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Internal corrosion of carbon steel pipelines for dense phase CO_2 transport in Carbon Capture and Storage (CCS) – A review

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Abstract

Carbon Capture and Storage (CCS) has been highlighted as a potential method to enable the continued use of fossil-fuelled power stations through the abatement of carbon dioxide (CO_2). A complete CCS cycle requires safe, reliable and cost effective solutions for the transmission of CO_2 from the capturing facility to the location of permanent storage.

This publication presents a detailed review of the integrity risks posed to dense phase CO_2 pipelines in the form of internal corrosion. To begin, the current worldwide experience in handling dense phase CO_2 and the anthropogenic stream compositions expected from the different combustion techniques currently available are discussed. The anticipated compositions are then related to a number of tentative CO_2 stream compositions available in open literature proposed by research institutes and pipeline operators.

In subsequent sections, early laboratory and field corrosion experience relating to natural dense phase CO_2 transport for the purposes of enhanced oil recovery (EOR) are summarised along with more recent research efforts which focus on identifying the role of anthropogenic impurities in the degradation processes. For each system impurity, the reaction rates, mechanisms and corrosion product composition/morphology expected at the steel surfaces are discussed, as well as each component's ability to influence the critical water content required to initiate corrosion. Potential bulk phase reactions between multiple impurities are also evaluated in an attempt to help understand how the impurity content may evolve along a long distance pipeline.

The likelihood of stress-corrosion cracking and hydrogen-induced cracking is discussed and the various corrosion mitigation techniques which exist to control degradation to acceptable

levels are reviewed. Based on the current research performed in the context of impure dense phase CO_2 corrosion, issues associated with performing laboratory experiments to replicate field conditions and the challenges such limitations present in terms of defining the safe operating window for CO_2 transport are considered.

1 Introduction

1.1 General overview

Fossil fuels will continue to be the dominant source of the world's energy production for the foreseeable future. There has been increased concern that the combustion of carbon-based fuels produces greenhouse gases (particularly CO_2) which adversely affects the global climate.

The implementation of Carbon Capture and Storage (CCS) technology has the potential to enable the continued use of fossil fuels through the abatement of carbon dioxide (CO_2), preventing emissions into the atmosphere, whilst also presenting itself as an opportunity to facilitate the recovery of hydrocarbons through the application of enhanced oil recovery (EOR). Currently, CCS is the only process available to create a significant and immediate impact on the CO_2 level in the Earth's environment.

CCS refers to a number of technologies which essentially involve capturing CO_2 from large point sources (i.e. power generation, refineries and industrial applications), followed by compressing and transporting the fluid to geological reservoirs or depleted oil and gas fields for sequestration or EOR.[1] Numerous industrial processes, most notably cement manufacture, iron/steel making and natural gas treatment also intrinsically produce CO_2 and can be fitted with CO_2 capture technologies.[1]

Although CO_2 can be transported by pipeline, ship, rail or road, the mode of transport will be dictated by the quantity of CO_2 requiring sequestration, the distance travelled, and the CO_2 stream composition produced after capture, processing and purification.[1] It is estimated that for the abatement of climate change, approximately 10 Gt/year of CO_2 will need to be transported and sequestered in 2050.[2] Furthermore, researchers have suggested that the only logical choice to achieve such deep reductions in CO_2 emission would be to construct an extensive pipeline network from carbon steel.[3]

CO_2 pipelines must be constructed and designed at an optimal cost such that they are reliable and safe to operate, posing minimal risk to the local population and environment.[1] One of the most notable risks to pipeline integrity during operation is internal corrosion; carbon steel is the principal material of construction and is susceptible to corrosion in flue gas environments because of the presence of CO_2, H_2O, O_2, SO_x, H_2S, NO_x and various other constituents that are capable of forming corrosive products.[4]

Currently, there is no universally agreed upon specification for the CO_2 stream composition to ensure safe transport. It is also apparent that there is a distinct lack of industrial experience associated with *anthropogenic* CO_2 transmission. Consequently, the purpose of this review article is two-fold:

i. Firstly, to review the current literature focusing on the internal corrosion threats posed to carbon steel pipelines in impure dense phase CO_2 environments.
ii. Secondly, to evaluate the extent of knowledge in the various subject areas pertaining to pipeline integrity and to use this information to identify where research efforts should be focused and concentrated to enable the safe design, construction and operation of CO_2 pipelines.

2 Industrial experience in handling CO_2 and pipeline incidents

2.1 Industrial experience worldwide

The transportation of CO_2 has been practiced for over 40 years and currently, over 6000 km of pipeline exist for EOR purposes. The majority of these pipelines are located in the USA and Canada, with some projects also being undertaken in Norway, Algeria, Hungary and Turkey.[5] Nearly all of these pipelines transport CO_2 from natural sources; however a few pipelines do transport anthropogenic CO_2, but these tend to have very stringent specified water content limits imposed, as will be discussed in due course. In North America, CO_2 has been used for EOR since 1972, but the majority of CO_2 is transported from naturally occurring gas fields along the mid-continental mountain ranges and Mississippi Basin.[5]

In terms of European experience with CO_2 transport, this currently rests with Statoil at Sleipner and Snovhit. However, the expectation is that European CCS will evolve to target offshore storage sites, developing in a network format due to the potential for CCS clusters.[5] Some studies have suggested that the infrastructure for European CCS could reach between 30,000 and 150,000 km.[5]

2.2 Pipeline incidents – the importance of corrosion management

It is perhaps worth reflecting on the past number of failures attributed to corrosion in dense phase CO_2 pipelines to highlight the importance of understanding material susceptibility to such environments. Statistics on pipeline incidents in the USA can be found at the Office of Pipeline Safety (OPS) within the US Department of Transportation, Pipeline and Hazardous

Materials Safety Administration (PHMSA).[6] CO_2 pipeline failure information is contained within the hazardous liquid accident data and is specifically related to the transmission of compressed supercritical CO_2. However, operational problems are not necessarily reported in the public domain unless a release occurs. Consequently, this limitation slightly inhibits the ability for people outside of industry to learn from operational sources.

Regardless of this fact, Det Norske Veritas (DNV)[7] analysed the data provided by the PHMSA thoroughly from 1986 to 2008. During this period, 29 incidents relating to CO_2 transport were reported, with one fatality and two injuries. The failure modes of all the 29 reported incidents from 1986-2008 are summarised in Figure 1, which has been adapted from the work of Johnson et al.[7]. The results indicate that between 1986 and 2008 the single greatest cause of pipeline failures was attributed to corrosion.

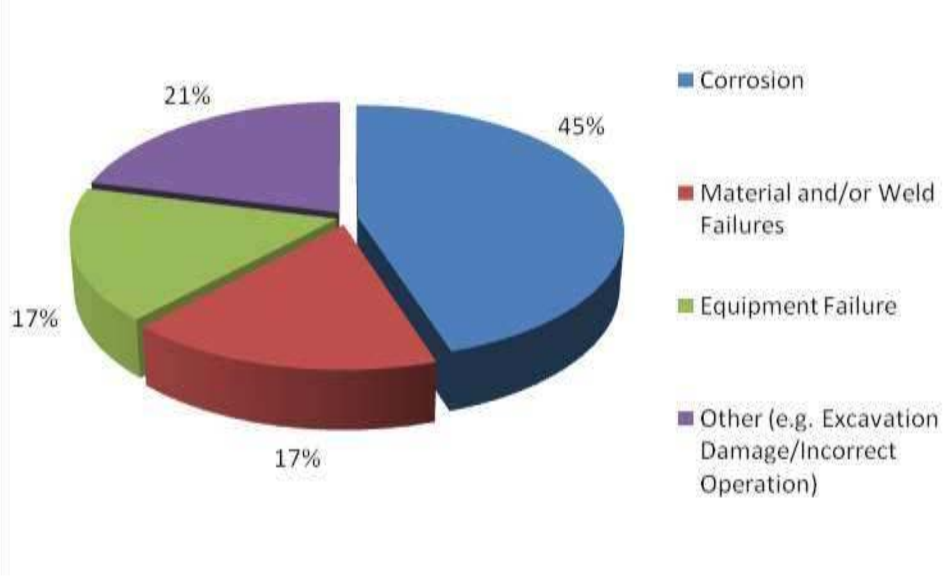


Figure 1: Failure modes for CO_2 pipeline systems in the US – adapted from Johnson et al.[7]

In comparison to the statistics provided for CO_2 pipelines, 5,610 accidents causing 107 fatalities and 520 injuries relating to natural gas and hazardous liquid (excluding CO_2) pipelines occurred from 1986-2006 in the USA.[7] Of these accidents, 32% were attributed to corrosion.

A mile-by-mile comparison was also performed by Gale and Davidson[8] between natural gas, hazardous liquid and CO_2 pipelines. According to their study, CO_2 pipelines have a frequency of incident of 0.32 per 1000 km per year based on data collected between 1990 and 2001, whereas natural gas and hazardous liquid pipelines have a frequency of 0.17 and 0.82, respectively.[8] Table 1 summarises the data collated by Gale and Davidson[8] from 1990 to 2001 in comparison to more recent data collected from the PHMSA website[6] for

1994 to 2013. Figure 2 also depicts the number of CO_2 pipeline incidents recorded per year in the USA between the same period.

Table 1: Statistics relating to pipeline incidents in the USA – adapted from Gale et al.[8] and the US Department of Transportation, Pipeline and Hazardous Materials Safety Administration (PHMSA)[6]

	Natural Gas Transmission		Hazardous Liquid Transmission		CO_2 Transmission	
	1990-2001[8]	1994-2013[6]	1990-2001[8]	1994-2013[6]	1990-2001[8]	1994-2013[6]
No. of incidents	1287	1891	3035	5897	10	64
No. incidents per 1000 km pipeline per year	0.17	0.19	0.82	1.06	0.32	0.64*

*assuming 5000 km as average US pipeline distance between 1994 and 2013

The statistics in Table 1 show that the frequency of incidents on CO_2 pipelines from 1990 to 2001 was greater than that of natural gas transport, but less than that of hazardous liquids. Furthermore, the results indicate that the rate of incidents associated with CO_2 transmission increased from 0.32 between 1990 and 2001 to 0.64 per 1000 km per year for 1994-2013. However, certain authors[8] have cautioned on drawing conclusions from the small sample size of CO_2 pipelines in the USA. The fact that only 6000 km of CO_2 pipelines are in place is often pointed out as a limitation by not providing an extensive knowledge base, especially when compared to the 490,000 km of gas pipelines or the 278,000 km of hazardous liquid pipelines in the US alone.[5]

Figure 2 shows the number of CO_2 pipeline incidents reported per year in the USA between 1994 and 2013 from the PHMSA website. From this figure, it does appear that the number of reported incidents has been generally increasing over the last 20 years. Whether this is related to complacency, lack of reliable information or supply of incorrect information is not known.

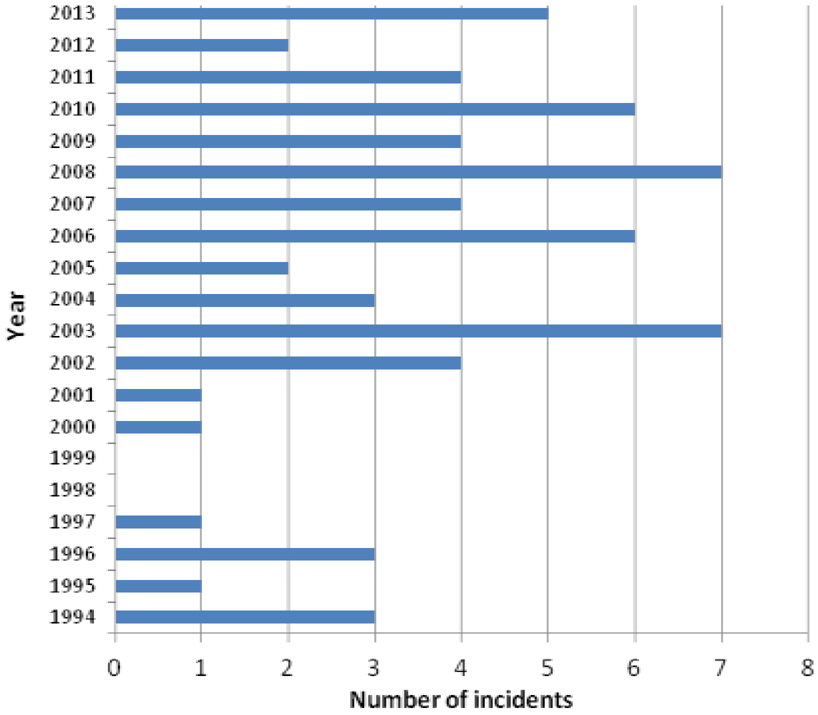


Figure 2: CO_2 pipeline incidents between 1994 and 2013[6]

3 Early corrosion studies in supercritical CO_2 and experience from the SACROC pipeline

One of the key examples of early research into corrosion as well as field observations was that undertaken by the Scurry Area Canyon Reef Operators Committee (SACROC) project. The unit consists of a 352 km long CO_2 injection pipeline network, initially commenced in 1972.[9-11]

Research into the potential for corrosion within the SACROC pipelines was performed by Schremp and Roberson[10] who tested a number of stream compositions to determine the anticipated internal corrosion rates within the system. Samples for the experiments consisted of full size X60 carbon steel 12-inch and 16-inch pipe sections which were exposed to CO_2 streams consistent with the real SACROC pipeline conditions. Corrosion tests were performed at two design temperatures (22 and 3℃) and a pressure of 13.8 MPa. Impurities within the CO_2 stream included 600-800 ppm H_2S (twice the pipeline concentration) and a water content of 1000 ppm, which was 20 times the specified pipeline concentration.

