity CH4 can lower the water solubility limit in dense CO2 (1). The modelling results showed below.
The lines are the calculated results obtained with the Soave–Redlich–Kwong equation of state with the Huron–Vidal mixing rule (SRK–HV) model, and the points are experimental data from Song and Kobayashi (2).



A similar effect in terms of lowering water solubility limit was found for N_2 by Foltran et al. (3).
Similar effect of HCl on the solubility of water in dense CO_2 was also found by Cole et al. (4).

1. Munkejord ST, Jakobsen JP, Austegard A, et al. Thermo- and fluid-dynamical modelling of two-phase multi-component carbon dioxide mixtures. Int J Greenh Gas Con. 2010;4(4):589–596.

2. Song KY, Kobayashi R. The water content of a CO_2-rich gas mixture containing 5.31 mol% methane along the three-phase and supercritical conditions. J Chem Eng Data. 1990;35(3):320–322.

3. Foltran S, Vosper ME, Suleiman NB, et al. Understanding the solubility of water in carbon capture and storage mixtures: an FTIR spectroscopic study of H2O+CO2+N2 ternary mixtures. Int J Greenh Gas Con. 2015;35:131–137.

4. Cole IS, Paterson DA, Corrigan P, et al. State of the aqueous phase in liquid and supercritical CO_2 as relevant to CCS pipelines. Int J Greenh Gas Con. 2012;7:82–88.

Impurity Sulphur

- Dugstad et al. (1) found that there was some elemental sulphur in the autoclave after the test for steel corrosion in supercritical CO_2 containing NO_2, SO_2, H_2O, H_2S, and O_2.
- Brown et al. (2) also suggested a similar reaction between H_2S and O_2 at very low H_2S and O_2 concentrations to produce sulphur.
- Fang et al. reported that sulphur in a CO_2 environment can lead to pitting corrosion (3), which indicates that sulphur initiated pitting may also occur in a supercritical CO_2 environment.
- Elemental sulphur can react with H_2O to produce H_2S and sulphuric acid (4): $8S + 8H_2O \rightarrow 6H_2S + 2H_2SO_4$
- Dugstad et al. (1) also discussed the interaction between NO_2 and SO_2 can generate HNO_3 that can increase corrosion rate.

1. Dugstad A, Halseid M, Morland B. Experimental techniques used for corrosion testing in dense phase CO_2 with flue gas impurities. CORROSION/2014, San Antonio, TX, USA. Paper No. 4383, 2014.

2. Brown J, Graver B, Gulbrandsen E, et al. Update of DNV recommended practice RP-J202 with focus on CO_2 corrosion with impurities. Energy Proc. 2014;63:2432–2441.

3. Fang H, Young D, Nešić S. Elemental sulfur corrosion of mild steel at high concentrations of sodium chloride. CORROSION/ 2009, Atlanta, GA, USA, Paper No. 2592, 2009, NACE International.

4. Boden PJ, Maldonado-Zagal SB. Hydrolysis of elemental sulfur in water and its effects on the corrosion of mild steel. Br Corros J. 1982;17:116–120.

Impurity Mercury

- Mercury (Hg) gas can exist in the CO_2 stream as atomic or oxidised, Hg^0, Hg^{++}.[1]
- CO_2 corrosion activity will not be influenced by both elemental and ionic Hg.[2]
- Effect of mercury on CO_2 and H_2S corrosion[2]
  The ionic Hg reduce the H_2S formed protective sulphide scale significantly and leading to higher corrosion rate on pipeline. The reason is ionic Hg may react with sulphide to form HgS which might have interfered the formation of passive layer on the metal resulted to high corrosion rate.
- The main finding is that Hg^0 reacts readily with NO_2 formed from NO oxidation at high pressure. This reaction was shown to be kinetically limited and occurred without the presence of water (either water vapour or liquid water). [2]

1. Terry W., Rohan S., Tim T., Dunyu L., Gas quality impacts, assessment and control in oxy-fuel technology for CCS Final report, Chemical Engineering, the University of Newcastle, NSW, Australia, Nobember 2013.

2. Rohana J., Azmi M. N., Amir S. M. S., Ahmad M. A. R., Noor L. R., Noraina S. M. A., Suhor M. F., Ahmad Z. A., Hasan H. M., The effect of mercury to carbon steel in CO2, and H2S environment, Offshore Technology Conference Asia, OTC- 30258-MS, 27 October 2020.

Impurity organic amines

- Since most of the CO_2 is captured by organic amines, it is possible that organic amines will be present in the CO_2 stream.
- The results of Thodla et al. (1) indicated that the presence of monoethanolamine (MEA) decreased the corrosion rate, while Collier et al. (2) found that the presence of diethanolamine (DEA) increased the corrosion rate. MEA might serve as an inhibitor, adsorbing on the steel surface (3), while DEA might provide cathodic depolarising agents.

1. Thodla R, Francois A, Sridhar N. Materials performance in supercritical CO_2 environments. CORROSION/2009, Atlanta, GA, 03/22/2009, 2009, NACE International.

2. Collier J, Shi C, Papavinasam S, et al. Effect of impurities on the corrosion performance of steels in supercritical carbon dioxide: optimization of experimental procedure. CORROSION/2013, NACE International, Orlando, FL, USA, 2013.

3. Xiang Y, Yan M, Choi Y-S, et al. Time-dependent electrochemical behaviour of carbon steel in MEA-based CO_2 capture process. Int J Greenh Gas Con. 2014;30:125–132.

Impurities synergistic effect: NO_2 + SO_2

- NO_2 and SO_2 were reported to have a synergistic effect that can intensify atmospheric corrosion.(1)

The effect of NO_2 is indirect given that nitrogen compounds have not been detected among the corrosion products and its influence is related with the increase in the rate of SO2 oxidation to sulphate (2). The global process of sulfur dioxide oxidation to sulfate and the catalytic action of nitrogen dioxide would correspond to the following general reactions:

$SO_2 + H_2O = SO_3^{2-} + 2H^+$

$SO_3^{2-} + NO_2 = SO_4^{2-} + NO$

$NO + \frac{1}{2} O_2 = NO_2$

$SO_2 + \frac{1}{2} O_2 + H_2O = SO_4^{2-} + 2H^+$

where nitrogen dioxide would act as an oxygen carrying agent. The greater oxygen availability would produce an increase in the sulfur dioxide and sulfite oxidation (3).

1. Corvo F, Reyes J, Pérez T, et al. Role of NOx in materials corrosion and degradation. Rev Cenic Ciencias Químicas.2010;41:1–10.
2. J.G. Castaño, D. de la Fuente, M. Morcillo, A laboratory study of the effect of NO2 on the atmospheric corrosion of zinc, Atmospheric Environment 41, 8681– 8696, 2007.
3. G. Castaño, C. Arroyave, M. Morcillo, Characterization of atmospheric corrosion products of zinc exposed to SO2 and NO2 using XPS and GIXD, J Mater Sci. 42, 9654–9662, 2007.

Impurities synergistic effect: O_2 +H_2S+SO_2

Recently, Sun et al. (1) found that the synergistic effect of O_2, H_2S, and SO_2 impurities on the corrosion behaviour of X65 steel in water-saturated supercritical CO_2 systems was remarkable.

The corrosion scales consisted of FeOOH, $FeSO_3 \cdot 2H_2O$, $FeSO_4 \cdot 4H_2O$, FeS, $FeCO_3$, and S , which implied a complex corrosion mechanism. The weak protective ability of the product scale might be one of the reasons for the synergistic increase in the effect of impurities on the corrosion rates.

1. Sun C, Sun J, Wang Y, et al. Synergistic effect of O2, H2S and SO2 impurities on the corrosion behavior of X65 steel in water-saturated supercritical CO2 system. Corros Sci. 2016;107:193–203.

Impurities synergistic effect: SO_2+O_2+H_2O and HIC

- For the case with SO_2, O_2, and H_2O impurities can produce sulphuric acid and iron oxyhydroxide. This reaction will lead to fast metal loss. (1)
- To date, there is no open published model that can predict the synergistic reactions are thermodynamically and kinetically possible and favourable under supercritical CO_2 test conditions . (2)
- The hydrogen-induced cracking (HIC) have to be considered when an aqueous phase and impurities such as H_2S and NO_x exist. (3)

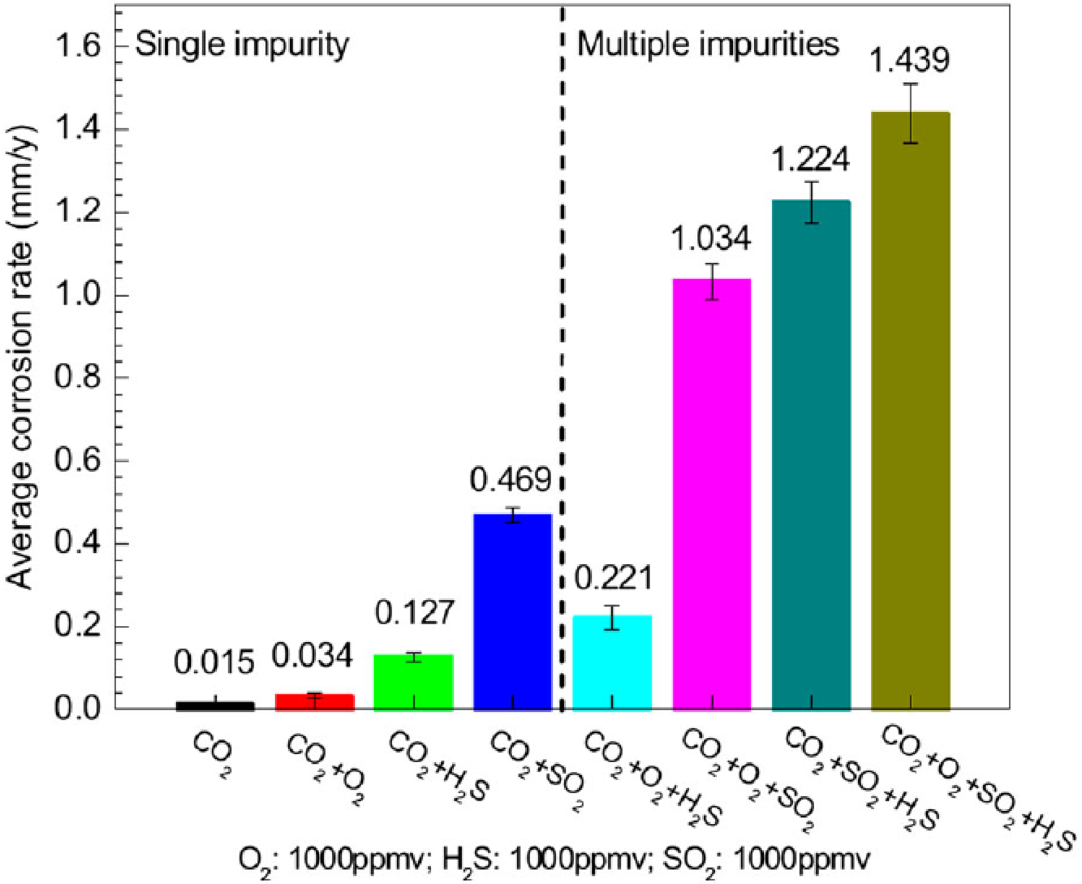
1. Allam IM, Arlow JS, Saricimen H. Initial stages of atmospheric corrosion of steel in the Arabian Gulf. Corros Sci. 1991;32

2. Dugstad A, Halseid M, Morland B. Testing of CO2 specifications with respect to corrosion and bulk phase reactions. Energy Proc. 2014;63:2547–2556.