Specimens recovered from the tests after 4-6 weeks exposure showed no evidence of pitting or localised attack and general corrosion rates were below 0.5 µm/year. These results aligned very well with operation experience on the SACROC pipeline which, after 12 years with a 50 ppm water content limit, recorded a corrosion rate between 0.25 and 2.5

µm/year.[5, 11] That being said, there have been incidents with corrosion on a spur line from the SACROC pipeline[12] which occurred as a result of free-standing water remaining from a hydrostatic test, generating high levels of corrosion.

The operation of the SACROC pipeline over the last 44 years, along with a number of other CO_2 pipelines across the USA demonstrates a considerable amount of experience associated with dense phase CO_2 transport. However, despite CO_2 transport having been practiced successfully for decades, there is a limited amount of experience in relation to anthropogenic CO_2 transport, as nearly all US involvement lies with transporting CO_2 from natural sources.

4 Typical CO_2 stream compositions and anticipated impurity contents

4.1 Typical stream compositions available in open literature

Although the composition of CO_2 streams currently being transported through pipelines is not readily available in the open literature, Table 2 provides a summary of information compiled from various authors.[8, 10, 13-17] This covers a selection of existing pipelines which transport either natural or anthropogenic sources of CO_2.

CO_2 from natural sources is typically high purity, will require minimal gas treatment prior to injection and only impurities such as CO_2, N_2, CH_4, water (potentially containing salts) and H_2S are to be expected.[1] Considering anthropogenic sources, there can be a distinct difference in composition, as the stream can become further contaminated by various flue gas impurities (SO_x, NO_x, O_2, CO, Ar, H_2 and others) due to the associated combustion process. Regrettably, the presence of some of these compounds is not reflected in the list of anthropogenic sources in Table 2; and it is unclear from the literature whether this is because these components are not present, or the streams were not analysed for these particular compounds. Despite this, it is clear there will be significant differences in stream composition between natural and anthropogenic CO_2 and the exact composition of man-made CO_2 will inevitably vary depending upon the type of capture process, the source and the level of gas treatment applied.

Table 2: CO_2 compositions transported in existing pipelines

	Canyon Reef Carriers Pipeline[1, 8, 10, 13, 14]	**Central Basin Pipeline[1, 13-15]**	**Sheep Mountain Pipeline[1, 8, 14]**	**Bravo Pipeline[1, 8, 13, 14]**	**Cortez Pipeline[1, 8, 13, 14]**	**Weyburn Pipeline[1, 16]**	**NEJD Pipeline[13]**	**Sleipner[1, 16] (Offshore Pipelines)**	**Snohvit[1, 13, 17] (Offshore Pipelines)**
Location	USA	USA	USA	USA	USA	USA and Canada	USA	Norway	Norway
Operator	Kinder Morgan	Kinder Morgan	Occidental	BP/Occidental	Kinder Morgan	Dakota Gasification Company	Denbury Resources	Statoil	Statoil
Length (km)	~225	~278	~772	~350	~803	~328	~295	<1	~160
Capacity (Mt/y)	4.4	20	9.2	7.3	19.3	5	n/a	1	0.7
Source	Anthropogenic - Gasification Plant	Natural	Natural	Natural	Natural	Anthropogenic - Gasification Plant	Natural	Separation from Natural Gas	Separation from Natural Gas
CO_2 (vol.%)	85-98	98.5	96.8-97.4	99.7	95	96	98.7-99.4	93-96	Not specified
CH_4 (vol.%)	2-15 (C_6H_{14})	0.2	1.7	-	1-5	0.7	0.3	0.5-2.0 total hydrocarbons	Not specified
N_2 (vol.%)	<0.5	1.3	0.6-0.9	0.3	4	<300 ppm	0.3	3-5 non-condensable	Not specified
H_2S	<260 ppm	<26 ppm	-	-	20 ppm	9000 ppm	-	150 ppm	Not specified
C_2+ (vol.%)	-	-	0.3-0.6	-	Trace	2.3	-	0.5-2.0 total hydrocarbons	Not specified
CO (vol.%)	-	-	-	-	-	0.1	-	-	Not specified
O_2	-	<14 ppm	-	-	-	<70 ppm	-	-	Not specified
NO_X	Not specified	-	-	-	-	Not specified	-	-	Not specified
SO_X	Not specified	-	-	-	-	Not specified	-	-	Not specified
H_2 (vol.%)	-	-	-	-	-	Trace	-	3-5 non-condensable	Not specified
Ar (vol.%)	-	-	-	-	-	-	-	3-5 non-condensable	Not specified
Water content (mole)	50 ppm	~630 ppm	315 ppm	Not specified	~630 ppm	20 ppm	418 ppm	Water-saturated (Corrosion Resistant Alloy pipeline)	50 ppm

Table 3 is extracted from a publication by the EDGAR (Energy Delta Gas Research) CO_2 purity project[18] which indicates the concentrations of impurities expected in flue gases and their dependency on the combustion process and form of purification technique employed. The table itself is compiled from numerous publications[19-22] and demonstrates the large variation in the level of impurities expected in the captured CO_2 stream from the various combustion processes.

In addition to the compounds mentioned in Table 3, there may exist the potential for amine carry-over from the capture plant (for post and pre-combustion) that could influence the internal corrosion of pipeline materials. Thodla et al.[23] and Kanimozhi et al.[24] demonstrated that the presence of Monoethanolamine (MEA) can be beneficial or detrimental to internal corrosion depending upon its concentration in the CO_2 stream.

Table 3: Composition ranges for CO_2 streams for different combustion processes – from EDGAR CO_2 purity project – adapted from Walspurger et al.[18]

	Post-combustion	**Pre-combustion**				**Oxyfuel combustion**
	Amine scrubbing	Selexol IGCC[20]	Reactisol IGCC[19]	Amine scrubbing[21]	Sour SEWGS	Oxyfuel and double flashing[22]
CO_2	99.8-99.9%	98.1-99.7%	95-98.5%	>97.2%	>99%	97%
H_2	-	1.5%	20 ppm	<1%	<1%	-
O_2	150-300 ppm	-	-	-	-	1.2%
N_2	450-900 ppm (inc. Ar)	195 ppm	< 1%	<1%	<1%	1.6%
Ar	450-900 ppm (inc. N_2)	178 ppm	150 ppm	<1%	<1%	0.4%
Sulphur compounds	10-20 ppm (SO_2 predominantly)	2<H_2S<1700 ppm	0.2-20 ppm	H_2S<200 ppm for 2-stage plant	<5000 ppm to ppm level with H_2S stage	35ppm SO_2
NO_x	20-40 ppm	-	-	-	-	150 ppm
CO	10-20 ppm	100-1300 ppm	400 ppm	<1%	<1%	-
CH_4	-	112 ppm	100 ppm	<1%	<1%	-
MeOH	-		20-200 ppm	-	-	-
H_2O	100-600 ppm	376 ppm	0.1-10 ppm	1.8%	500 ppm (drying step)	-

4.2 Recommended impurity limits (enhanced oil recovery vs sequestration)

A number of tentative CO_2 purity specifications exist in literature, two of which are provided in Table 4. These are from the European project 'ENCAP – ENhanced CAPture of CO_2' from the DYNAMIS project[16], and a set of compiled data from Alstom which was referred to in a publication by Dugstad et al.[25]. Currently, no universally agreed upon specification for CO_2 quality exists, yet it is critical to accurately define the safe operating window before more

CO_2 lines are constructed or old natural gas lines are converted, as an overly conservative limit will impose unnecessary costs during capture and purification, whilst a liberal limit will cause pipeline integrity and storage issues.

Table 4: DYNAMIS CO_2 quality recommendations and Alstom CO_2 quality tolerances (the justification behind each limitation is also provided)

Component	**DYNAMIS CO_2 quality recommendations (adapted from de Visser et al.[16])**		**Alstom CO_2 quality tolerances (extracted from Dugstad et al.[25])**		
	Concentration Limit	**Reason for Limit**	**Low Limit**	**High Limit**	**Reason for Limit**
CO_2	>95.5 vol.%	Balanced with other compounds in CO_2	>90% vol.% (storage)	>95% vol.% (EOR)	Low – Storage requirement High – EOR requirement
N_2/Ar/ H_2	< 4 vol.%	As proposed in ENCAP	<4 vol.%		EOR requirement
O_2	Aquifer < 4 vol.%, EOR 100 – 1000 ppm	Technical: range for EOR due to lack of practical experiments on effect of O_2 underground	<10 ppm	<1000 ppm	Unclear
CH_4	Aquifer < 4 vol.%, EOR < 2 vol.%,	As proposed in ENCAP	<4%	<4%	EOR requirement
H_2O	500 ppm	Technical: below solubility limit of H_2O in CO_2. No significant cross effect of H_2O and H_2S, cross effect of H_2O and CH_4 is significant but within limits for water solubility.	<10 ppm	<600 ppm	Corrosion prevention requirement
H_2S	200 ppm	Health and Safety	<10 ppm	<15000 ppm	Low – Health and Safety High – EOR requirement
CO	2000 ppm	Health and Safety	<100 ppm	<40000 ppm	Low – Health and Safety High – EOR requirement
SO_x	100 ppm	Health and Safety	<100 ppm	<1500 ppm	Low – Health and Safety High – EOR requirement
NO_x	100 ppm	Health and Safety	<100 ppm	<1500 ppm	Low – Health and Safety High - Unclear

It is worth noting that the specifications outlined in Table 4 do not fully take into account cross-reactions between impurities (except for H_2S and CH_4 impact on water solubility through the DYNAMIS study) and no interactions between H_2O, SO_x and NO_x were considered in the development of these guidelines.[26] It is also important to stress that the NO_x and SO_x limits recommended by DYNAMIS were justified based on health and safety in the event of a sudden release, not from the perspective of maintaining pipeline integrity.

It is important to keep in mind when considering the purification of the CO_2 stream, in the case of EOR, that there is an economic incentive to remove certain impurities down to very low levels to enable optimum oil recovery by preventing adverse reactions with hydrocarbons in the reservoir and maintaining the minimum miscibility pressure. However, transporting CO_2 for solely storage purposes does not share the same relationship, and removing impurities down to such low concentrations may impose a significant energy and cost penalty which could be avoided.[1]

5 Water content specifications, water solubility and dehydration

5.1 Pipeline water content specifications, water solubility and rationale for a water concentration limit

Referring back to Table 2, it can be observed that the water content within each CO_2 stream for the different sources varies from 20 ppm to ~630 ppm (with the exception of Sleipner which transports water-saturated CO_2 using corrosion resistant alloy pipelines).

When the acceptable water content is discussed, the proposed limit is usually related to the solubility of water in the system. Putting this into context, the solubility limit of water in pure CO_2 over the range of conditions expected for CCS (5-85℃ and 7.3-30.0 MPa), is around 1700 ppm or higher before free water precipitation occurs.[16, 27] Figure 3, which is extracted from a publication by de Visser et al.[16] outlines in more detail how the solubility of water varies as a function of temperature and pressure over the range of -10 to 25℃ and 1.0 to 20.0 MPa. The figure shows that increasing temperature serves to increase the solubility limit of water in CO_2. Furthermore, a noticeable increase in solubility is observed due to increasing pressure when CO_2 makes the transition from gas to liquid phase. Before this transition, the minimum solubility is observed for each specific temperature profile.

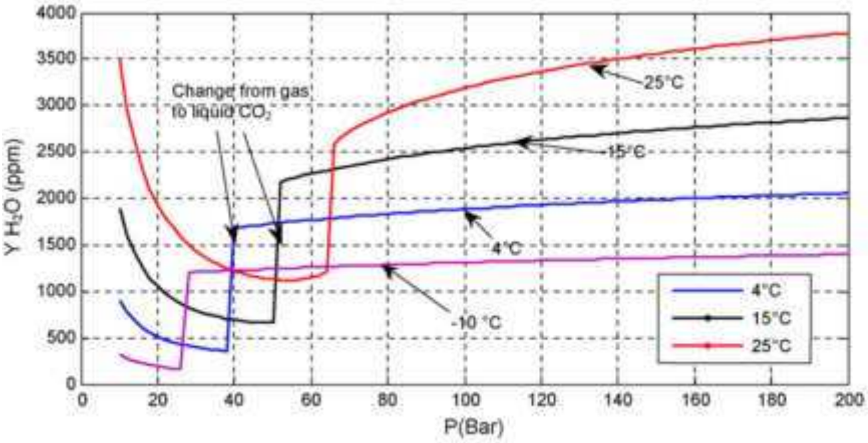


Figure 3: Water solubility in pure CO_2 for varying temperatures as a function of pressure - Figure from de Visser et al.[16] as part of the DYNAMIS report

If the water content within the CO_2 stream locally exceeds the specified solubility limit, water will break free from the CO_2 phase and a separate aqueous phase will exist. If such a phase were to form on the pipeline wall, it will invariably become saturated with CO_2, creating carbonic acid (H_2CO_3) which will pose a threat to pipeline integrity, even without the presence of additional flue gases such as SO_x, O_2, H_2S and NO_x.[28] Consequently, because of the inherent risk associated with corrosion, pipeline operators set their own limits for water content in CO_2 streams, with some limits being as strict as 50 ppm. According to Dugstad et al.[3], 500 ppm tends to be the accepted limit in literature, although little reasoning exists behind this specific value.