3. Y. Xiang, M. Xu, Y.-S. Choi, “State-of-the-Art Overview of Pipeline Steel Corrosion in Impure Dense CO2 for CCS Transportation: Mechanisms and Models,” Corros. Eng. Sci. Techn. 52, 7 (2017): pp. 485-509.

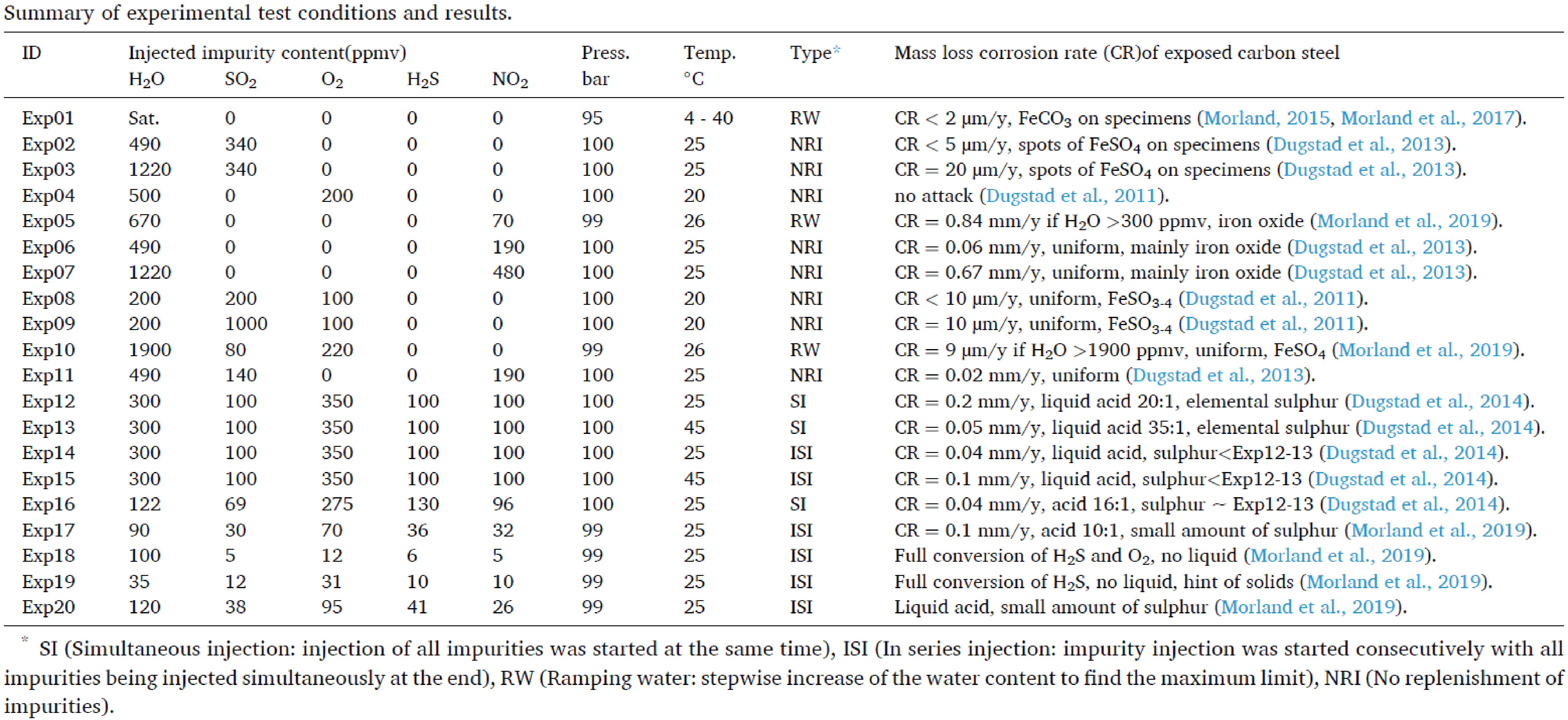
Synergistic effects summary charts

Sun summarised synergistic effects (1)



1. Sun C, Sun J, Wang Y, et al. Synergistic effect of O2, H2S and SO2 impurities on the corrosion behavior of X65 steel in water-saturated supercritical CO2 system. Corros Sci. 2016;107:193–203.

Summary of impurities combinations test (1)



Summary of experimental test conditions and results.

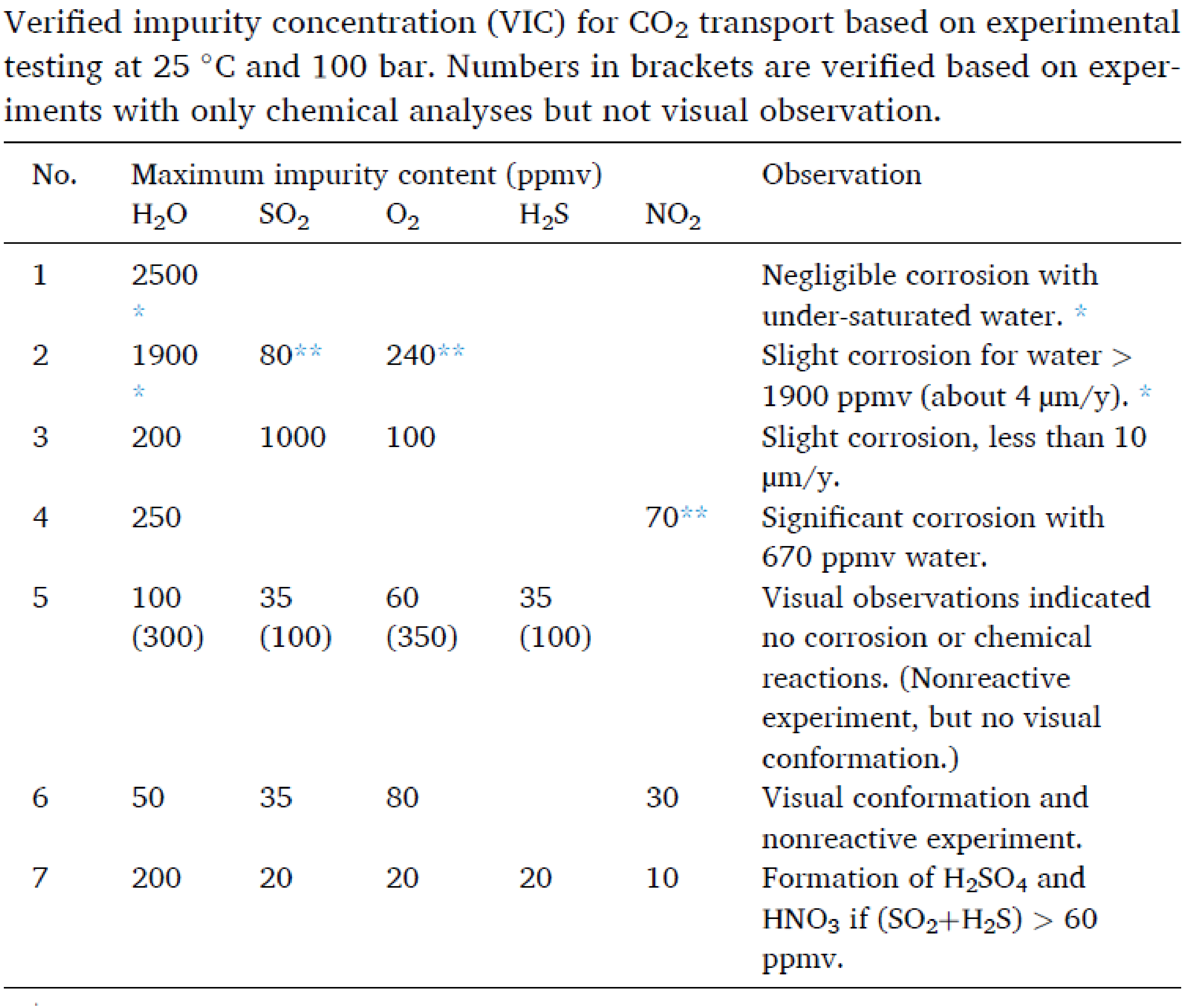
ID	Injected impurity content(ppmv)					Press.	Temp.	Type*	Mass loss corrosion rate (CR)of exposed carbon steel
	H_2O	SO_2	O_2	H_2S	NO_2	bar	°C		
Exp01	Sat.	0	0	0	0	95	4 - 40	RW	CR < 2 μm/y, $FeCO_3$ on specimens (Morland, 2015, Morland et al., 2017).
Exp02	490	340	0	0	0	100	25	NRI	CR < 5 μm/y, spots of $FeSO_4$ on specimens (Dugstad et al., 2013).
Exp03	1220	340	0	0	0	100	25	NRI	CR = 20 μm/y, spots of $FeSO_4$ on specimens (Dugstad et al., 2013).
Exp04	500	0	200	0	0	100	20	NRI	no attack (Dugstad et al., 2011).
Exp05	670	0	0	0	70	99	26	RW	CR = 0.84 mm/y if H_2O >300 ppmv, iron oxide (Morland et al., 2019).
Exp06	490	0	0	0	190	100	25	NRI	CR = 0.06 mm/y, uniform, mainly iron oxide (Dugstad et al., 2013).
Exp07	1220	0	0	0	480	100	25	NRI	CR = 0.67 mm/y, uniform, mainly iron oxide (Dugstad et al., 2013).
Exp08	200	200	100	0	0	100	20	NRI	CR < 10 μm/y, uniform, $FeSO_{3\text{-}4}$ (Dugstad et al., 2011).
Exp09	200	1000	100	0	0	100	20	NRI	CR = 10 μm/y, uniform, $FeSO_{3\text{-}4}$ (Dugstad et al., 2011).
Exp10	1900	80	220	0	0	99	26	RW	CR = 9 μm/y if H_2O >1900 ppmv, uniform, $FeSO_4$ (Morland et al., 2019).
Exp11	490	140	0	0	190	100	25	NRI	CR = 0.02 mm/y, uniform (Dugstad et al., 2013).
Exp12	300	100	350	100	100	100	25	SI	CR = 0.2 mm/y, liquid acid 20:1, elemental sulphur (Dugstad et al., 2014).
Exp13	300	100	350	100	100	100	45	SI	CR = 0.05 mm/y, liquid acid 35:1, elemental sulphur (Dugstad et al., 2014).
Exp14	300	100	350	100	100	100	25	ISI	CR = 0.04 mm/y, liquid acid, sulphur<Exp12-13 (Dugstad et al., 2014).
Exp15	300	100	350	100	100	100	45	ISI	CR = 0.1 mm/y, liquid acid, sulphur<Exp12-13 (Dugstad et al., 2014).
Exp16	122	69	275	130	96	100	25	SI	CR = 0.04 mm/y, acid 16:1, sulphur ~ Exp12-13 (Dugstad et al., 2014).
Exp17	90	30	70	36	32	99	25	ISI	CR = 0.1 mm/y, acid 10:1, small amount of sulphur (Morland et al., 2019).
Exp18	100	5	12	6	5	99	25	ISI	Full conversion of H_2S and O_2, no liquid (Morland et al., 2019).
Exp19	35	12	31	10	10	99	25	ISI	Full conversion of H_2S, no liquid, hint of solids (Morland et al., 2019).
Exp20	120	38	95	41	26	99	25	ISI	Liquid acid, small amount of sulphur (Morland et al., 2019).

* SI (Simultaneous injection: injection of all impurities was started at the same time), ISI (In series injection: impurity injection was started consecutively with all impurities being injected simultaneously at the end), RW (Ramping water: stepwise increase of the water content to find the maximum limit), NRI (No replenishment of impurities).

Corrosion rates are also expected to vary around the pipeline circumference, particularly if strong acids are present.

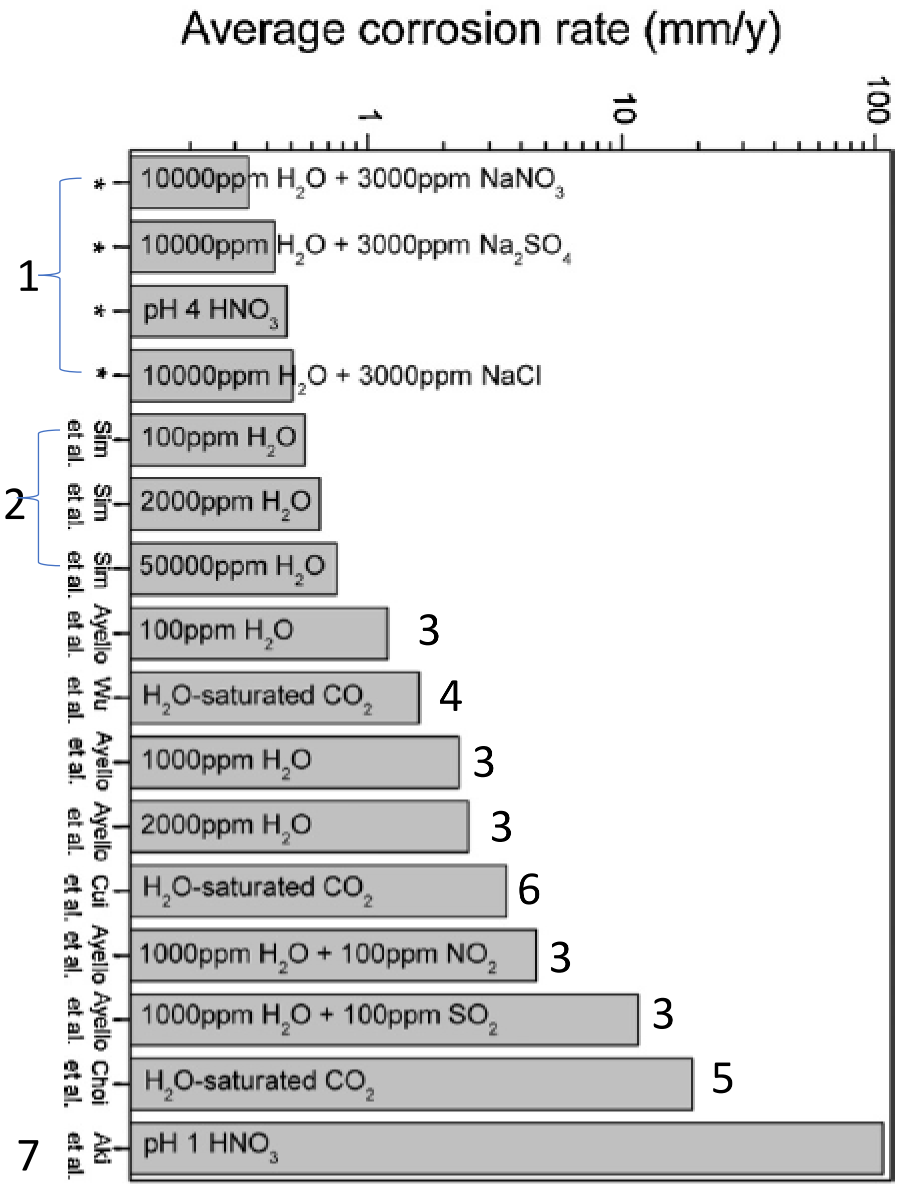
1. Bjorn H. M., Arne D., Gaute S., Experimental based CO_2 transport specification ensuring material integrity, Institute for Energy Technology, P.O. Box 40, Kjeller NO-2027, Norway, International Journal of Greenhouse Gas Control, 119 (2022) 103697.

Not lead to corrosion impurities combinations



Verified impurity concentration (VIC) for CO_2 transport based on experimental testing at 25 °C and 100 bar. Numbers in brackets are verified based on experiments with only chemical analyses but not visual observation.

No.	Maximum impurity content (ppmv)					Observation
	H_2O	SO_2	O_2	H_2S	NO_2	
1	2500 *					Negligible corrosion with under-saturated water. *
2	1900 *	80**	240**			Slight corrosion for water > 1900 ppmv (about 4 μm/y). *
3	200	1000	100			Slight corrosion, less than 10 μm/y.
4	250				70**	Significant corrosion with 670 ppmv water.
5	100 (300)	35 (100)	60 (350)	35 (100)		Visual observations indicated no corrosion or chemical reactions. (Nonreactive experiment, but no visual conformation.)
6	50	35	80		30	Visual conformation and nonreactive experiment.
7	200	20	20	20	10	Formation of H_2SO_4 and HNO_3 if $(SO_2+H_2S) > 60$ ppmv.



Overall comparison of corrosion rates from tests in supercritical CO_2 and tests conducted in other studies (1)

1 Sim S., Cole I.S., Bocher F., Corrigan P., Gamage R.P., Ukwattage N., Birbilis N., Investigating the effect of salt and acid impurities in supercritical CO_2 as relevant to the corrosion of carbon capture and storage pipelines, International Journal of Green House Gas Control, 17 (2013) 534-541.

2. Sim, S., Bocher, F., Cole, I.S., Birbilis, N., 2013. Investigating the effect of water content in supercritical CO2 as relevant to the corrosion of carbon capture and storage pipelines. Corrosion (submitted for publication).

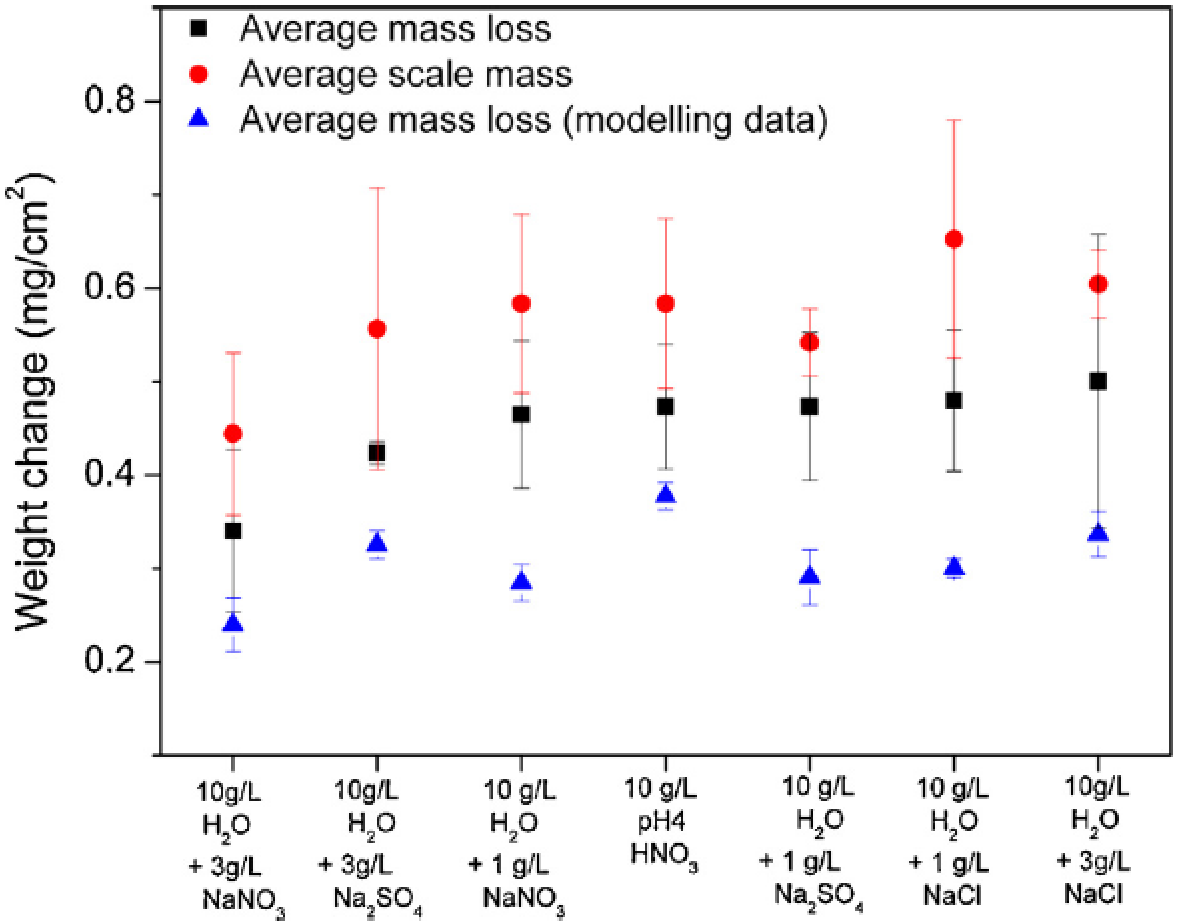
3. Ayello, F., Sridhar, N., Evans, K., Thodla, R., 2010b. Effect of liquid impurities on corrosion of carbon steel in supercritical CO2. In: Proceedings of the 8th International Pipeline Conference, Calgary, Canada.