6 Influence of impurities on bulk CO_2 stream properties and water solubility

Unfortunately, the added complication brought about by impurities is that they influence the physical properties of the CO_2 which can have a significant effect the extent/occurrence of both corrosion and hydrate formation.[29] This aspect is reviewed within this section, with focus directed towards the impact of impurities on water solubility within the CO_2 stream.

6.1 Effect of impurities on the critical properties and phase envelope of CO_2

Modelling of phase behaviours requires the use of Equation of State (EOS), but there no universal agreement regarding the EOS model that should be used for CO_2 pipelines. It has been suggested that the models selected should be based on reliable experimental data.[30] Both Li and Yan[31] and Seevam et al.[30] indicated through the use of different EOS models that the presence of SO_2 and H_2S impurities increase the critical temperature of the CO_2 stream, whilst CH_4, Ar, N_2 and O_2 all serve to lower the critical temperature of the mixture. In terms of the critical pressure, Seevam et al.[30] reported an increase in critical pressure with the introduction of 5% SO_2, N_2, O_2, CO, CH_4, H_2S, H_2, NO_2 and Ar in CO_2. Such observations agreed with the findings of Li and Yan[31] for SO_2 and CH_4, but in contrast they reported that N_2 and H_2S caused a reduction in critical pressure with increasing concentration from 0 to 5%. The contrast in results highlights the importance of selecting an appropriate EOS model and suggests further research is required to determine the most appropriate models to use to predict phase behaviour.

Although the location of the critical point is important, the entire phase envelope of CO_2 can change when impurities are introduced into the system, and this also requires consideration. For efficient transport, it is important that CO_2 remains in the dense phase. Consequently, the implication of impurities on the whole phase envelope (as well as the critical point) needs to be understood, as this envelope defines where CO_2 exists as a supercritical fluid. On the basis of this information, Seevam et al.[30] implemented the Peng-Robinson equation to perform a study into the influence of impurities (5% of SO_2, N_2, O_2, CO, CH_4, H_2S, H_2, NO_2

and Ar individually in combination with CO_2) on the phase envelope. Their constructed phase diagrams for all these binary combinations generally showed that the impurities increase the width of the phase envelope, resulting in the formation of a two-phase gas-liquid region. Impurities such as H_2 and NO_2 were shown to generate very large envelopes, whilst H_2S and N_2 produced much smaller changes. Ternary mixtures analysed for 90% CO_2 with 5% N_2 and 5% NO_2 produced a dramatic effect on increasing the size of the phase envelope whilst also increasing critical pressure and temperature significantly. However, it could be argued that some of the concentrations considered in these systems (e.g. 5% SO_2/NO_2) are unrealistic in terms of what is actually likely to be transported. Nonetheless, they highlight an important point that certain impurities may have notable effects on the optimum pipeline operating region. The general observations suggested that as the impurity contents increases, so does the size of the phase envelope, and the critical pressure. It is also important to note that the pipeline will contain mixtures of numerous impurities and the interactions between these species need to be taken into account, as discussed later in this review.

6.2 Effect of impurities on water solubility

An additional complexity associated with the presence of impurities is that they not only influence the physical properties and phase boundaries of CO_2, but they can have an effect on the solubility of water in the process stream. At present, very little data exists relating to water solubility in impure CO_2. Such data has been identified by the UK Carbon Capture and Storage Research Council (UKCCSRC) as being crucial for the development of safe CO_2 transportation pipelines in both the gaseous and dense phase, as this is believed to be related to the likelihood of corrosion and hydrate formation.

In terms of understanding the influence of species such as N_2 and H_2, Foltran et al.[32] established the water solubility limit in CO_2 containing 5 and 10% N_2 at 40℃ and from 80 to 18.0 MPa. Their research indicated that the presence of N_2 was able to significantly lower the solubility of water in CO_2. In particular, at 40℃ and 10.21 MPa, the addition of 10% N_2 reduced solubility of water from 4450 ppm to 3400 ppm (approximately a 30% reduction). Figure 4 (from the publication by Foltran et al.[32]) shows in more detail how N_2 influences the solubility behaviour of water in CO_2 at 40℃ over the pressure range of 8.0 to 18.0 MPa.

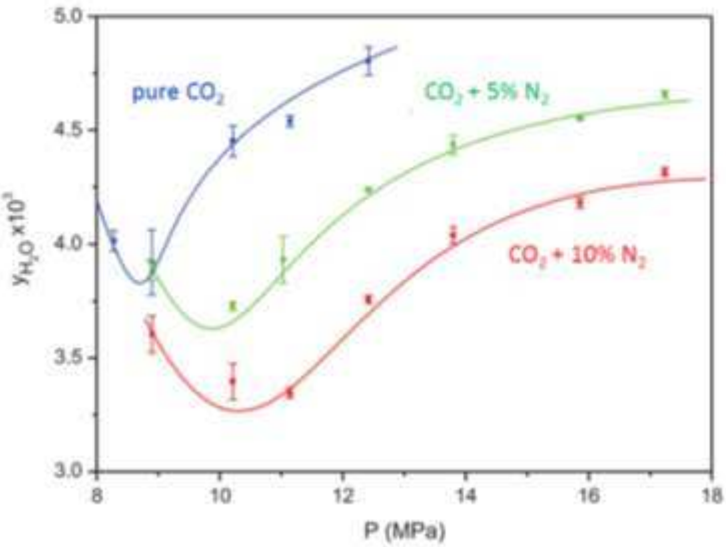


Figure 4: Water solubility expressed as a mole fraction in pure CO_2, CO_2 + 5% N_2 and CO_2 + 10% N_2 as a function of pressure at 40°C determined using FT-IR spectroscopy – Figure from Foltran et al.[32]

7 Influence of impurities on corrosion of carbon steel in dense phase CO_2

When considering CO_2 corrosion of carbon steel in supercritical environments, there are two main types of corroding system that can be considered. The stream can consist of an aqueous/water-rich phase saturated with supercritical CO_2 (representative predominantly of oil and gas production), or the dominant phase can be dense phase CO_2 (representative of CO_2 transport in the context of CCS) containing considerably much smaller quantities of water (i.e. typically from 50 to a few thousand ppm). Only a review of corrosion in systems dominated by dense phase CO_2 is provided within this work as this is typical of the conditions encountered during normal CO_2 service in the context of CCS and EOR. Although some studies by Sim et al.[33] and Ruhl et al.[34-36] seek to understand corrosion behaviour in supercritical systems through aqueous and/or ambient pressure testing, they are not reviewed in detail here as focus is directed towards experiments performed at high pressures.

7.1 CO_2-H_2O and CO_2-H_2O-O_2 environments

The impact of CO_2 corrosion on carbon steel in aqueous systems has been covered extensively at pressures relevant to oil and gas transport (up to 2.0 MPa) and has been an active area of study for the past 50 years.[37-43] However, less research has been afforded to high pressure CO_2 corrosion where CO_2 is the dominant phase[44], especially in conditions above the critical point of 31.1°C and 7.38 MPa.[45] That being said, the corrosion of carbon steel in systems where supercritical CO_2 is the dominant fluid has received considerably more attention over the last few years due to the emerging potential of CCS.

The mechanism of CO_2 corrosion in CCS is similar to that encountered in oil and gas production and is capable of being divided into both anodic and cathodic processes which are outlined in the following sections.

7.1.1 Cathodic reactions

When CO_2 dissolves in water, it is hydrated to produce carbonic acid (H_2CO_3).[46] Although CO_2 is very soluble in water, only a small proportion of the dissolved CO_2 in the aqueous phase is hydrated to form H_2CO_3:[47]

$$CO_{2(g)} + H_2O_{(l)} \leftrightarrow H_2CO_{3(aq)} \tag{1}$$

H_2CO_3 is diprotic and partially dissociates in two stages to form bicarbonate and carbonate ions[46, 48] (Reactions 2a and 2b). The dissociation of carbonic acid (Reaction 2a) in particular is very fast in comparison to CO_2 dissolution, meaning that hydration generally becomes the rate-determining step, limiting the corrosion reaction rate:[47]

$$H_2CO_3 \leftrightarrow H^+ + HCO_3^- \tag{2a}$$

$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-} \tag{2b}$$

In terms of reactions at the steel surface, the main cathodic reaction (under oil and gas transportation and normal CO_2 service) is hydrogen evolution:

$$2H^+ + 2e^- \rightarrow H_2 \tag{3}$$

This reaction depends strongly on the solution pH, however, it is often limited by the rate at which H^+ ions can be transported to the steel surface by mass-transfer (i.e. diffusion limited), making the reaction flow-dependant[47]. In terms of dense phase CO_2 transport, the acceleration of corrosion rate due to flow is less of a concern within the condensate on the pipe wall as it is typically stationary.

In CO_2 systems at low pH (i.e. less than pH of 4), which is typical for pure CO_2-saturated water at the pressures associated with dense phase transport, the dominant process is the cathodic reduction of H^+ because of its high concentration. At intermediate concentrations ($4 < pH < 6$), the limiting diffusion rate of H^+ is smaller because of its low concentration. Such a pH range can be achieved within the condensate if it becomes contaminated with Fe^{2+} ions from corrosion or if amine carry-over occurs. Both processes result in increased alkalinity of the electrolyte.

In addition to hydrogen evolution, another cathodic reaction pathway is also suggested to be important; the direct reduction of H_2CO_3:[48]

$$2H_2CO_3 + 2e^- \rightarrow H_2 + 2HCO_3^- \tag{4}$$

Again, in this reaction the distinction is only the pathway and hence, the kinetics of the reaction (which is limited by the slow CO_2 hydration step). The reaction is a strong function of partial pressure, which means it can potentially play a substantial role in the acceleration of corrosion in dense phase CO_2 systems.[47] However, Reaction (4) has recently become subject to debate regarding whether or not it actually occurs to any significant degree, or whether it is purely attributed to a buffering effect at the steel surface.[49, 50]

Given that HCO_3^- is also a weak acid, then reduction of H^+ from HCO_3^- is another reaction pathway (Reaction 5), although experience indicates that this reaction is much slower than the direct reduction of carbonic acid in the pH range 4 to 6, and consequently, it can be ignored under oil and gas and CO_2 service. However, in neutral and alkaline systems, the concentration of HCO_3^- can become higher than H_2CO_3, making the direct reaction of HCO_3^- significant.

$$2HCO_3^- + 2e^- \rightarrow H_2 + 2CO_3^{2-} \tag{5}$$

A final additional reaction is the direct reduction of water i.e. the reduction of H^+ ions from the water molecules adsorbed on the steel surface:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{6}$$

Although this reaction is thermodynamically equivalent to hydrogen evolution, the difference in the reaction pathway means that this reaction is much slower and generally does not contribute significantly towards the total cathodic reaction under typical CO_2 service conditions where the aqueous pH will be typically less than 4.[47] This reaction tends to only play a significant role at very high pH, or very low partial pressures of CO_2.

7.1.2 Anodic reactions

In terms of anodic reactions, the electrochemical dissolution of iron in acid solutions:

$$Fe \rightarrow Fe^{2+} + 2e^- \tag{7}$$

has been studied extensively by researchers, with several multi-step mechanisms being used to explain experimental results. A detailed discussion of such steps is outside of the scope of this review. However, more detail on the proposed multi-step models can be found in the publication by Nešić et al.[51] who demonstrate the iron dissolution reaction is much more complicated than that shown in Reaction (7). The two electrons involved in the reaction are not released in one step, more a sequence of intermediate steps.

Considering both the anodic and cathodic reactions, the overall corrosion reaction can be represented as:

$$Fe + 2H_2CO_3 \rightarrow Fe^{2+} + 2HCO_3^- + H_2 \tag{8}$$

providing the solution does not become saturated with respect to $FeCO_3$.

7.1.3 $FeCO_3$ precipitation

In aqueous CO_2 environments when the concentration of Fe^{2+} and CO_3^{2-} ions exceed the solubility product it becomes thermodynamically favourable for $FeCO_3$ to form as a corrosion product on the steel surface.