4. Wu, S.L., Cui, Z.D., Zhao, G.X., Yan, M.L., Zhu, S.L., Yang, X.J., 2004. EIS study of the surface film on the surface of carbon steel from supercritical carbon dioxide corrosion. Applied Surface Science 228, 17–25.

5. Choi, Y.-S., Neˇsi ´ c, S., 2011. Determining the corrosive potential of CO2 transport pipeline in high pCO2–water environments. International Journal of Greenhouse Gas Control 5, 788–797.

6. Cui, Z.D., Wu, S.L., Zhu, S.L., Yang, X.J., 2006. Study on corrosion properties of pipelines in simulated produced water saturated with supercritical CO2. Applied Surface Science 252, 2368–2374.

7 Ruhl, A.S., Kranzmann, A., 2012. Corrosion in supercritical CO2 by diffusion of flue gas acids and water. Journal of Supercritical Fluids 68, 81–86.



Average scale mass and mass loss of steel samples exposed to supercritical CO2 in a variety of salt and acid solutions for a period of 7 days. The scale mass is a weight gain, which is then removed via the cleaning procedure according to NACE standard RP0775-2005. The mass loss is the actual mass lost after cleaning of products, and determined from final specimen weight and after exposure and cleaning compared to the mass of the specimen prior to exposure. The diamonds represent results derived from a neural network model (1) developed from testing in aqueous conditions.

- The corrosion product of each solution tested is different; hence not all scales produced had an impact on mass loss. NaCl crystals deposited on the steel sample surface aided in retarding mass loss, where a decrease in scale mass from 1 to 3 g/L NaCl saw an increase in average mass loss.
- Pitting corrosion analysis using the optical profilometer shows that the lowest pit depth rate was recorded by the 1 g/L NaCl solution, with an average of 0.12 mm/year. The highest pit depth rate recorded was from exposure to pH 4 HNO3, with a maximum rate exceeding 3 mm/year. Corrosion mechanism (uniform or localised) differs for each test solution exposed to a supercritical CO2 environment.

1. Sim, S., Cavanaugh, M.K., Corrigan, P., Cole, I.S., Birbilis, N., 2012a. Aqueous corrosion testing and neural network modelling to simulate corrosion of supercritical CO2 pipelines in the CCS cycle. Corrosion 69.5, 477–486.

Pressure

- Choi and Nesic (1) preliminarily studied the effect of total pressure on the corrosion rate of X65 steel in a high pressure CO_2 environment with saturated water, and the experimental results revealed that the corrosion rate increased when the total pressure increased from 6.0 to 8.0 MPa, with the CO_2 phase changing from gas to a supercritical state. Moreover, the increase in O_2 partial pressure can also generally increase the corrosion rate in a supercritical CO_2 system; however, the corrosion rate reaches a maximum value at 3.3 bar O_2 (2).
- Meanwhile, increasing the partial pressure of SO_2, which means increasing the SO_2 concentration, can also dramatically increase the corrosion rate of X70 steel and iron in a supercritical CO_2 system (3).
- Xu et al. [113] showed that the corrosion rates of pipeline steels at 8 MPa are higher than at 10 MPa when the water concentration is below 3000 ppmv, while the situation is the opposite when the water content was 3000 ppmv. They also found that the pitting rates were high, especially for the cases with 3000 ppmv water concentration.

1. Choi Y-S, Nesic S. Determining the corrosive potential of CO2 transport pipeline in high pCO2-water environments. Int J Greenh Gas Con. 2011;5(4):788–797.

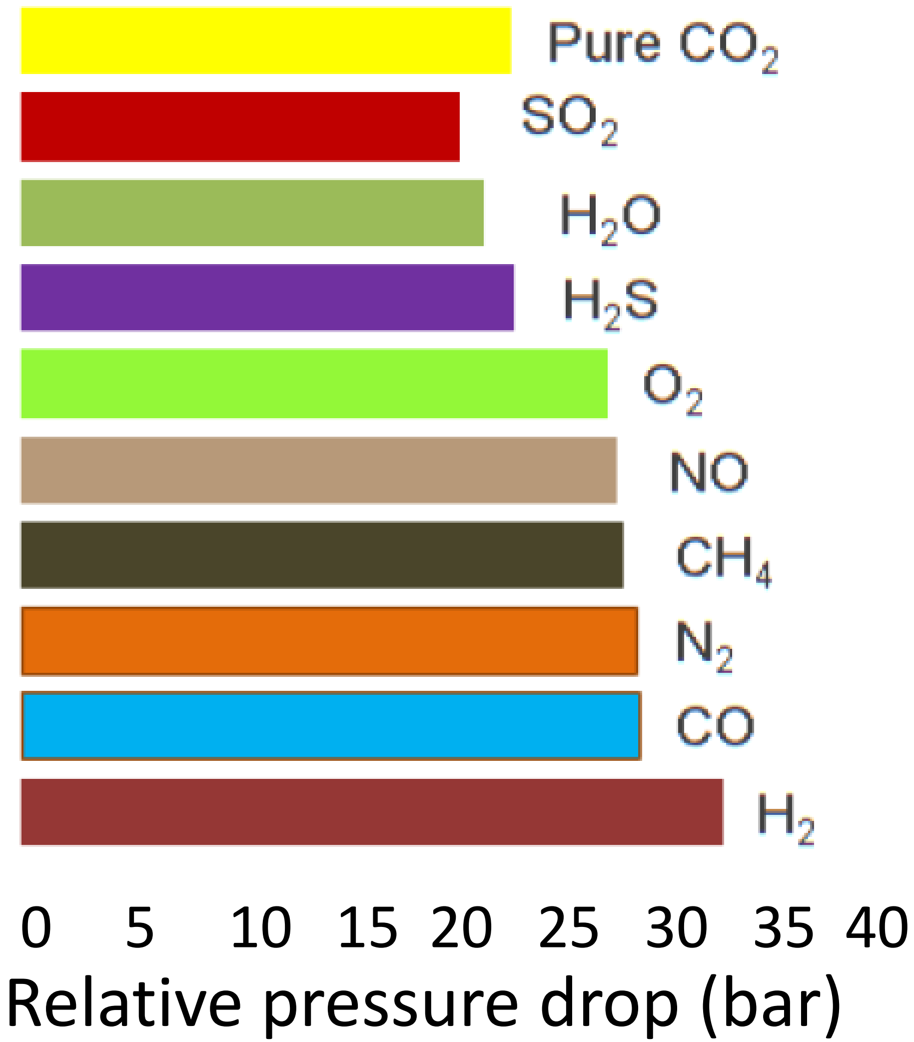
2. Choi YS, Nesic S, Young D. Effect of impurities on the corrosion behavior of CO2 transmission pipeline steel in supercritical CO2- water environments. Environ Sci Technol. 2010;44(23):9233–9238.

3. Y. Xiang, Z. Wang, C. Xu, C. Zhou, Z. Li, and W. Ni: ‘Impact of SO2 concentration on the corrosion rate of X70 steel and iron in water-saturated supercritical CO2 mixed with SO2’, J Supercrit Fluids. 2011;58(2): 286–294.

4. Xu M, Li W, Zhou Y, et al. Effect of pressure on corrosion behaviour of X60, X65, X70, and X80 carbon steels in water-unsaturated supercritical CO2 environments. Int J Greenh Gas Con. 2016;51:357–368.

Pressure drop with 10% single impurity in CO_2 fluid (1)

Test in a 70km, 457.2 mm diameter pipeline with flow rate of 100kg/s and input pressure of 150 bar



1. Suoton P. P, Nejat R., Iqbal M.M., Effects of impurities on CO_2 pipelines performance, Vol. 57 2017, Chemical Engineering Transactions.

Temperature

- The temperature in a dense CO_2 transportation system can vary from −56.7 to above 31°C, with the CO_2 phase changing from liquid to supercritical based on CO2phase diagram(1).
- Temperature directly influences the corrosion reaction rate by affecting exchange current density, chemical reaction equilibrium constants, chemical reaction rate constants, fluid viscosity, and fluid density. It can also affect morphology and properties of product layers and the component diffusion coefficients.
- The corrosion rates of X70 steel in supercritical CO_2 mixtures first increased with temperature, reaching a peak value near 75°C, and then decreased (2). Those findings have similar trend of temperature on the corrosion rate of pipeline steel in a low partial pressure CO_2 environment (3).
- Meanwhile, Hua et al. (4) revealed that the corrosion rate of X65 steel increased as the temperature decreased from 50 to 35°C when the water content was lower than 1600 ppm (mol).
- Moreover, temperature can affect the morphology and properties of product layers and the component diffusion coefficients, thus indirectly influencing the corrosion behaviours.
- Under supercritical CO_2 conditions, the porosity test results of the product scales indicated that the loose product layer with poor protectiveness was related to low temperature, while a more compact product layer with better protectiveness was related to high temperature (5).

1. Y. Xiang, M. Xu, Y.-S. Choi, “State-of-the-Art Overview of Pipeline Steel Corrosion in Impure Dense CO2 for CCS Transportation: Mechanisms and Models,” Corros. Eng. Sci. Techn. 52, 7 (2017): pp. 485-509.

2. Xiang Y, Wang Z, Li Z, et al. Effect of temperature on the corrosion behavior of X70 steel in high pressure CO2/SO2/O2/ H2O environments. Corros Eng Sci Technol. 2013;48(2):121– 129.

3. Ikeda A, Ueda M, Mukai S, et al. CO2 behavior of carbon and Cr steels. In: Hausler RH, editor. Advances in CO2 corrosion. Houston (TX): NACE; 1984. p. 39.

4. Hua Y, Barker R, Neville A. Effect of temperature on the critical water content for general and localised corrosion of X65 carbon steel in the transport of supercritical CO2. Int J Greenh Gas Con. 2014;31:48–60.

5. Xiang Y, Wang Z, Li Z, et al. Effect of temperature on the corrosion behaviour of X70 steel in high pressure CO2/SO2/O2/ H2O environments. Corros Eng Sci Technol. 2013;48(2):121– 129.

Flow rate

- CO_2 corrosion studies for low partial pressure conditions have shown that the increase in flow velocity would usually increase the corrosion rate (1). However, after the formation of the corrosion product layers, the impact of flow velocity on the corrosion rate was found to be weakened (2).
- Flow-induced localised corrosion and erosion problems in the presence of particulates may also occur in dense CO_2 environments.
- The work by Dugstad et al. (3) revealed that in supercritical CO_2 at 50°C, the corrosion rate of X65 steel at a flow velocity of 3 m/s condition was approximately 10 times the value with no flow. The similar effect of the flow on the corrosion rate was also found in liquid $CO_{2.}$
- In contrast, the work by Farelas et al. (4) revealed that a 1000 r/min rotating speed in the autoclave can depress the corrosion rate of X65 in the supercritical CO_2 system distinctly. Hua et al. (5) stated that the flow can reduce the amount of water condensing onto the sample surface, thereby depressing the corrosion.
- Meanwhile, only a few of the existing supercritical CO_2 corrosion tests were completed in the flow loop (6, 7), and the test results in the flow loop were believed to show better reliability than the test results obtained in the sealed autoclaves. There is no doubt that more studies under different flow conditions in the flow loop are needed, especially for multiphase flow conditions in the CO_2 pipeline with different flow regimes, which may represent a gas–liquid flow in the worst-case scenario.

1. Chen C. Research on electrochemical behavior and corrosion scale characteristics of CO2 corrosion for tubing and casing steel [PhD thesis]. Xi'an: Northwestern Polytechnical University; 2002.

2. Eriksrud E, Sontvedt T. Effect of flow on CO2 corrosion rates in real and synthetic formation waters. In: Hausler RH, editor. Advances in CO2 corrosion. Houston (TX): NACE; 1984. p. 20.

3. Dugstad A, Morland B, Clausen S. Corrosion of transport pipelines for CO2-effect of water ingress. Energy Proc. 2011;4:3063– 3070.

4. Farelas F, Choi YS, Nesic S. Effects of CO2 phase change, SO2 content and flow on the corrosion of CO2 transmission pipeline steel. CORROSION/2012, Salt Lake City, UT, USA, 2012, NACE International, Paper No. C2012-0001322.

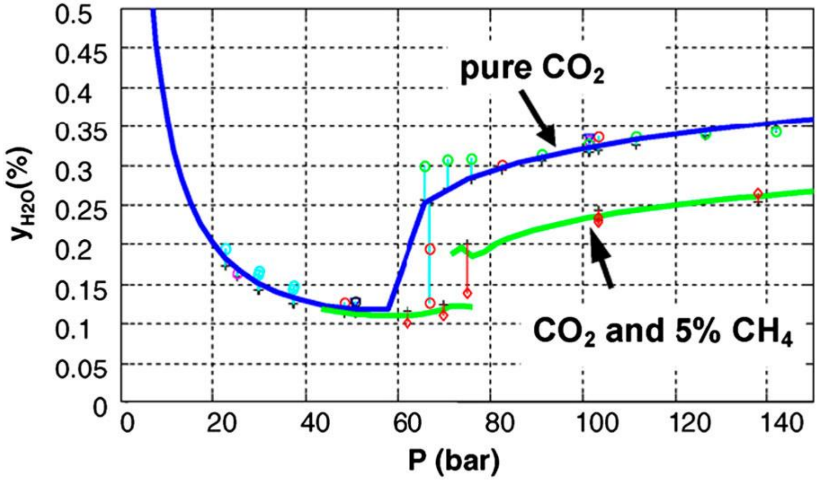
5. Hua Y, Barker R, Neville A. Understanding the influence of SO2 and O2 on the corrosion of carbon steel in water-saturated supercritical CO2. Corrosion. 2015;71(5):667–683.

6. Yevtushenko O, Bäßler R. Water impact on corrosion resistance of pipeline steels in circulating supercritical CO2 with SO2- and NO2- impurities. CORROSION/2014, NACE International, San Antonio, TX, USA, Paper No. 3838, 2014.

7. Yevtushenko O, Bäßler R, Carrillo-Salgado I. Corrosion stability of piping steels in a circulating supercritical impure CO2 environment. CORROSION/2013, Orlando, FL, USA, 2013, NACE International, Paper No. 2372.

Impurities affect the H_2O solubility

The impurity CH_4 can lower the water solubility limit in dense CO_2 (1). The modelling results showed below.
The lines are the calculated results obtained with the Soave–Redlich–Kwong equation of state with the Huron–Vidal mixing rule (SRK–HV) model, and the points are experimental data from Song and Kobayashi (2).



A similar effect in terms of lowering water solubility limit was found for N_2 by Foltran et al. (3). Similar effect of HCl on the solubility of water in dense CO_2 was also found by Cole et al. [78].

1. Munkejord ST, Jakobsen JP, Austegard A, et al. Thermo- and fluid-dynamical modelling of two-phase multi-component carbon dioxide mixtures. Int J Greenh Gas Con. 2010;4(4):589–596.

2. Song KY, Kobayashi R. The water content of a CO2-rich gas mixture containing 5.31 mol% methane along the three-phase and supercritical conditions. J Chem Eng Data. 1990;35(3):320–322.

3. Foltran S, Vosper ME, Suleiman NB, et al. Understanding the solubility of water in carbon capture and storage mixtures: an FTIR spectroscopic study of H2O+CO2+N2 ternary mixtures. Int J Greenh Gas Con. 2015;35:131–137.

4. Cole IS, Paterson DA, Corrigan P, et al. State of the aqueous phase in liquid and supercritical CO2 as relevant to CCS pipelines. Int J Greenh Gas Con. 2012;7:82–88.

Impurity C_4, N_2, O_2

- Increase bulk density or viscosity require higher compressor power capacity of the pipeline in transporting CO_2. (1)

1. Heggum, G., 2005, CO2 conditioning and transportation. D.C. Thomas and S.M. Benson. Carbon Dioxide Capture for Storage in Deep Geologic Formations: Elsevier.

Localised corrosion

- Localised corrosion problem can occur in dense CO_2 corrosion, even without acidic gas impurities and with high enough water content (1).
- Most of the literature reports the localised corrosion issue only note the pitting occurred without determine the penetration rates (2).
- Localised corrosion also has a great impact on determining the upper limit of water content to avoid corrosion. Hua et al. (1) noted that the critical water content required to minimise the significant localised attack was substantially lower than the value required to prevent general corrosion When other impurities exist, such as NO_x, HCl, and H_2S, this estimated tolerable water content needs to be re-evaluated
- Barker et al. (3) discussed a series of fundamental questions relating to the localised corrosion of steel in dense CO_2. They suggested the investigation of the initiation, propagation, and stability of pits in a dense CO_2 environment to verify whether they would be the real threat to long-term operation in the field. Currently, there is no literature identifying whether the pits are stable and continue to propagate, and the propagation kinetics also needs further investigation.
- The localised penetration rates under the corrosion product were much higher than the general corrosion rates. It is essential to investigate the evolution rules of the corrosion products on the sample surface and their relation to the initiation and propagation of pits in dense CO_2 environments (2).

1. Hua Y, Barker R, Neville A. The influence of SO_2 on the tolerable water content to avoid pipeline corrosion during the transportation of supercritical CO_2. Int J Greenh Gas Con. 2015;37:412–423.

2. Y. Xiang, M. Xu, Y.-S. Choi, “State-of-the-Art Overview of Pipeline Steel Corrosion in Impure Dense CO_2 for CCS Transportation: Mechanisms and Models,” Corros. Eng. Sci. Techn. 52, 7 (2017): pp. 485-509.

3. Barker R, Hua Y, Neville A. Internal corrosion of carbon steel pipelines for dense-phase CO_2 transport in carbon capture and storage (CCS) – a review. Int Mater Rev. 2016: 1–31.

Steel chemistry

- Russick et al. [1] showed that carbon steel suffered corrosion problems in water-saturated supercritical CO_2, while 316 SS and 304L SS are corrosion resistant in the same environment
- Hua et al. [2] found that when O_2 is present in water-saturated supercritical CO_2, 5Cr offers more resistance to pitting corrosion than X65 steel
- They also found that with a concentration of O_2 above 500 ppm, the general corrosion rate of 5Cr steel was less than 0.04 mm/y, half the value measured for X65 steel [2]
- However, the experimental results by Choi et al. [3] showed that the corrosion rates of X65 steel and 13Cr steel showed no outstanding differences in water-saturated supercritical CO_2 with SO_2 and O_2 impurities, revealing that 13Cr steel does not show higher corrosion resistance in the water saturated dense CO_2 environment with SO_2 and O
- Yevtushenko and Bäßler [4] also found that X20Cr13 steel showed severe pitting problems in supercritical CO_2 with H_2O, SO_2 NO, CO, and O_2 impurities
- It was indicated that the ions generated from the pipeline steel alloy elements, such as Mn^{2+}, would be a catalyst to accelerate the oxidation reaction of SO_2^{3-} to SO_2^{4-} . The differences between the physical properties of the $FeSO_3$ hydrate and the $FeSO_4$ hydrate products, such as the different solubility in water, may indirectly affect the corrosion process
- Dugstad et al. [5] even found that high concentrations (>1000 mg L^{-1}) of Ni, Mo, and Cr were dissolved in the greenish liquid after corrosion testing, which indicated that the Hastelloy C autoclave was attacked in liquid CO_2 with H_2O, SO_2, NO_2, H_2S, and O_2 impurities

1. Russick EM, Poulter GA, Adkins CLJ, et al. Corrosive effects of supercritical carbon dioxide and cosolvents on metals. J Supercrit Fluids. 1996;9(1):43–50.
2. Hua Y, Barker R, Neville A. The effect of O_2 content on the corrosion behaviour of X65 and 5Cr in water-containing supercritical CO_2 environments. Appl Surf Sci. 2015;356:499–511.
3. Choi YS, Nesic S, Young D. Effect of impurities on the corrosion behavior of CO_2 transmission pipeline steel in supercritical CO_2- water environments. Environ Sci Technol. 2010;44(23):9233– 9238.
4. Yevtushenko O, Bäßler R. Water impact on corrosion resistance of pipeline steels in circulating supercritical CO_2 with SO^{2-} and NO^{2-} impurities. CORROSION/2014, NACE International, San Antonio, TX, USA, Paper No. 3838, 2014.
5. Dugstad A, Halseid M, Morland B. Testing of CO_2 specifications with respect to corrosion and bulk phase reactions. Energy Proc. 2014;63:2547–2556.