$FeCO_3$ precipitation is a common occurrence in the oil and gas industry (particularly at high pH and high temperature) and is believed to occur via a one stage reaction with carbonates, or via a two stage reaction with bicarbonates[52, 53]:

$$\mathrm{Fe^{2+} + CO_3^{2-} \rightarrow FeCO_3} \tag{9}$$

$$\mathrm{Fe^{2+} + 2HCO_3^- \rightarrow Fe(HCO_3)_2} \tag{10}$$

$$\mathrm{Fe(HCO_3)_2 \rightarrow FeCO_3 + CO_2 + H_2O} \tag{11}$$

The driving force for precipitation of $FeCO_3$ is the supersaturation (S) which measures the extent to which the solubility of $FeCO_3$ is exceeded within the solution. Typically, a high degree of supersaturation is required in the bulk solution to obtain appreciable levels of precipitation onto the steel surface. The supersaturation is defined as:

$$S = \frac{[Fe^{2+}][CO_3^{2-}]}{K_{sp}} \tag{12}$$

where

$$K_{sp} = [Fe^{2+}]_{eq}[CO_3^{2-}]_{eq} \tag{13a}$$

$[\mathrm{Fe}^{2+}]$ and $[\mathrm{CO}_3^{2-}]$ (in mol/dm^3) are the concentrations of ferrous and carbonate ions, respectively. K_{sp} (in mol^2/dm^6) is the solubility product for $FeCO_3$, which is a function of ionic strength and temperature. $[\mathrm{Fe}^{2+}]_{\mathrm{eq}}$ and $[\mathrm{CO}_3^{2-}]_{\mathrm{eq}}$ are the concentrations of the species in equilibria.

The value of K_{sp} can be calculated using a unified equation developed by Sun and Nesic[54]:

$$log(K_{sp}) = -59.3498 - 0.041377(T_K) - \frac{2.1963}{T_K} + 24.5724log\,(T_K) + 2.518(I^{0.5}) - 0.657(I) \tag{13b}$$

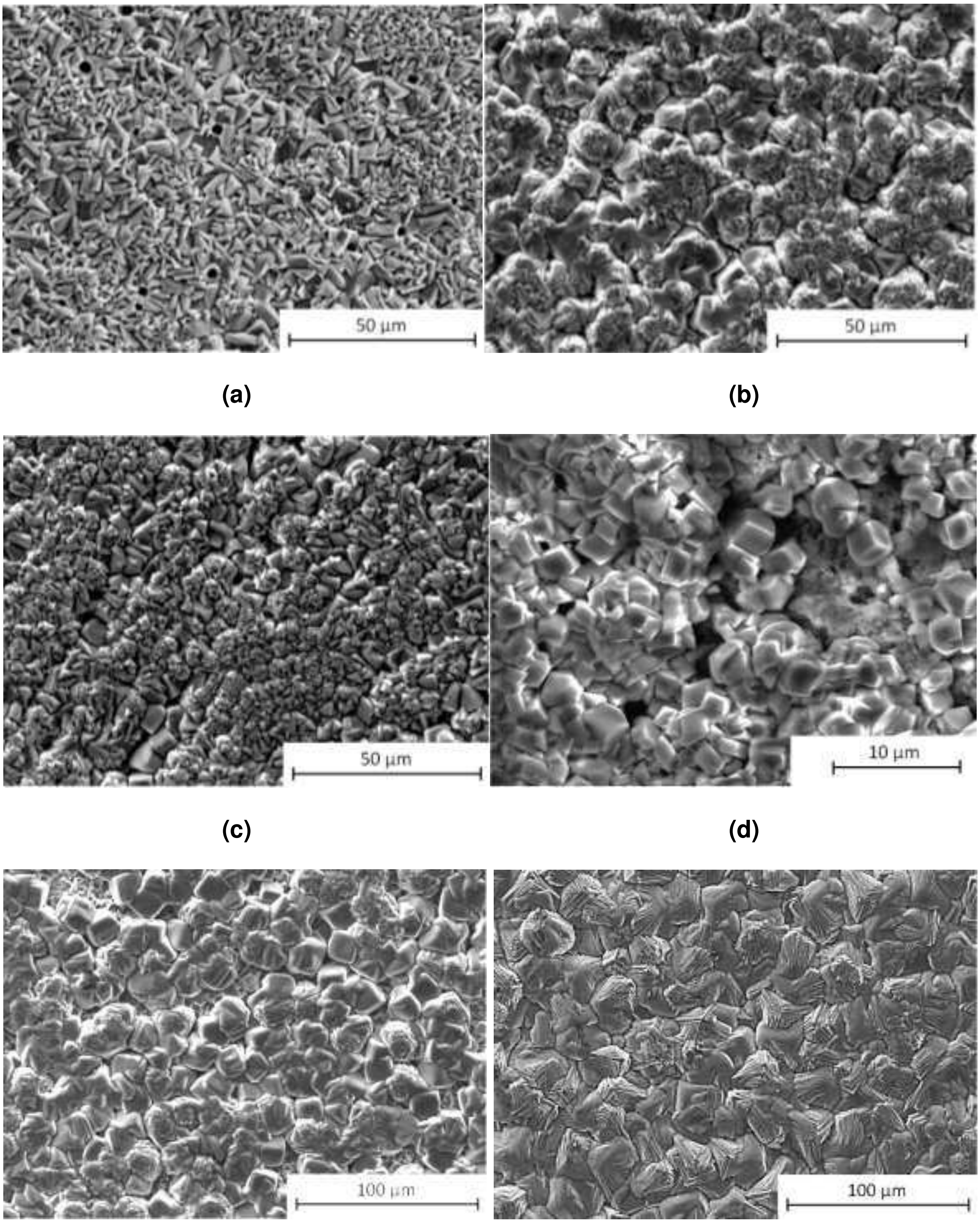
where T_K is the temperature in Kelvin and I is the ionic strength of the solution.

$FeCO_3$ films possess an interesting property in that they are capable of slowing down the corrosion kinetics at the steel surface by acting as a diffusion barrier to electrochemically active species, but also by a surface coverage effect where the $FeCO_3$ crystals adhere to the substrate. In some instances, the $FeCO_3$ layer is capable of reducing the corrosion rate of the underlying steel by over two orders of magnitude.

Understanding the factors which influence the rate of formation of this corrosion product are essential as part of a corrosion management strategy within the oil and gas industry and could be an important consideration in CO_2 pipeline transportation. Numerous studies have focused on determining factors which influence the protectiveness and kinetics of $FeCO_3$ formation under various oil and gas conditions as many operators are reliant on the protective properties of this film to minimise internal corrosion.[54-67] The question remains as to the ability for $FeCO_3$ to form and offer protection under the conditions typical of CCS, as much less information is known regarding the precipitation kinetics, formation and protective nature of $FeCO_3$ at higher pressure.

That being said, a number of authors have reported $FeCO_3$ precipitation onto carbon steel in supercritical CO_2 experiments under CCS conditions.**[4, 68-70]** Images of these observed films are provided in Figure 5 and bear a strong resemblance to those which develop under aqueous oil and gas conditions. The question which remains is whether such films are also capable of stifling the corrosion rate at the steel surface. Recent work by Hua et al.[70] has highlighted that specific morphologies of $FeCO_3$ formed under dense phase CO_2 are indeed capable of preventing both general and localised corrosion. Consequently, understanding the conditions conducive to the formation of $FeCO_3$ and how other impurities may influence

$FeCO_3$ precipitation kinetics, morphology and protectiveness is important for accurately determining the threat of internal corrosion in CO_2 pipelines.



(a) (b)

(c) (d)

(e) (f)

Figure 5: Examples of $FeCO_3$ films precipitated onto carbon steel surfaces under pure dense-phase CO_2 conditions with water; (a) from Choi et al.[4] – 8.0 MPa water-saturated CO_2 at 50°C after 24 h, (b) from Choi et al.[68] - 6.0 MPa water-saturated CO_2

at 50°C after 24 h, (c) from Choi et al.[68] - 4.0 MPa water-saturated CO_2 at 50°C after 24 h, (d) from Sim et al.[69] – 8.0 MPa CO_2 at 90°C with 50,000 ppm water after 7 days, (e) from Hua et al.[71] – 8.0 MPa water-saturated CO_2 at 50°C after 48 h and (f) from Hua et al.[70] – 8.0 MPa water-saturated CO_2 at 35°C after 7 days.

Although all the aforementioned anodic, cathodic and precipitation reactions outlined are capable of occurring during dense phase CO_2 transport when water condenses onto the steel surface and becomes saturated with CO_2, the corrosion rates and corrosion product precipitation kinetics can be markedly different to those observed in systems where water is the dominant phase. In a system where the dominant fluid is CO_2 and is at considerably higher pressures, the water content in the system is critical in influencing the extent of degradation observed. Understanding how the different process fluid and operating conditions change the degradation and precipitation kinetics is crucial towards developing a robust pipeline integrity management strategy.

7.1.4 Influence of O_2 on CO_2 corrosion

The introduction of O_2 to CO_2 corrosion systems has been evaluated in the context of oil and gas transportation and has been reported to have a two-fold effect on corrosion behaviour; firstly, by introducing an additional cathodic reaction (for acidic solutions)[41], which can potentially accelerate the level of corrosion:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \tag{14}$$

and secondly, through the ability of O_2 to inhibit the formation of protective $FeCO_3$ by oxidising ferrous ions to ferric ions, resulting in the formation of non-protective iron oxide.[4] Observations on the effect of O_2 at high pressure appear contradictory in the literature and are discussed in the following sections.

7.2 Anticipated corrosion rates in CO_2-H_2O and CO_2-H_2O-O_2 environments

In relation to the literature focusing on carbon steel corrosion specifically in dense phase CO_2-H_2O-O_2 systems, a full summary of recent studies is provided in Table 5 and is discussed within the following paragraphs. A number of studies have been performed considering the degradation of carbon steel in both water-saturated and under-saturated environments over the past few years. The overall consensus from the corrosion rate data in Table 5 for CO_2-H_2O and CO_2-H_2O-O_2 systems is that *uniform* corrosion rates are generally very low (<0.08 mm/year) when water is below the solubility limit. However, when the CO_2

phase becomes saturated with water or approaches the saturation limit, the level of attack becomes significantly greater.

One concern in terms of pipeline integrity is the magnitude of localised corrosion rates reported by some researchers in the end column of Table 5. It is apparent that the extent of pitting/localised attack on the surface can be approximately one order of magnitude greater than the general corrosion rates, even when water content is well below the solubility limit. For example, Sim et al.[69] found that a molar concentration of ~900 ppm water in supercritical CO_2 at 40°C and 8.0 MPa produced a general corrosion rate of ~0.08 mm/year, whereas the localised corrosion rate was recorded at a maximum of ~0.65 mm/year over 168 hours of exposure. Similarly, Hua at al.[71] recorded general corrosion rates increasing from 0.003 to 0.1 mm/year as water content was increased from 700 ppm to water-saturated conditions at 35°C and 8.0 MPa, while localised corrosion rates ranged from 0.29 to 0.92 mm/year based on 48 hour experiments.

Given these high penetration rates it is important to stress that the stated pitting rates are only a reflection on the average mm/year over the test duration. Whether the pits identified are stable and continue to propagate at the same rate indefinitely is a fundamental question and requires further research. Nonetheless, the results highlight the potential severity and importance of understanding the extent of localised attack in such systems. It is also clear from a review of the work of Dugstad et al.[3, 25] Hua et al.[70-72] and Sim et al.[69] that localised corrosion of mild steel does appear to be prevalent in supercritical CO_2 systems containing water. Hence, it is critical that the occurrence of localised corrosion in such environments is taken into account when defining the safe water content. Furthermore, it is important to have in place a procedure to allow systematic and accurate quantification of the extent of attack to ensure that the pitting rates determined are indicative of the test conditions. It is also essential to understand the initiation, propagation and stability of pits in such environment to ascertain whether they would present themselves as a long term threat in the field. It is clear that very little attention has been directed towards quantifying *localised* corrosion in supercritical CO_2 systems where CO_2 is the dominant phase, yet pitting/localised corrosion have the potential to be a key concern in such environments if pits remain stable and continue to propagate.

Another interesting observation from Table 5 is that the effect of pressure appears not to have a particularly significant influence on corrosion rate in conditions typical of CCS. Choi and Nesic[68] found that the increase in CO_2 pressure from 4.0 to 8.0 MPa produced only a marginal effect on general corrosion rate in water-saturated experiments, increasing the uniform thickness loss rate from approximately 0.2 to 0.4 mm/year.

With regards to the influence of temperature, research has indicated that for the same total system pressure, a change in temperature can have a significant influence on the critical water content required to initiate corrosion in a particular system. Hua et al.[71] showed that X65 samples exposed to conditions at 50°C and 80 bar produced no corrosion when water content was below 1600 ppm, whilst small levels of corrosion were recorded at as low as 300 ppm water at 35°C under the same pressure.