Mechanism difference for different CO_2 phase conditions

- The corrosion mechanism differences between low partial pressure and supercritical condition (aqueous phase) have been studied by Zhang et al. (1). They found that under both low CO_2 partial pressure and supercritical CO_2 condition, the corrosion behaviours of X65 steel, including characteristics of CO_2 corrosion product scale and the variation rule of corrosion rate with temperature, were similar. They concluded that the change in CO_2 partial pressure does not change the corrosion mechanism. They also explained that the corrosion rate was enhanced under supercritical CO_2 condition due to the higher carbonic acid concentration. Zhang et al. (2) stated that there was no essential difference in the electrochemical corrosion mechanism under supercritical CO_2 and non-supercritical CO_2 environments for the N80 steel in the aqueous phase.
- While, Xiang (3) stats that the corrosion mechanism will be totally different with CO_2 phase change. Corrosion in CO_2 environments can be divided into six circumstances: corrosion in aqueous phase with low CO_2 partial pressure (gas CO_2), wet gas phase with low CO_2 partial pressure (gas CO_2), aqueous phase with high CO_2 partial pressure (liquid CO_2), liquid CO_2 phase, aqueous phase with high CO_2 partial pressure (supercritical CO_2), and supercritical CO_2 phase. When the phase state of CO_2 is changed, the corresponding parameters (solubility, diffusion coefficient, viscosity, ionic strength, etc.) will change. With the presence of acidic gas impurities (SO_2, NO_2, H_2S, etc.), the corrosion mechanism will be thoroughly altered. The carbonic acid corrosion will change to sulphurous acid corrosion, nitric acid corrosion, and H_2S corrosion, or a mixed type of them. The corrosion products will also vary for different acidic gas impurities, which will affect the corrosion process in turn.
- For the corrosion in the dense CO_2 phase, the corrosion happened in the confined aqueous phase (water film), which is apparently different from the corrosion in the bulk aqueous phase. This characteristic has notable impact on the mass transport of species, and also affects the solubility of corrosion products, which will eventually affect the protectiveness of product layers to the substrate. The investigations on the effects of multiple acidic gas impurities on the corrosion behaviours and their effects on the corrosion mechanisms are necessary and urgent, which is required by establishing the mechanistic prediction models. (3)

1. Zhang Y, Pang X, Qu S, et al. Discussion of the CO2 corrosion mechanism between low partial pressure and supercritical condition. Corros Sci. 2012;59:186–197.
2. Zhang GA, Liu D, Guo XP. Corrosion behaviour of N80 carbon steel in formation water under dynamic supercritical CO2 condition. Corros Sci. 2017. DOI:10.1016/j.corsci.2017.02.012.
3. Y. Xiang, M. Xu, Y.-S. Choi, “State-of-the-Art Overview of Pipeline Steel Corrosion in Impure Dense CO_2 for CCS Transportation: Mechanisms and Models,” Corros. Eng. Sci. Techn. 52, 7 (2017): pp. 485-509.

Corrosion product layer

- In CO_2 corrosion, if a protective layer forms on the steel surface, a diffusion process controlled by the product layer may become the rate-determining step (RDS) in the corrosion process (1).
- Four characteristics are generally used to judge the protectiveness of the product layer: layer density, adhesion, stability, and surface coverage (2).
- To date, there have been limited studies on the formation mechanisms of the product layer in supercritical CO_2 environments with impurities and their properties, while studies related to the $FeCO_3$ layer formation in supercritical CO_2-saturated water environments have been performed in detail (3, 4). If the supersaturation exceeds the solubility of $FeCO_3$ in the solution, $FeCO_3$ will precipitate on the steel surface.
  The solubility product of $FeCO_3$ according to the following equation (5)

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

  where Ksp is the solubility product of FeCO3, TK is the temperature in Kelvin and I is the ionic strength of the solution.
- Another study conducted by Hua et al. (4) indicated that the $FeCO_3$ layer formed in a supercritical CO_2-saturated water environment consisted of two layers: the loose amorphous $FeCO_3$ inner layer and the compact $FeCO_3$ crystal outer layer. However, the localised corrosion rates were still high, even though the layers seemed to be compact, in water-saturated supercritical CO_2.
- The composition of the product layer and the effect on corrosion behaviour become more complicated when the acidic gases are contained in a dense CO_2 stream. Taking SO_2 as an example, $FeSO_3 \cdot xH_2O$ and $FeSO_4 \cdot xH_2O$ crystals are usually detected in the product layers (6), while $FeCO_3$ cannot be found in the product unless the SO_2 concentration in the corrosion environment is fairly low (7). A mixed product layer containing $FeSO_3 \cdot 3H_2O$ and $FeCO_3$ was found under conditions of 50 and 100 ppm SO_2 and 20 ppm O_2, and the ratio of $FeSO_3 \cdot 3H_2O$ to $FeCO_3$ increased with increasing SO_2 concentration (7). Moreover, Ruhl and Kranzmann (8) suggested that the inner part of the $FeSO_3 \cdot xH_2O$ and $FeSO_4 \cdot xH_2O$ layers changed to iron sulphide (FeS) under ambient pressure. The changing process was characterised by the following equation (9): $SO_2 \rightarrow SO_3^- \rightarrow S_2O_4^- \rightarrow S_4O_6^- \rightarrow S_2O_3^- \rightarrow S \rightarrow S_5^- \rightarrow S_4^- \rightarrow S_3^- \rightarrow S_2^- \rightarrow S^-$
  When NO_x and SO_x were present, ammoniojarosite ($(NH_4)Fe_3(SO_4)2(OH)_6$) was found to be the main corrosion product under ambient conditions (10), while $Fe(NO_3)_3.9H_2O$ and $Fe_2O_3.H_2O$ were detected as the main corrosion products for X65 steel in water-saturated supercritical CO_2 with 1000 ppmv NO_2 (11). NO_3^- present in the solution might be reduced to ammonium (NH_4^+) within the aqueous film and in the presence of hydronium ions (H_3O^+) (12), according to the following equation (13): $4Fe + NO_3^- + 10H^+ \rightarrow 4Fe^{2+} + NH_4^+ + 3H_2O$

1. Chen C. Research on electrochemical behavior and corrosion scale characteristics of CO2 corrosion for tubing and casing steel [PhD thesis]. Xi'an: North western Polytechnical University; 2002.
2. Kermani MB, Morshed A. Carbon dioxide corrosion in oil and gas production – a compendium. Corrosion. 2003;59(8):659–683.
3. Zhang Y, Pang X, Qu S, et al. The relationship between fracture toughness of CO2 corrosion scale and corrosion rate of X65 pipeline steel under supercritical CO2 condition. Int J Greenh Gas Con. 2011;5(6):1643–1650.
4. Hua Y, Barker R, Neville A. Comparison of corrosion behaviour for X-65 carbon steel in supercritical CO2-saturated water and water-saturated/unsaturated supercritical CO2. J Supercrit Fluids. 2015;97:224–237.
5. Sun W, Nesic S, Woollam RC. The effect of temperature and ionic strength on iron carbonate (FeCO3) solubility limit. Corros Sci. 2009;51(6):1273–1276.
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7. Hua Y, Barker R, Neville A. Understanding the influence of SO2 and O2 on the corrosion of carbon steel in water-saturated supercritical CO2. Corrosion. 2015;71(5):667–683.
8. Ruhl AS, Kranzmann A. Investigation of corrosive effects of sulphur dioxide, oxygen and water vapour on pipeline steels. Int J Greenh Gas Con. 2013;13:9–16.
9. Hemmingsen T, Vangdal H, Valand T. Formation of ferrous sulfide film from sulfite on steel under anaerobic conditions. Corrosion. 1992;48(6):475–481.
10. Ruhl AS, Kranzmann A. Corrosion behavior of various steels in a continuous flow of carbon dioxide containing impurities. Int J Greenh Gas Con. 2012;9(0):85–90.
11. Sun C, Wang Y, Sun J, et al. Effect of impurity on the corrosion behavior of X65 steel in water-saturated supercritical CO2 system. J Supercrit Fluids. 2016;116:70–82.
12. Ruhl AS, Kranzmann A. Corrosion in supercritical CO2 by diffusion of flue gas acids and water. J Supercrit Fluids. 2012;68:81–86.
13. Alowitz MJ, Scherer MM. Kinetics of nitrate, nitrite, and Cr(VI) reduction by iron metal. Environ Sci Technol. 2002;36:299–306.