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. Some of the first experimental work to determine the corrosion rates of carbon steel in water-saturated CO_2-H_2O-O_2 environments was performed by Choi and co-workers[4]. Tests conducted over 24 hours at a pressure of 8.0 MPa and temperature of 50°C indicated that the presence of up to 0.33 MPa O_2 resulted in an increase in general corrosion rate by delaying the onset of $FeCO_3$ film formation on the steel surface and providing an additional cathodic reaction. Corrosion rates recorded by Choi and colleagues[4] for X65 steel ranged from 0.38 to 1.05 mm/year as a result of increasing O_2 concentration. In contrast, Hua et al.[73] evaluated the influence of lower O_2 contents (0, 20, 500 and 1000 ppm) on both the general and localised corrosion of X65 steel at 8.0 MPa CO_2 and 35°C. The introduction of O_2 under these conditions was shown to reduce the general corrosion rate of X65 due to the establishment of an iron oxide film, but promoted severe localised/pitting corrosion. The difference in behaviour could be attributed to the lower operating temperature as other authors have reported O_2 to both reduce general corrosion but accelerate localised attack at lower temperatures.[74] There appears to be a balance between the passivating effect of iron oxides and the enhancement of the cathodic reaction due to O_2 presence which could be largely dependent upon the operating temperature and the concentration of O_2 in the system. It is clear that further research is required to elucidate the effect of O_2 presence at the concentrations anticipated for CO_2 transport.

Table 5: Summary of literature relating to corrosion rates in supercritical CO_2 with H_2O and O_2 as impurities

	CO_2 pressure (MPa)	**O_2 pressure (MPa unless stated)**	**Temp (°C)**	**Test period**	**Water content (ppm in mole)**	**Corrosion Rate (mm/year)**	
						General (test rotation speed in brackets)	**Localised**
Choi, Nesic and Young[4]	8.0	0	50	24 h	Water-saturated CO_2 (10 g water added to autoclave)	~0.4	n/a
		0.16				~0.6	n/a
		0.33				~1.05	n/a
		0.51				~0.9	n/a
Choi and Nesic[68]	4.0	0	50	24 h	Water-saturated CO_2 (400 ml water added to autoclave)	~0.2	n/a
	6.0					~0.2	n/a
	8.0					~0.4	n/a
Choi and Nesic[27]	8.0	0.33	50	24 h	650 ppm	<0.01	n/a
					2000 ppm	<0.01	n/a
					3000 ppm	<0.01	n/a
Dugstad et al.[75]	10.0	0	20	30 days	500 ppmw (~1200 ppm)	No attack (3 rpm)	No attack
		200 ppm				No attack (3 rpm)	No attack
Sim et al.[69]	8.0	0	40	168 h	~900 ppm	~0.08	Av. ~0.22 Max ~ 0.65
					~1800 ppm	~0.07	Av. ~ 0.30 Max ~ 0.64
					~2600 ppm	~0.06	Av. ~ 0.22 Max ~ 0.55
					~3500 ppm	~0.08	Av. ~ 0.22 Max ~ 0.65
					Water-saturated CO_2 (1.5g water added to autoclave)	~0.08	Av. ~ 0.19 Max ~ 0.50
Brown et al.[76]	10.0	500 ppm	4	168 h	500 ppm	0.008 (3 rpm)	n/a
			4			<0.005 (3 rpm)	n/a
			50			0.006 (3 rpm)	n/a
			50			<0.005 (3 rpm)	n/a
Hua et al.[71]	8.0	0	35	48 h	300 ppm	0.003	0
					700 ppm	0.005	~0.29
					1770 ppm	0.027	~0.62
					2800 ppm	0.068	~0.85
					Water-saturated CO_2 (3 g water added to autoclave)	0.10	~0.92
			50		700 ppm	No attack	No attack
					1600 ppm	No attack	No attack
					2650 ppm	0.014	0.20
					Water-saturated CO_2 (3 g water added to autoclave)	0.024	1.99
Hua et al.[70]	8.0	0	35	14 h	Water-saturated CO_2 (3 g water added to autoclave)	0.10	0.92
				48 h		0.10	0.92
				96 h		0.03	0.96

Hua et al.[73]	8.0	0 ppm	35	48 h	Water-saturated CO_2 (10 g water added to autoclave)	0.10	0.92
		20 ppm				0.09	1.10
		500 ppm				0.07	1.24
		1000 ppm				0.03	3.13
		1000 ppm	35	48 h	300 ppm	0	0
					650 ppm	0	0
					1200 ppm	0.002	0
					1770 ppm	0.005	0.39
					2800 ppm	0.012	0.77

7.3 CO_2-H_2O-SO_2-O_2 environments

Any additional contaminants entering the CO_2 stream (such as SO_2 and NO_x in particular) will segregate into the aqueous phase, potentially lowering the solution pH further and increasing the corrosivity of the environment.[77]

When SO_2 and O_2 are present together, the formation of sulphurous (H_2SO_3) and/or sulphuric (H_2SO_4) acid is permitted, which can play a key role in, not only the corrosion mechanisms, but also in the nature and morphology of any corrosion products formed on the steel surface which may indirectly inhibit or accelerate the corrosion kinetics.

7.3.1 Additional corrosion and precipitation reactions in CO_2-H_2O-SO_2-O_2 environments

Currently, the minimum water content required in dense phase CO_2 for acid formation in the presence of SO_2 is not known[26], but the detection of $FeSO_3$ and $FeSO_4$ on the steel surface in numerous experiments indicate that reactions occur at water contents considerably lower than the water solubility in pure CO_2-H_2O systems[3, 4, 26, 76, 78, 79]. It is still not clear whether SO_2 reacts with water in the bulk solution to form an acid, or if a thin condensed layer of water is initially formed on the steel surface which then reacts with SO_2. However, the postulated reaction mechanisms associated with $FeSO_3$ formation have been suggested using the following steps:[80]

i. Firstly, SO_2 is believed to dissolve into the condensed water film on the surface and subsequently becomes ionised:

$$H_2O + SO_2 \rightarrow H^+ + HSO_3^{2-} \tag{15a}$$

$$HSO_3^{2-} \rightarrow H^+ + SO_3^{2-} \tag{15b}$$

ii. The cathodic reaction then occurs via the direct reduction of hydrogen ions:

$$2H^+ + 2e^- \rightarrow H_2 \tag{16}$$

iii. The formation of $FeSO_3$ then occurs via a precipitation process:

$$Fe^{2+} + SO_3^{2-} \rightarrow FeSO_3 \tag{17}$$

$FeSO_3 \cdot 3H_2O$ has been observed on carbon steel surfaces by both Choi et al.[4], Xiang et al.[80] and Hua et al.[78, 81] in SO_2-containing dense phase CO_2 experiments. Additionally, both Choi et al.[4] and Xiang et al.[80] detected the presence of $FeSO_4$ when O_2 was introduced into the system. It was suggested by Choi and co-workers[4] that the addition of O_2 not only results in an additional cathodic reaction (Equation 18a), but it also enables the oxidation of sulphite ions to sulphate ions (Equation 18b):

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \tag{18a}$$

$$2SO_3^{2-} + O_2 \rightarrow 2SO_4^{2-} \tag{18b}$$

Enabling $FeSO_4$ to form via the following reaction:

$$Fe^{2+} + SO_4^{2-} \rightarrow FeSO_4 \tag{19}$$

$FeSO_4$ was also believed by Choi et al.[4] to undergo further oxidation to become FeOOH in the presence of O_2 in an acid regeneration process:

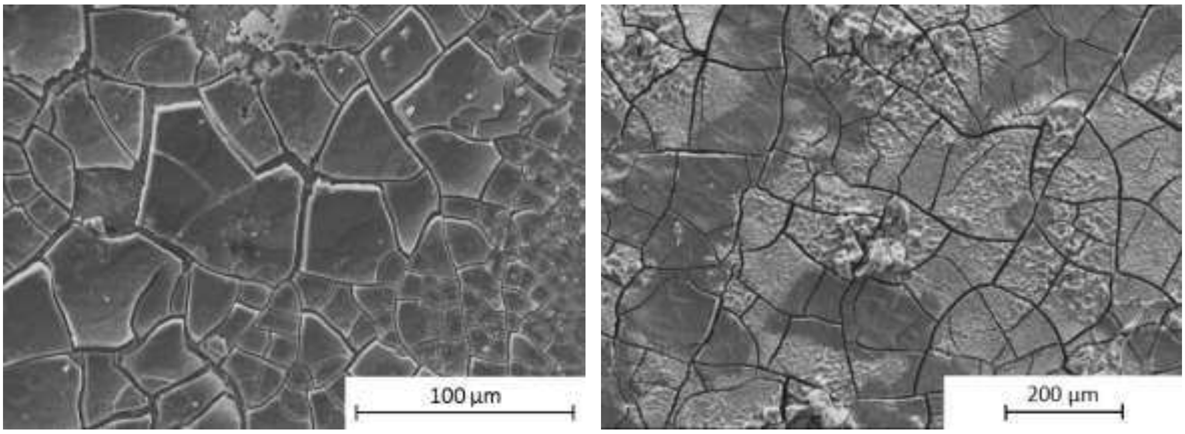
$$4\,FeSO_4 + 6H_2O + O_2 \rightarrow 4\,FeOOH + 4H_2SO_4 \tag{20}$$

Examples of the typical corrosion product films encountered by numerous authors in CO_2-H_2O-SO_2-O_2 environments are provided in Figure 6. In general, three typical corrosion morphologies are reported in literature; a thin sulphur-rich cracked film[27, 78, 82, 83] (Figures 6(a), (b) and (c)), columnar/spherical crystals of $FeSO_3$/$FeSO_4$[4, 78, 84] (Figures 6(d), (e) and (f)), and globular crystals of $FeCO_3$[78, 81] (Figures 6(g) and (h)).

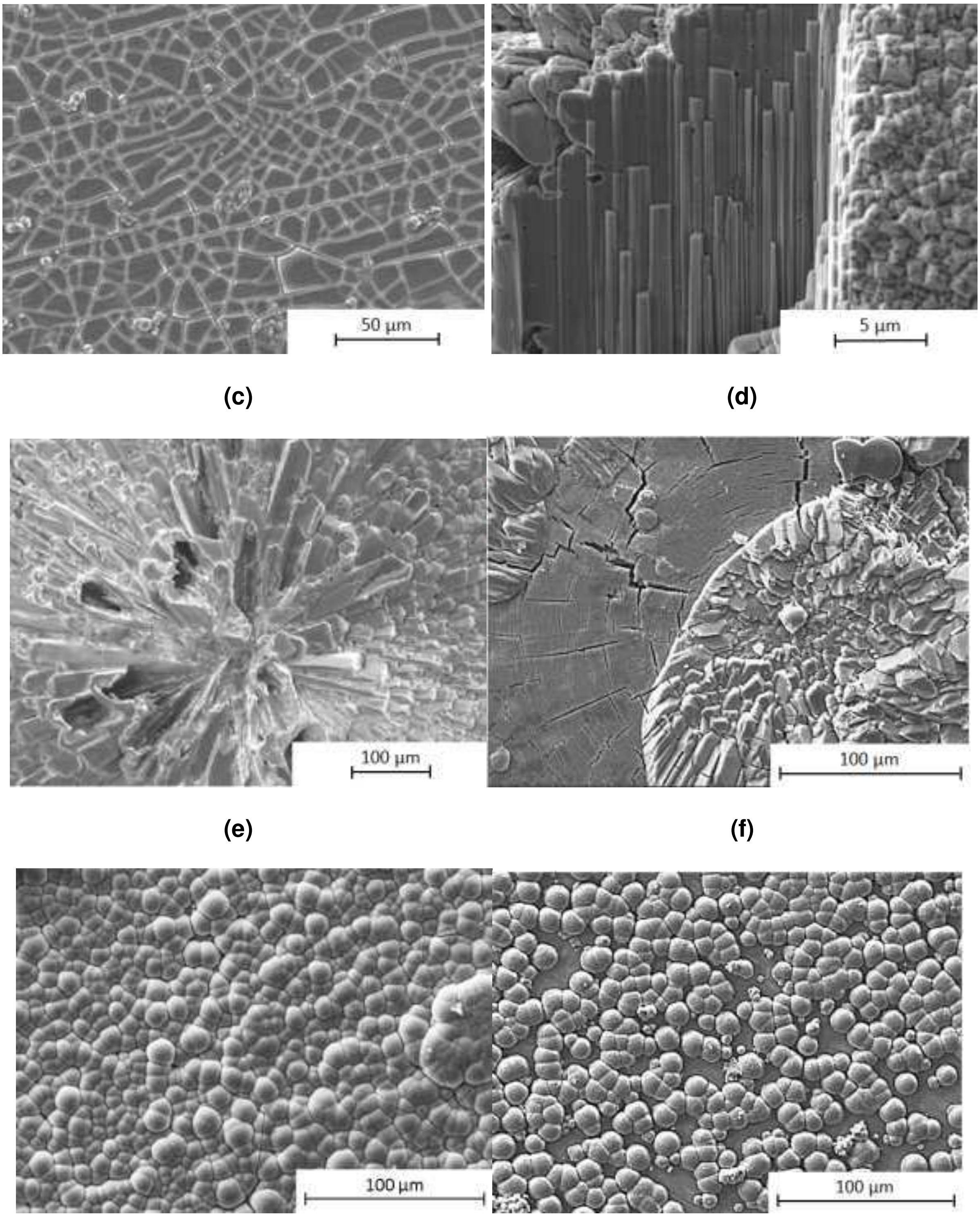
The presence of the thin sulphur-rich film (which has presented difficulty in terms of characterisation) is believed to offer little protection to the steel substrate by some authors[85] as the cracks in the film are considered to provide channels required for the transport of reactants and products to and from the steel surface, respectively. However, no evidence exists to support this statement and it is not clear as to whether these cracks appear due to dehydration of the film upon removal from the autoclave after testing is complete.

In terms of the columnar and spherical crystals of $FeSO_3$ and $FeSO_4$, little evidence has been provided to support the protectiveness of such a corrosion product. However, Xiang et al.[84] have utilised focused ion beam etching to look into the structure of a spherical $FeSO_4$ corrosion product (shown in Figure 6(d)). Observations from the etching process revealed that small micro-pores existed within the crystalline film, but these were not connected and could not provide necessary channels to facilitate the corrosion process. It was therefore postulated that such a film could offer corrosion protection. To support this statement, further work by Xiang et al.[85] involved understanding the corrosion rate of X70 steel as a function of immersion time in water-saturated CO_2 at 10.0 MPa and 50°C in the presence of 1000 ppm O_2 and 0.2 MPa SO_2. Exposure times of 24, 72, 120 and 192 hours were considered and results indicated that the corrosion rate reduced as a function of time from 2.0 to 0.7 mm/year in conjunction with the formation and growth of a hydrated $FeSO_3/FeSO_4$ crystalline surface scale. The authors believed that the results suggested the corrosion deposits were capable of reducing the dissolution of the underlying steel. However, the reduction in corrosion rate could potentially be attributed to consumption of SO_2 throughout the experiment as it reacted with the steel surface, and this fact should not be discounted.

With regards to the $FeCO_3$ films observed in Figures 6(g)and (h), this particular morphology of corrosion product has only been observed at low concentrations of SO_2 (2 to 100 ppm range) as higher concentrations of SO_2 have been shown to completely dominate the corrosion process and prevent any formation of $FeCO_3$.[34, 35] At low concentration, the presence of SO_2 is capable of changing the structure of the $FeCO_3$ film from that typically observed in Figure 5. Again, further work is required to define whether such a film is capable of offering protection to the steel substrate.



(a) **(b)**



(c) (d)

(e) (f)

(g) (h)

Figure 6: Examples of corrosion products formed on carbon steel surfaces under dense-phase CO_2 conditions containing water, SO_2 and O_2; (a) thin cracked sulphur-rich film from Hua et al.[78] – water-saturated CO_2 at 8.0 MPa and 35 °C containing 50 ppm SO_2 and 20 ppm O_2 after 48 h; (b) thin cracked sulphur-rich film from Choi et al.[27] – 8.0 MPa CO_2, 0.33 MPa O_2 and 0.08 MPa SO_2 and 50 °C with 650 ppm water after

24 h; (c) thin cracked sulphur-rich film from Farelas et al.[83] – 8.0 MPa CO_2, 0.08 MPa SO_2 and 50°C with 650 ppm water after 24 h; (d) focused ion beam etching through $FeSO_4$ spherical agglomeration of crystals from Xiang et al.[84]] – water-saturated CO_2 at 10.0 MPa and 93°C containing 0.2 MPa SO_2 and 0.002 MPa O_2 (e) $FeSO_3$ crystals from Choi et al.[4] - water-saturated CO_2 at 8.0 MPa and 50°C containing 0.08 MPa SO_2 after 24 h; (f) $FeSO_3$ crystals from Hua et al.[78] - water-saturated CO_2 at 8.0 MPa and 35°C containing 100 ppm SO_2 and 20 ppm O_2 after 48 h; (g) Globular $FeCO_3$ crystals from Hua et al.[78] - water-saturated CO_2 at 8.0 MPa and 35°C containing 100 ppm SO_2 and 20 ppm O_2 after 48 h; (h) Globular $FeCO_3$ crystals from Hua et al.[81] - water-saturated CO_2 at 8.0 MPa and 35°C containing 2 ppm SO_2 and 20 ppm O_2 after 48 h

7.3.2 Anticipated corrosion rates in CO_2-H_2O-SO_2-O_2 environments

In reference to the literature relating to the corrosion of carbon steel in supercritical CO_2-H_2O-SO_2-O_2 systems, Table 6 provides a summary of corrosion experiments performed by numerous authors. The results within this table are discussed within the following paragraphs.

Referring to Table 6, a number of authors are in agreement that the presence of SO_2 and SO_2/O_2 are detrimental to pipeline integrity if a particular water content is exceeded. Investigators have shown that increasing SO_2 concentration in dense phase CO_2 results in an increase in general corrosion rate[4, 83, 86] and can also promote localised corrosion under $FeSO_3/FeSO_4$ deposits.[76] Some authors have also demonstrated a noticeable synergy existing between SO_2 and O_2 which results in the synergistic corrosion rate being greater than the sum of the individual corrosion rates from the presence of SO_2 and O_2 individually.[4] This observation is attributed to the ability of O_2 to react with SO_2 and water to produce sulphuric acid (H_2SO_4), as will be discussed later.

Table 6 also shows that SO_2 or SO_2 and O_2 combined are capable of increasing the corrosion rate in under-saturated conditions. In particular, Choi and Nesic[27] evaluated the corrosion behaviour of X65 carbon steel in conditions with a water content of 650 ppm whilst SO_2 and O_2 content were varied in a 8.0 MPa/50°C system containing supercritical CO_2. After 24 hours of exposure, the corrosion rate of X65 in the absence of O_2 and SO_2 at 650 ppm water was less than 0.01 mm/year. Increasing SO_2 content to 0.08 MPa without the presence of O_2 increased corrosion rate to 3.48 mm/year and further addition of 0.33 MPa O_2 along with 0.08 MPa SO_2 increased general corrosion rate to 3.70 mm/year, demonstrating that corrosion can be excessive in the presence of SO_2 and SO_2/O_2 combinations, even at low water contents recommended by pipeline operators. However, SO_2 and O_2 concentrations of this magnitude are unlikely to be encountered during typical

CO_2 service. The SO_2 impurity concentrations evaluated by Choi and Nesic[27] and Farelas et al.[86] could be regarded as being very high when compared with the proposed impurity limits outlined by the DYNAMIS project and Alstom in Table 4, which suggest a lower limit of 100 ppm.

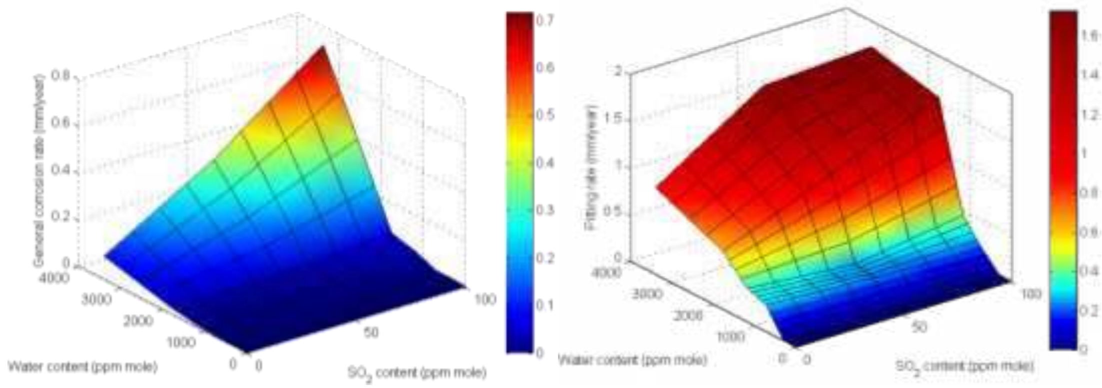
Under conditions which could be argued to be more reflective of the field, Dugstad et al.[75] performed a study to understand the effect of SO_2 and O_2 on the corrosion of carbon steel. In this work, SO_2 and O_2 contents of 200 and 100 ppm, respectively were chosen. For initial tests involving pure CO_2 with 1220 ppm water at 10.0 MPa and 20℃, no corrosion was observed after 30 days of exposure. Likewise, when 200 ppm O_2 was introduced to the same system at the same water content, no corrosion was recorded over the same test duration. However, introducing 200 ppm SO_2 and 100 ppm O_2 to the autoclaves at a lower water content of 200 ppm resulted in corrosion rates of approximately 0.01 mm/year, indicating SO_2 can enhance the corrosion process and lower the critical water content required for corrosion to occur under realistic SO_2/O_2 combinations expected under normal CO_2 service conditions for anthropogenic transport.

Two studies in literature have also considered the influence of SO_2 on the critical water content required to prevent substantial corrosion during CO_2 service. Xiang et al.[79] performed a series of experiments on X70 steel at 10.0 MPa and 50℃ over 120 hours. A partial pressure of 0.2 MPa SO_2 and an O_2 content of 1000 ppm were added to supercritical CO_2 and relative humidity values of 9, 50, 60, 70, 88 and 100% (414 to 4600 ppm) were considered. The results indicated that the onset of appreciable levels of corrosion (>0.1 mm/year) occurred when a humidity content of 60% (2760 ppm) was exceeded. In a another study, Hua et al.[78] evaluated the minimum water content required to avoid both general and localised corrosion of X65 carbon steel in the presence of SO_2 and O_2. Corrosion experiments were performed in autoclaves containing supercritical CO_2 at 8.0 MPa and 35℃ in the presence of 0, 50 and 100 ppm SO_2 and water contents from 0 ppm to water-saturated CO_2. Figure 7 shows a selection of the results obtained and indicates the importance of considering localised corrosion rates of carbon steel in supercritical CO_2 systems by providing a comparison between the general and localised attack on X65 steel under various stream compositions. Again, it is perhaps worth noting that the localised corrosion rates are based on pit depths over 48 hours of exposure and there is no certainty that the pitting rates can be extrapolated to provide realistic rates over the lifetime of the pipeline.

Table 6: Summary of literature relating to corrosion rates in supercritical CO_2 with H_2O, SO_2 and O_2 as impurities

	CO_2 pressure (MPa)	O_2 content (MPa unless stated)	SO_2 content (MPa unless stated)	Temp (°C)	Test period	Water content (ppm in mole)	Corrosion Rate (mm/year)	
							General (test rotation speed in brackets)	Localised
Choi, Nesic and Young[4]	8.0	0.33	0.08	50	24 h	0 ppm	No attack	No attack
		0	0			Water-saturated CO_2 (10 g water added to autoclave)	~0.4	n/a
		0.33	0				~1.0	n/a
		0	0.08 (1%)				~5.6	n/a
		0.33	0.08 (1%)				~7.0	n/a
Choi and Nesic[27]	8.0	0	0	50	24 h	650 ppm	< 0.01	n/a
		0	0.08 (1%)				3.48	n/a
		0.33	0.08 (1%)				3.70	n/a
Dugstad et al.[75]	10.0	0	0	20	30 days	500 ppmw (~1220 ppm)	No attack	No attack
		200 ppm	0		30 days	500 ppmw (~1220 ppm)	No attack	No attack
		100 ppm	1000 ppm		7 days	200 ppmw (~488 ppm)	0.01	n/a
		100 ppm	200 ppm		7 days	200 ppmw (~488 ppm)	< 0.01	n/a
Dugstad et al.[3]	10.0	0	0	25	14 days	488 ppm	No attack (3 rpm)	No attack
		0	0			1220 ppm	No attack (3 rpm)	No attack
		0	100 ppm			488 ppm	< 0.005 (3 rpm)	n/a
		0	344 ppm			488 ppm	< 0.005 (3 rpm)	n/a
		0	344 ppm			1220 ppm	0.02 (3 rpm)	n/a
Farelas et al.[86]	8.0	0	0	50	24 h	650 ppm	0	n/a
			0.008 (0.1%)				0.03	n/a
			0.004 (0.05%)				0.05	n/a
			0.008 (0.1%)	25 (Liquid CO_2)			0.1	6.8
			0.004 (0.05%)				~0	2.4
			0.008 (0.1%)				~0.019 (1000 rpm)	n/a
			0.008 (0.1%)				~0.013 (1000 rpm)	n/a
Xiang et al.[80]	10.0	1000 ppm	0.02 (0.2%)	50	288 h	Water-saturated CO_2 (6 g water added to autoclave to ensure saturation)	0.2 (120 rpm)	n/a
			0.07 (0.7%)				0.7 (120 rpm)	n/a
			0.14 (1.4%)				0.85 (120 rpm)	n/a
			0.2 (2%)				0.9 (120 rpm)	n/a
Xiang et al.[85]	10.0	1000 ppm	0.2 (2%)	50	24 h	Water-saturated CO_2 (3 g water added to autoclave to ensure saturation)	2.0 (120 rpm)	n/a
					72 h		1.8 (120 rpm)	n/a
					120 h		1.4 (120 rpm)	n/a
					192 h		0.7 (120 rpm)	n/a
Xiang et al.[79]	10.0	1000 ppm	0.2 (2%)	50	120 h	414 ppm	~0 (120 rpm)	n/a
						2300 ppm	~0.04 (120 rpm)	n/a
						2760 ppm	~0.08 (120 rpm)	n/a
						3220 ppm	~0.35 (120 rpm)	n/a
						4048 ppm	~0.9 (120 rpm)	n/a
						Water saturated CO_2 (~4600 ppm)	~1.5 (120 rpm)	n/a
Brown et al.[76]	10.0	0	200 ppm	4	7 days	500 ppm	0.022 (3 rpm)	n/a
		0					0.022 (3 rpm)	n/a
		500 ppm					0.006 (3 rpm)	n/a
		500 ppm					0.009 (3 rpm)	n/a