Corrosion product layer

- Ammoniojarosite ($(NH_4)Fe_3(SO_4)_2(OH)_6$) formed according to (1):
  $3Fe^{3+} + NH_4^+ + 2SO_4^{2-} + 6H_2O \rightarrow NH_4Fe_3(SO_4)_2(OH)_6 + 6H^+$
  For the case with SO_2, H_2S, and O_2 impurities, the complex product has been identified by Sun et al. (2), while for the case with NO_x, SO_x, H_2S, O_2, and HCl coexisting, there is still no experimental result that can be cited here to clearly show the exact composition of the product layers. The following equations describe the other potential corrosion products of mild steel in the supercritical CO2 environments:
  $Fe + SO_2 + H_2O \rightarrow FeSO_3 + H_2$
  $2Fe + 2SO_2 + 2H_2O + O_2 \rightarrow 2FeSO_4 + 2H_2$
  $xFe + yH_2S \rightarrow Fe_xS_y + yH_2$
  $Fe + 2HCl \rightarrow FeCl_2 + H_2$
- A protective corrosion product layer, on the one hand, tends to reduce the flux of corrosive media reaching the metal surface, and on the other hand, may directly isolate part of the substrate metal from the corrosive media completely, thus substantially lowering the corrosion rate. Vitse and Nesic proposed the concept of surface coverage to describe the ability of the product layer to isolate the steel from the corrosive media (3).
- The mechanisms of product layer formation under different conditions also need to be specified. Sun et al. (4) speculated the mechanisms of water layer and product layer formation for a water-saturated supercritical CO_2 system with O_2 and H_2S impurities, as shown below.
- Xu et al. (5) found that the initial surface roughness has no influence on the corrosion rate at a RH of 88% (88, 100%). However, a rougher surface leads to higher corrosion rate at a RH between 60 and 75%.

1. Das GK, Anand S, Acharya S, et al. Preparation and decomposition of ammoniojarosite at elevated temperatures in H2O-(NH4)2SO4-H2SO4 media. Hydrometallurgy. 1995;38 (3):263–276.
2. Sun C, Sun J, Wang Y, et al. Synergistic effect of O2, H2S and SO2 impurities on the corrosion behavior of X65 steel in water-saturated supercritical CO2 system. Corros Sci. 2016;107:193–203.
3. Vitse F, Nesic S, Gunaltun Y, et al. Mechanistic model for the prediction of top-of-the-line corrosion risk. Corrosion. 2003;59 (12):1075–1084.
4. Sun J, Sun C, Zhang G, et al. Effect of O2 and H2S impurities on the corrosion behavior of X65 steel in water-saturated supercritical CO2 system. Corros Sci. 2016;107:31–40.
5. Xu M, Zhang Q, Yang X, et al. Impact of surface roughness and humidity on X70 steel corrosion in supercritical CO2 mixture with SO2, H2O, and O2. J Supercrit Fluids. 2016;107:286–297.

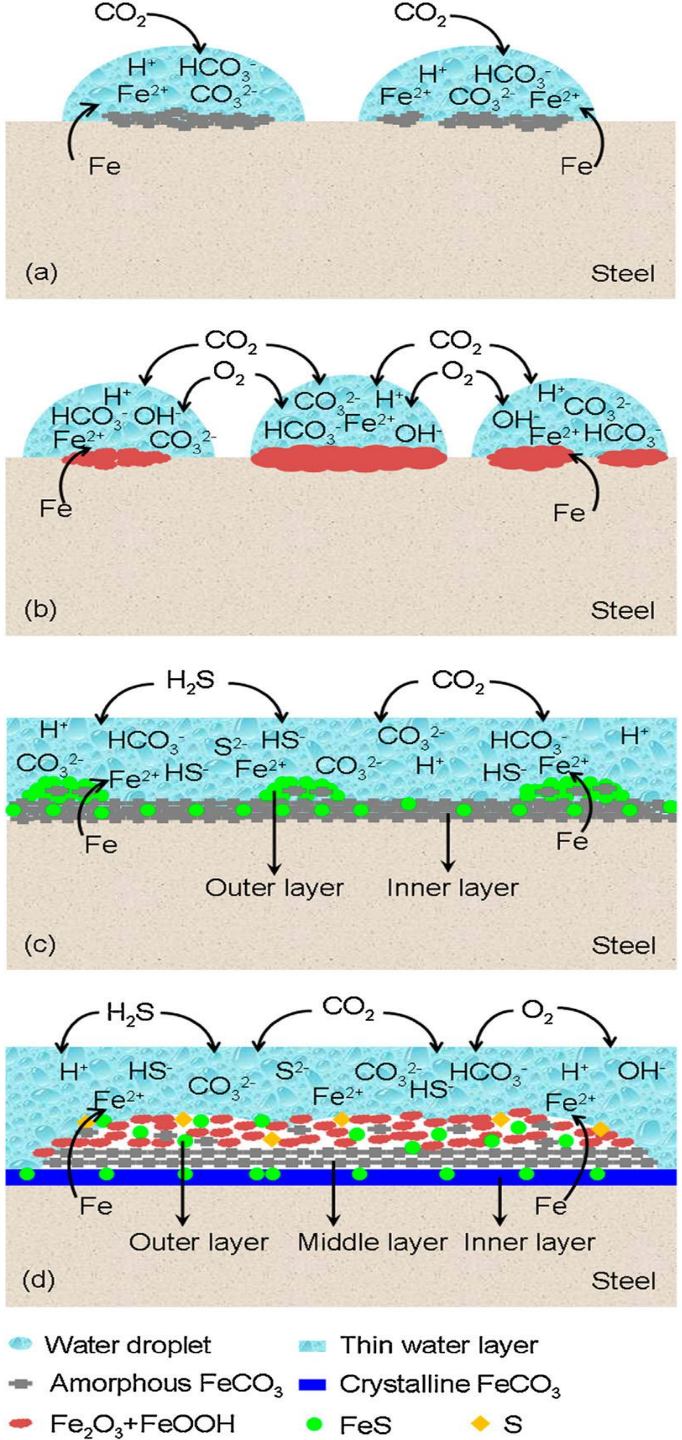
Schematic diagram of the corrosion of X65 steel in water-saturated supercritical CO_2 system:

(a) CO_2–H_2O system;

(b) CO_2–H_2O–O_2 system;

(c) CO_2–H_2O–H_2S system and

(d) CO_2–H_2O–O_2–H_2S system (1).



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1. Sun J, Sun C, Zhang G, et al. Effect of O2 and H2S impurities on the corrosion behaviour of X65 steel in water-saturated supercritical CO2 system. Corros Sci. 2016;107:31–40.

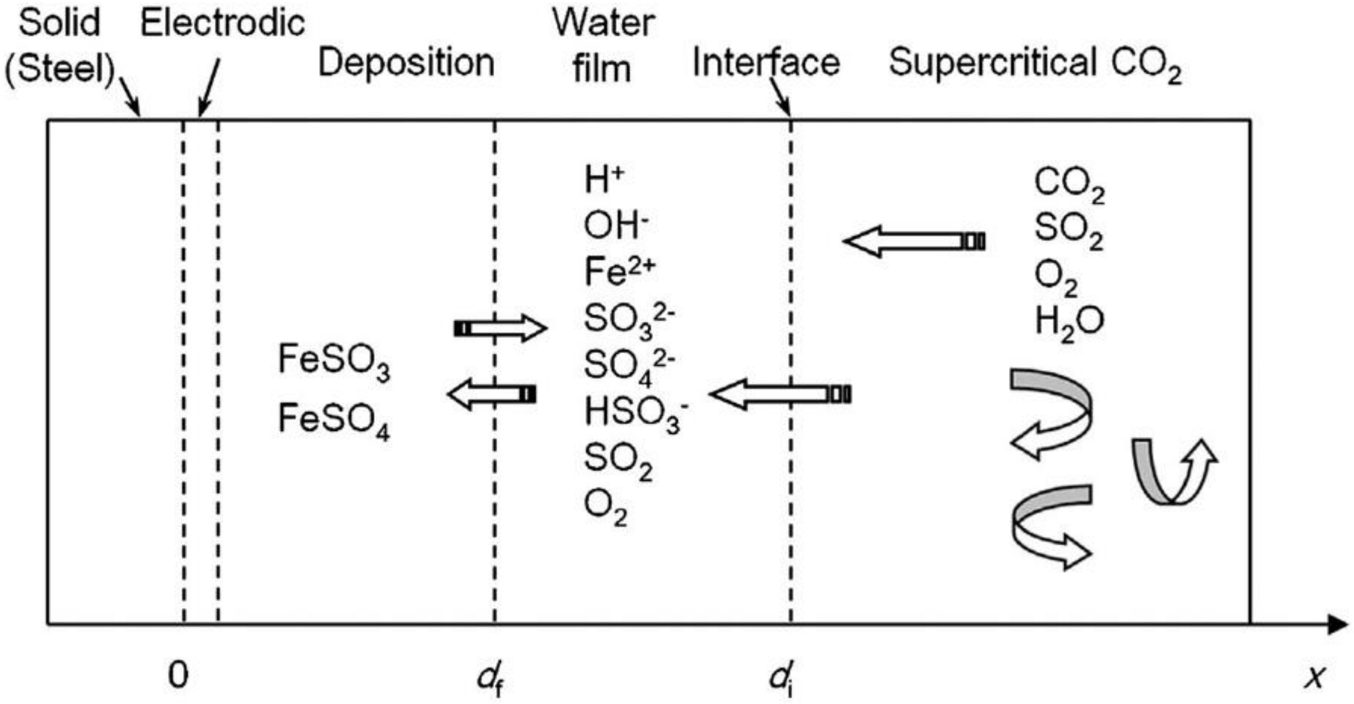
CO_2 and H_2S corrosion prediction models

- Zheng et al. (1) established mechanistic prediction model for CO_2/H_2S corrosion is a useful reference when establishing supercritical CO_2 corrosion with H_2S and other impurities.
- They investigate the electrochemistry of mild steel corrosion in a mixed H_2S/CO_2 aqueous environment, and develop an electrochemical model to simulate the experimental results. The experiments were designed to determine the effect of H_2S on CO_2 corrosion for short-term exposures of a few hours before any interference from iron sulfide corrosion product layers happened. An electrochemical model was developed for a mixed H_2S/CO_2 system, which was calibrated with new experimental results and compared to data found in the open literature. The model predictions fit experimental data well for short exposures (measured in hours) but overestimate the experimental results for longer term exposures (measured by days and weeks) due to the formation of an iron sulfide corrosion product layer, which is not accounted for in the present model.

1. Zheng Y, Ning J, Brown B, et al. Electrochemical model of mild steel corrosion in a mixed H2S/CO2 aqueous environment in the absence of protective corrosion product layers. Corrosion. 2015;71(3):316–325.

Mechanistic prediction models in dense CO_2 with SO_2-O_2-H_2O corrosion prediction models

- Xiang et al. (1) developed one mechanistic model that specifically addresses the prediction of carbon steel corrosion in dense CO_2 phase with SO_2–O_2–H_2O impurities. They integrating the traditional CO_2 corrosion models and the atmospheric corrosion model. The schematic diagram of the six-region model shows below.