		500 ppm					0.013 (3 rpm)	n/a
		0	100 ppm	50			No attack (3 rpm)	n/a
		0	200 ppm				<0.005 (3 rpm)	n/a
		0	100 ppm	4		50 ppm	No attack (3 rpm)	n/a
		0					No attack (3 rpm)	n/a
		200 ppm					No attack (3 rpm)	n/a
		10000 ppm					No attack (3 rpm)	n/a
		0		50			<0.005	n/a
		200 ppm					No attack (3 rpm)	n/a
		500 ppm					No attack (3 rpm)	n/a
							No attack (3 rpm)	n/a
Hua et al.[81]	8.0	0	0	35	48 h	Water-saturated CO_2 (3 g water added to autoclave)	0.10	0.92
		20 ppm	2 ppm				0.12	1.26
		20 ppm	50 ppm				0.37	1.66
		20 ppm	100 ppm				0.72	1.72
Hua et al.[78]	8.0	0	0	35	48 h	310 ppm	0.003	n/a
						1185 ppm	0.005	0.29
						1770 ppm	0.009	0.36
						3400 ppm	0.027	0.62
						Water-saturated CO_2 (3 g water added to autoclave)	0.100	0.92
		20 ppm	50 ppm			310 ppm	0.003	n/a
						1185 ppm	0.006	0.23
						1770 ppm	0.009	0.26
						3400 ppm	0.028	1.09
						Water-saturated CO_2 (3 g water added to autoclave)	0.368	1.66
		20 ppm	100 ppm			310 ppm	0.003	n/a
						1185 ppm	0.004	0.18
						1770 ppm	0.039	0.44
						3400 ppm	0.067	1.55
						Water-saturated CO_2 (3 g water added to autoclave)	0.716	1.72



(a) **(b)**

Figure 7: Surface plots for X65 carbon steel to indicate the variation of (a) general and (b) pitting/localised corrosion rates as a function of SO_2 and water content in static dense phase CO_2 at 35℃ and 8.0 MPa over 48 h of exposure – from Hua et al.[78]

From the information produced by Hua et al.**[78]** in Figure 7 it was possible to establish the critical water content to maintain general and localised corrosion rates below a threshold of 0.1 mm/year, as shown in Figure 8. The results obtained indicated that the presence of SO_2 significantly reduces the critical water content required to maintain a general corrosion rate below 0.1 mm/year, from ~3400 ppm to ~1850 ppm. However, the water content required to avoid excessive localised corrosion was far less than that to prevent significant general corrosion and reduced from approximately 500 ppm to 400 ppm as SO_2 content was increased from 0 to 100 ppm. These results are in agreement with a systematic study performed by Brown et al.[76]. In their extensive parametric study, water content was maintained at 500 ppm in a 10.0 MPa system. Only temperatures of 4 and 50°C were considered whilst O_2 and SO_2 content were varied from 0 to 10000 ppm and from 100 to 200 ppm, respectively (see Table 6 for further details). At 500 ppm water, all experiments produced general corrosion rates below 0.03 mm/year regardless of operating temperature. However, most of the specimens experienced localised attack or produced small visibly stained regions on the surface. The local corrosion rates under the clusters of $FeSO_3$/$FeSO_4$ corrosion product were much higher than those reported by mass loss, but were not determined.

In additional tests, Brown et al.[76] reduced the water content to 50 ppm. At such low water content, all general corrosion rates were below 0.005 mm/year for SO_2 contents up to 100 ppm and O_2 concentrations up to 10000 ppm (at 10.0 MPa and 4/50℃). These results suggest that a water concentration limit of 500 ppm may not be substantial enough to completely prevent corrosion in systems where SO_2 content can be as high as 200 ppm.

The research by Hua et al.[78] and Brown et al.[76] highlight that reducing water content is a more favourable option compared to reducing SO_2 content to minimise internal pipeline corrosion during transportation, as significant level of pitting corrosion were still observed in the absence of SO_2 when water content was high enough.

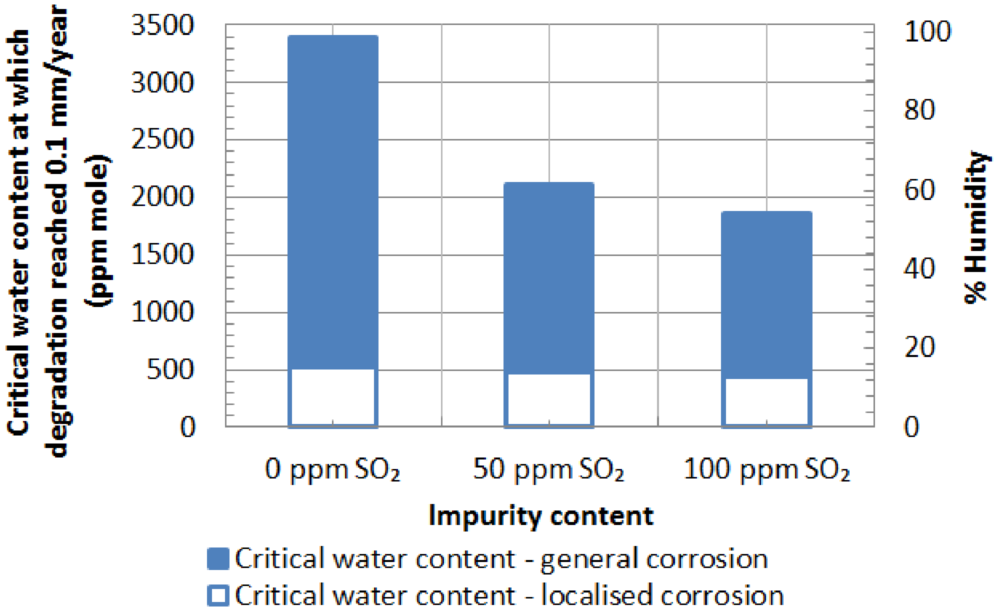


Figure 8: Critical water content at which 0.1 mm/year corrosion rate is reached from the perspective of general and localised corrosion for X65 steel. Conditions are 35°C and 8.0 MPa in supercritical CO_2 with 48 h exposure – from Hua et al.[78]

7.4 CO_2-H_2O-O_2-NO/NO_2 environments

The lack of experimental data in impure dense phase CO_2 is particularly noticeable for systems containing NO_x as an impurity. It is known that NO_2 is highly soluble in water and capable of reacting to produce nitric acid and NO under atmospheric conditions[26] and it has been suggested that the following reaction could also occur in dense phase CO_2[26]:

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO \tag{21}$$

Which will serve to reduce the pH of the aqueous phase and accelerate the rate of the cathodic hydrogen evolution reaction.

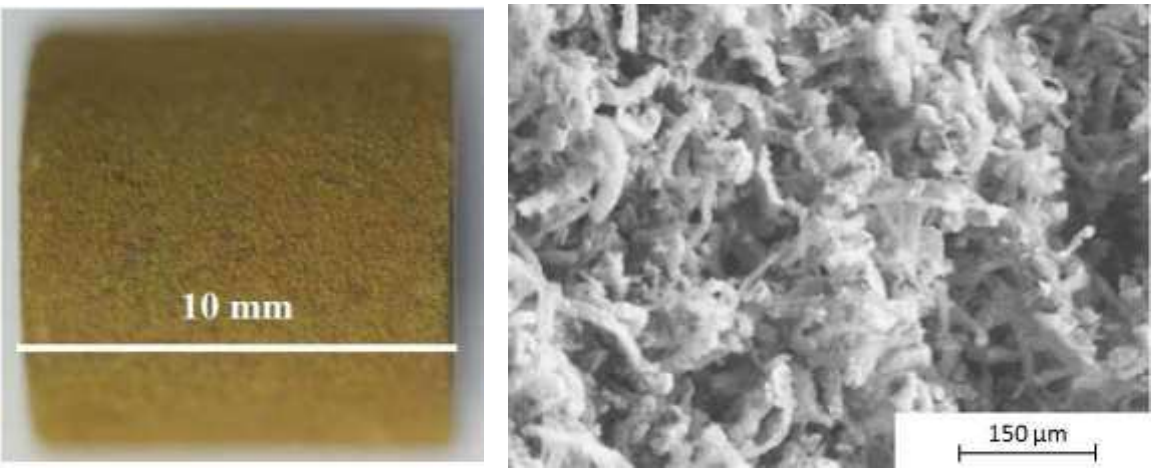
Some of the most recent work performed to evaluate the influence of NO and NO_2 has been performed by Brown et al.[76] (as part of the second phase of the CO_2PIPETRANS Joint Industry Project) as well as by Dugstad et al.[3]. The results from these two studies are provided in Table 7 and discussed in the following sections.

Brown et al.[76] presented results from 16 different carbon steel corrosion experiments involving various concentrations of O_2, NO and NO_2 at a pressure of 10.0 MPa and temperatures of 4 and 50℃ (see Table 7). Out of a total matrix of 31 experiments performed (which also included assessing the effect of SO_2 and H_2S without NO_x present) Brown et al.[76] reported that corrosion rates were the highest in the presence of NO and NO_2. Specific tests in the presence of 200 ppm NO_2 and 500 ppm O_2 resulted in the general corrosion rate reaching 0.275 mm/year with only a water content of 500 ppm. A distinct trend was noticed in that corrosion rates rapidly reduced as a function of test duration from 1 to 7 days in such experiments. It is postulated that the reduction in corrosion rate is attributed to the rapid consumption of impurities within the system, as opposed to the formation a protective corrosion product. This was based on evidence that the presence of NO_2 results in the formation of a brown/orange coloured dusty, porous film which was very easily removed from the steel surface.[3, 76] The appearance and morphology of typical corrosion products produced on the steel surface during NO_2 experiments is provided in Figure 9 which is from the work of Dugstad et al.[3].

Table 7: Summary of literature relating to corrosion rates in supercritical CO_2 with H_2O, NO_2, NO and O_2 as impurities

	CO_2 pressure (MPa)	O_2 content (ppm unless stated)	NO_2 content (ppm unless stated)	NO content (ppm unless stated)	Temp (°C)	Test period	Water content (ppm in mole)	Corrosion Rate (mm/year)	
								General (test rotation speed in brackets)	Localised
Brown et al.[76]	10.0	0	200	0	4	7 days	500	0.017 (3 rpm)	n/a
		500	200	0		3 days		0.2 (3 rpm)	n/a
		500	200	0		3 days		0.21 (3 rpm)	n/a
		0	0	200		7 days		<0.05 (3 rpm)	n/a
		500	0	200		7 days		0.082 (3 rpm)	n/a
		0	50	0	50	1 day		0.127 (3 rpm)	n/a
		500	50	0		1 day		0.116 (3 rpm)	n/a
		0	100	0		7 days		0.02 (3 rpm)	n/a
		500	100	0		1 day		0.182 (3 rpm)	n/a
		0	200	0		1 day		0.205 (3 rpm)	n/a
		0	200	0		3 days		0.088 (3 rpm)	n/a
		0	200	0		7 days		0.025 (3 rpm)	n/a
		500	200	0		1 day		0.275 (3 rpm)	n/a
		500	200	0		7 days		0.09 (3 rpm)	n/a
		0	0	200		7 days		0.013 (3 rpm)	n/a
		500	0	200		7 days		0.03 (3 rpm)	n/a
Brown et al.[76]	10.0	0	100	0	4	7 days	50	0.011 (3 rpm)	n/a
		200	100	0				0.002 (3 rpm)	n/a
		500	100	0				0.005 (3 rpm)	n/a
		10000	100	0				No attack (3 rpm)	No attack
		500	100	0	50			0.005 (3 rpm)	n/a
		10000	100	0				No attack (3 rpm)	No attack
Dugstad et al.[3]	10.0	0	478	0	25	10 days	1220	1.6 (3 rpm)	n/a
		0	191	0		10 days	1220	0.67 (3 rpm)	n/a
		0	191	0		20 days	488	0.06 (3 rpm)	n/a
		0	96	0		3 days	488	0.17 (3 rpm)	n/a

In recent research by Dugstad et al.[3], four key experiments were performed involving various concentrations of NO_2 and water. Corrosion rates from weight loss measurements ranged between 0.06 and 1.6 mm/year with the highest rate recorded at a NO_2 content of 478 ppm over 10 days with a water content of 1220 ppm (the highest NO_2 content tested - image shown in Figure 9). After each experiment, the specimens were shown to be evenly corroded and contained a black/orange dusty film. The dust was spread within the autoclave and EDX analysis of the film revealed no nitrogen compounds present on the surface. It was suggested that the nitric acid oxidised Fe^{2+} ions within the solution to produce the rust-like corrosion product. Similar observations were made by Paschke et al.[87] who reported a yellow/brown surface colour of the specimen and supported the idea of Fe^{2+} oxidation. Dugstad et al.[3] also observed significantly lower corrosion rates over longer duration experiments (20 days vs 3 days) in agreement with Brown et al.[76]. It was suggested that the corrosion rates recorded would have been significantly higher if the water and NO_2 were replenished in the system at the same rate as they were consumed.