The accuracy of this model seems to be high, especially for cases with high SO_2 concentration and RH. However, for cases with extremely low SO_2 concentration, the accuracy of this model seems to be low. These results suggested that the effect of dissolved CO_2 should be considered for conditions with low SO_2 concentrations. For low-RH conditions, the results of this model were also not satisfactory. (2)

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1. Xiang Y, Wang Z, Xu M, et al. A mechanistic model for pipeline steel corrosion in supercritical CO2–SO2–O2–H2O environments. J Supercrit Fluids. 2013;82:1–12.
2. Y. Xiang, M. Xu, Y.-S. Choi, "State-of-the-Art Overview of Pipeline Steel Corrosion in Impure Dense CO_2 for CCS Transportation: Mechanisms and Models," Corros. Eng. Sci. Techn. 52, 7 (2017): pp. 485-509.

Knowledge gaps summary related to various impurities and other factors in supercritical CO_2 corrosion that require further research:

- For impurities such as mercury, NO_x, O_2, and sulfur, there is a lack of understanding of their specific mechanisms and conditions under which they induce corrosion in CO_2 pipelines. Further research is needed to investigate the effects of different concentrations and chemical compositions of these impurities and develop effective strategies for mitigating their corrosion.
- There is a lack of data on supercritical CO_2-water corrosion behaviour and the impact of impurities in the supercritical region. More research is needed to determine the conditions for which the formation of free water will be unlikely and to develop a fundamental understanding of the thermodynamics of CO_2/impurities corrosion mechanisms.

- The potential for CO to cause SCC in carbon dioxide pipelines is not clearly understood, and further research is needed to assess the relevant factors that affect the SCC susceptibility under different operating conditions.
- The flow rate in CO_2 pipelines is also an area that requires further investigation, especially for multiphase flow conditions, to better understand the reliability of test results and develop more accurate predictive models. Overall, these knowledge gaps highlight the need for further research to improve the understanding and predictability of supercritical CO_2 corrosion and to develop effective mitigation strategies.

Recommendations

- From the pipeline integrity management perspective, NO_x should be removed most thoroughly, among all the acidic gas impurities, due to its detrimental effect on the pipeline integrity. (1)
- For high pressure conditions in dense CO_2, the task of elucidating this issue remains. No evidence currently exists to show that CO can promote or depress general corrosion or induce localised corrosion in dense CO_2 environments.

1. Y. Xiang, M. Xu, Y.-S. Choi, “State-of-the-Art Overview of Pipeline Steel Corrosion in Impure Dense CO_2 for CCS Transportation: Mechanisms and Models,” Corros. Eng. Sci. Techn. 52, 7 (2017): pp. 485-509.

Impurity H_2O Knowledge gaps (1):

- No comparative investigations involving CO_2 in the presence of impurities are available. O_2, H_2S, SO_2 and NO_x are all expected to increase corrosion rates.
- In addition, even for CO_2-water corrosion, no data in the supercritical region are available. The fact that supercritical CO_2 is an extremely efficient solvent (IPCC, 2004) poses serious uncertainties in extrapolating the current understanding of CO_2-water corrosion behaviour to pipelines transporting supercritical CO_2.
- The ultimate aim should be determining the conditions for which the formation of free water will be unlikely. This will require a fundamental approach involving the understanding of the thermodynamics of the CO_2/impurities corrosion mechanism in conjunction with careful experimentation.

1 Mike B., Solomon B., Michael F., Haroun M., ‘CO2 pipelines material and safety considerations’, IChemE, NO. 155, 2009.

Impurity mercury Knowledge gaps:

- There is lack of information on the specific mechanisms and conditions under which mercury-induced corrosion occurs. For example, while it is known that mercury can react with steel surfaces and form amalgams, there may be variations in the properties of these amalgams depending on factors such as the concentration and chemical composition of the environment. Additionally, the interactions between mercury and other contaminants in the environment, such as oxygen or sulfur compounds, may also impact the corrosion behavior of carbon steel. Further research may be needed to better understand these mechanisms and their interactions to develop more accurate models for predicting mercury-induced corrosion in CO_2 and H_2S environments.

Impurity NO_x Knowledge gaps:

- NO and NO_2 are common by-products of combustion processes and can be present in CO_2 emissions from industrial processes. These gases can react with water to form nitric and nitrous acids, which can accelerate the corrosion of steel and other metals. Therefore, their presence in a water-saturated CO_2 system have a significant impact on the corrosion behavior of X65 steel.
- Further research may be needed to investigate the allowable concentration of NO and NO_2 in CCS transportation system and to develop effective strategies for mitigating their effects. This could include studies to determine the concentrations of these gases in CO_2 emissions from different industrial processes, as well as investigations into the specific methods by which can monitor and reduce their corrosion.

Impurity O_2 Knowledge gaps:

- Different amounts of O_2 in dense CO_2 leading to different corrosion rate and corrosion patterns. Especially under conditions of multiple impurities, the general corrosion rate may not increase with O_2 increase due to localised corrosion rate has been ignored. These controversial results imply that more corrosion experiments related to different amounts of O_2 in dense CO_2 are needed to reveal the complex effects of O_2 on corrosion behaviours. (1)
- Further research is needed to clarify the impact of different oxygen concentrations on the corrosion behavior of steel in water-containing supercritical CO2 environments and to identify the underlying mechanisms that drive these effects.

1 Y. Xiang, M. Xu, Y.-S. Choi, "State-of-the-Art Overview of Pipeline Steel Corrosion in Impure Dense CO_2 for CCS Transportation: Mechanisms and Models," Corros. Eng. Sci. Techn. 52, 7 (2017): pp. 485-509.

Impurity sulphur Knowledge gaps:

- The impurity sulphur is not specifically studied under supercritical CO_2 conditions. Moreover, they do not provide detailed information on the experimental techniques used for studying the impurity sulfur. Furthermore, the sources do not discuss the procedures for preparing the test specimens, the exposure conditions, the analytical techniques for measuring the corrosion rates and the impurity sulfur content, and the interpretation of the results.
- Therefore, further research is needed to identify the most suitable experimental techniques for investigating the role of impurity sulfur in CO2 corrosion with flue gas impurities. This may involve developing new experimental setups or modifying existing ones to simulate the relevant conditions, such as temperature, pressure, and gas composition, and accurately measure the impurity sulfur content and its effects on corrosion. Additionally, advanced analytical techniques may be needed to detect and quantify trace amounts of impurity sulfur in the corrosion products and to elucidate its role in the corrosion mechanisms.

Impurity CO Knowledge gaps

- For high pressure conditions in dense CO_2 , the SCC issue is still not clear. No evidence currently exists to show that CO can promote or depress general corrosion or induce localised corrosion in dense CO_2 environments (1).
- The hydrogen-induced cracking (HIC) and SCC must be addressed in future standards related to the design and construction of pipelines for anthropogenic CO_2 transportation. (1)
- This may involve conducting laboratory experiments to simulate the transport conditions and determine the SCC threshold of pipeline materials in the presence of CO. It may also involve the development of predictive models that take into account the chemical reactions and transport processes involved in the pipeline system and the influence of operating conditions, such as temperature, pressure, and flow rate.

1 Y. Xiang, M. Xu, Y.-S. Choi, “State-of-the-Art Overview of Pipeline Steel Corrosion in Impure Dense CO2 for CCS Transportation: Mechanisms and Models,” Corros. Eng. Sci. Techn. 52, 7 (2017): pp. 485-509.

Flow rate research gap

- Only a few of the existing supercritical CO_2 corrosion tests were completed in the flow loop (1, 2), and the test results in the flow loop were believed to show better reliability than the test results obtained in the sealed autoclaves. There is no doubt that more studies under different flow conditions in the flow loop are needed, especially for multiphase flow conditions in the CO_2 pipeline with different flow regimes, which may represent a gas–liquid flow in the worst-case scenario (3).

1. Yevtushenko O, Bäßler R. Water impact on corrosion resistance of pipeline steels in circulating supercritical CO2 with SO2- and NO2- impurities. CORROSION/2014, NACE International, San Antonio, TX, USA, Paper No. 3838, 2014.

2. Yevtushenko O, Bäßler R, Carrillo-Salgado I. Corrosion stability of piping steels in a circulating supercritical impure CO2 environment. CORROSION/2013, Orlando, FL, USA, 2013, NACE International, Paper No. 2372.

3. Y. Xiang, M. Xu, Y.-S. Choi, "State-of-the-Art Overview of Pipeline Steel Corrosion in Impure Dense CO2 for CCS Transportation: Mechanisms and Models," Corros. Eng. Sci. Techn. 52, 7 (2017): pp. 485-509.

CO_2 corrosion prediction models gaps

- Most of CO_2 corrosion prediction models can only be employed within the CO_2 partial pressure range of 0–2 MPa. When these models were applied to higher CO_2 partial pressure conditions, the predicted values were almost an order of magnitude higher than the experimental values [20,70]. The reason for this discrepancy should be attributed to the different corrosion characteristics under high-pressure conditions (3).

1. Zhang Y, Gao K, Schmitt G, et al. Modeling steel corrosion under supercritical CO2 conditions. Mater Corros. 2013;64(6):478–485.

2. Kongshaug KO, Seiersten M. Baseline experiments for the modelling of corrosion at high CO2 pressure. CORROSION/2004, NACE International New Orleans, LA, Paper No. 04630, 2004.

3. Y. Xiang, M. Xu, Y.-S. Choi, “State-of-the-Art Overview of Pipeline Steel Corrosion in Impure Dense CO2 for CCS Transportation: Mechanisms and Models,” Corros. Eng. Sci. Techn. 52, 7 (2017): pp. 485-509.

Impurity H_2S corrosion prediction models knowledge gap

There are knowledge gap under specific conditions which the electrochemical model of mild steel corrosion in a mixed H_2S/CO_2 aqueous environment applies.

For example, it may be unclear whether this model is applicable to all concentrations or ratios of H_2S and CO_2, or whether other factors such as temperature, pressure, or the presence of other contaminants can affect the corrosion process. Further research may be needed to clarify these conditions and refine the electrochemical model accordingly. Additionally, the effectiveness of different corrosion mitigation strategies in this type of environment could be an area for further study.

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