(a) **(b)**

Figure 9: (a) Photograph and (b) SEM image of corrosion product found on the surface of carbon steel exposed to 478 ppm NO_2 and 1220 ppm water in dense phase CO_2 at 10.0 MPa and 25°C for 10 days. The recorded corrosion rate was 1.6 mm/year – Figure from Dugstad et al.[3]

Research by Ruhl et al.[88] showed that the mobility and corrosivity of acidic gases in supercritical CO_2 are very different for HCl, HNO_3 and H_2SO_4. Nitric acid was found to be very mobile and aggressive to low alloy steels, but not to the austenitic autoclave material. Furthermore, Cole et al.[77] implemented the use of equation of state based software to determine the pH of the aqueous phase formed in the presence of various concentrations of HCl, HNO_3, SO_3, NO_2 and SO_2. Their simulations suggested that HCl, HNO_3 and SO_3 would have a dramatic effect on the pH of the aqueous phase, even at very low concentrations, whilst NO_2 and SO_2 had only a marginal effect.

Based on the review within this section, it is clear that the least research attention has been directed towards understanding the influence of NO_x out of all the main impurities on the corrosion process, particularly in terms of its role on corrosion product formation and its potential synergy towards the corrosion kinetics with other species in the system. It does appear that NO and NO_2 do have the potential to be the most aggressive species in terms of how they influence the corrosion kinetics, and therefore it is paramount that the effects of these two compounds are clearly distinguished and that the reaction mechanisms at the steel surface are identified.

7.5 CO_2-H_2O-H_2S environments

The corrosion of carbon steel in mixed CO_2/H_2S aqueous environments is an important issue in the oil and gas industry and has been the subject of debate for a number of years. Although this form of corrosion has received significant attention in terms of quantifying corrosion rates for various systems, little progress has been made in understanding the mechanisms of corrosion involved during oil and gas transport.

The general consensus from research into the effects of H_2S presence in CO_2 systems is that low concentrations (approx. <500 ppm) of H_2S can dramatically reduce *general* corrosion rate.[89, 90] However, increasing H_2S content beyond this limit can result in an increase in uniform corrosion rate.[91, 92] The change in corrosion rate is as a result of H_2S influencing both the anodic and cathodic reactions. It also appears that the role of H_2S on localised and general corrosion behaviour of carbon steels is dependent, not only upon its concentration in the aqueous phase, but on various other environmental and physical parameters which can influence the corrosion mechanisms dramatically.[91, 92]

In terms of research into the effects of very low (<100 ppm) concentrations of H_2S, results by Brown et al.[89] strongly suggest that at pH<5 in *aqueous* environments (typical of oil and gas production), when there is no formation of carbonate or sulphide films, concentrations as low at 10 ppm H_2S in the gas phase will lead to rapid and significant reduction in corrosion rate. In instances where protective films did form, no effect was observed on the level of film protection for H_2S contents between 25 and 100 ppm. These observations were also supported by Videm et al.[90] and Ma et al.[92] who recorded very rapid reductions in anodic dissolution at low H_2S concentrations.

At low concentrations of H_2S (<500 ppm), the presence of the dissolved gas was shown by Zheng et al.[91] to hinder the rate of the H_2O and H_2CO_3 reduction reaction (in aqueous environments). However, increasing H_2S content beyond this value resulted in the direct reduction of H_2S accelerating the reaction kinetics.

The retardation effect of H_2S on general corrosion rate has been suggested to be attributed to two specific phenomenon. Various authors have proposed that the reduction in general corrosion rate is attributed to the very rapid formation of a thin mackinawite film, formed by the direct reduction of H_2S with Fe (referred to as a solid state reaction):[93, 94]

$$xFe_{(s)} + yH_2S \rightarrow Fe_xS_{y\,(s)} + yH_2 \tag{22}$$

However, other authors[91, 95, 96] have suggested that a very thin adsorbed iron sulphide layer which displaces H_2O and OH^- from the steel surface and influences the double layer composition may also be responsible for the low corrosion rates prior to the formation of a FeS film.

Caution has to be exercised when evaluating the role of H_2S on pipeline integrity as although the gas can reduce general corrosion, localised corrosion can become prevalent in such systems due to the nature of the iron sulphide films formed. Iron sulphide films are capable of adopting numerous morphologies with varying degrees of protectiveness and physical properties which can change over time as well as with environmental conditions. These include amorphous ferrous sulphide (FeS) and mackinawite ($Fe\,S_{1-x}$),which are able to form quickly while others such as cubic ferrous sulphide (FeS), smythite ($Fe_{3+x}S_4$), greigite (Fe_3S_4), pyrrhotite ($Fe_{1-x}S$), troilite (FeS), and pyrite (FeS_2) have been linked with a transition from the initially formed mackinawite phase.[43]

In the context of carbon steel corrosion in H_2S environments, a clear understanding of the level of influence and/or interaction of the combining gases on pitting corrosion in these systems has remained elusive. However, it has been reported that a thin initial layer of *mackinawite* forms in H_2S-containing environments which is very susceptible to failure and can lead to localised corrosion and/or pitting. Iron sulphide corrosion products formed in sour corrosion systems have also been reported to be electronically conductive with the ability to generate local galvanic cells around unprotected areas of steel surface, creating electrode potential gradients which are believed to drive the pitting process.[43]

Despite the literature in oil and gas production on the influence of H_2S, dense phase transport is a different system. Regrettably, research into the effect of H_2S on the corrosion of carbon steel in dense phase CO_2 systems is limited. Only two studies currently exist in literature considering the effect of H_2S. These were performed by Brown et al.[76] and Choi et al.[97] and are summarised in Table 8. In the work of Brown and colleagues[76], the general corrosion rate of carbon steel was evaluated in the presence of 200 ppm H_2S and 500 ppm

O_2 with a water content of 500 ppm at 10.0 MPa and 4/50°C. General corrosion rates were recorded at approximately 0.005 mm/year, although no measurements of localised corrosion were performed. Research by Choi et al.[97] determined the general corrosion rate of X65 carbon steel in water-saturated conditions at pressures of 8.0 and 12.0 MPa and temperatures of 25 and 80°C. Experiments were performed in the absence and presence of 200 ppm H_2S. When no H_2S was present in the system, general corrosion rates were below 0.01 mm/year at both temperatures. The introduction of H_2S resulted in corrosion rates rising to 0.07 mm/year at 25°C and 0.44 mm/year at 80°C and generated a corrosion product on the steel surface which possessed a bilayer structure. The film was believed to consist of an inner $FeCO_3$ layer and an outer iron sulphide layer.

Apart from the two independent studies performed by Brown et al.[76] and Choi et al.[97], there has been little consideration afforded to the effect of H_2S in *dense phase* CO_2 systems and its likely impact on carbon steel corrosion. This is especially from the view of localised corrosion (a form of corrosion known to be linked very strongly to the presence of H_2S in oil and gas production systems).

7.6 Complex mixture systems

7.6.1 Corrosion observations – NO_2 and SO_2 synergy

According to Corvo et al.[98], under atmospheric conditions, the combined presence of SO_2 and NO_2 can have a synergistic effect which can increase the corrosion and degradation of materials and is dependent upon the relative humidity. Corvo et al.[98] stated that nitrogen containing corrosion products are rarely reported under atmospheric corrosion conditions and that the primary purpose of NO_2 is to catalyse degradation reactions, although such behaviour has not, currently, been conclusively shown to occur under dense phase CO_2 conditions.

An interesting set of experiments was performed by Paschke et al.[87] whereby samples were mounted in an autoclave and studied visually. For a set of experiments, the samples were exposed to a CO_2 mixture containing 1000 ppm water and 4.7% O_2. Specimens exposed to this mixture showed no visible signs of corrosion. Additionally, no corrosion was observed when CO or SO_2 were subsequently added to the CO_2/O_2 mixture. In fact, significant corrosion only occurred once 100 ppm NO was introduced to the entire system, resulting in the formation of a yellow corrosion layer which turned brown after a few days. The reactions with NO were reported to occur a few minutes after injection, indicating the rapid corrosion kinetics in the system. An analysis of the corrosion products revealed the presence of an amorphous compound and α-FeOOH with no $FeCO_3$ or nitrates being reported. It was concluded that NO oxidised to NO_2 rapidly, reacting again with water to produce nitric acid, initiating corrosion. No formation of sulphuric acid was reported in the presence of SO_2 without NO, as it was believed to be hindered due to the low temperature. However, the combined presence of SO_2 and NO resulted in corrosion and the presence of sulphur within the oxide layer (from EDX analysis), suggesting the formation of sulphuric acid was catalysed by the oxidised NO. This evidence supports the catalytic behaviour of NO_2 on sulphuric acid formation, a process which is also referred to as the lead chamber effect:

$$NO_2 + SO_2 + H_2O \rightarrow NO + H_2SO_4 \tag{23}$$

Additional results of corrosion experiments performed in complex mixed impurity systems are provided in Table 9.

Table 8: Summary of literature relating to corrosion rates in supercritical CO_2 with H_2O and H_2S as impurities

	CO_2 pressure (MPa)	H_2S content (ppm)	O_2 content (ppm)	Temp (℃)	Test period	Water content (ppm in mole)	Corrosion Rate (mm/year)	
							General (test rotation speed in brackets)	Localised
Brown et al.[76]	10.0	200	500	4	7 days	500	<0.005 (3 rpm)	n/a
		200	500		7 days		<0.005 (3 rpm)	n/a
		200	500	5	7 days		0.005 (3 rpm)	n/a
		200	500		7 days		0.006 (3 rpm)	n/a
Choi et al.[97]	12.0	0	0	25	24 h	Water-saturated CO_2	<0.01	n/a
		0	0	80	24 h		<0.01	n/a
		200	0	80	48 h		0.41	n/a
		200	0	25	48 h		0.07	n/a
		200	0	25	24 h	100	<0.01	n/a
	8.0	200	0	80	24 h		<0.01	n/a

Table 9: Summary of literature relating to corrosion rates in supercritical CO_2 with complex mixtures of impurities

	CO_2 pressure (MPa)	O_2 content (ppm unless stated)	NO_2/NO content (ppm unless stated)	CO content (ppm unless stated)	SO_2 content (ppm unless stated)	H_2S content (ppm unless stated)	Temp (°C)	Test period	Water content (ppm in mole)	Corrosion Rate (mm/year)	
										General (test rotation speed in brackets)	Localised
Paschke et al.[87] (L485MB steel)	11.0	0.517 MPa (4.7%)	100 ppm NO	50	100	0	60	7 days	1000	0.072	n/a
									600	0.031	n/a
									100	0.019	n/a
									50	0.016	n/a
									0	0.004	n/a
Paschke et al.[87] (L360NB steel)	11.0	0.517 MPa (4.7%)	100 ppm NO	50	100	0	60	7 days	1000	0.050	n/a
									600	0.024	n/a
									100	0.003	n/a
									50	0.002	n/a
									0	0.004	n/a
Paschke et al.[87] (L485MB steel)	11.0	0	100 ppm NO	50	100	0	60	7 days	1000	0.009	n/a
Yevtushenko et al.[99] (L360NB steel)	10.0	8100	100 ppm NO_2	750	70	0	60	7 days	1000	0.003	n/a
Yevtushenko et al.[100] (X52 steel)	10.0	8100	100 ppm NO_2	750	70	0	60	30 days	1000	0.0013	n/a
									600	0.007	n/a
									500	0.004	n/a
Yevtushenko et al.[100] (X52 steel)	10.0	8100	100 ppm NO_2	750	70	0	60	7 days	1000	0.025	n/a
								30 days		0.013	n/a
								186 days		0.003	n/a
Dugstad et al.[3]	10.0	0	191 ppm NO_2	0	138	0	25	7 days	488	0.017 (3 rpm)	n/a

7.6.2 Bulk phase reactions

Chemical reactions are not just limited to those which occur at the electrolyte-steel interface. Dugstad[101] stated that numerous cross chemical reactions (Reactions 24 to 34) are capable of occurring within the bulk phase which can result in the formation of sulphuric/sulphurous acid, nitric acid and elemental sulphur when SO_2, NO_2, NO, O_2 and H_2S are present together:

$$2H_2S + SO_2 \rightarrow \frac{3}{x}S_x + 2H_2O \tag{24}$$

$$2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O \tag{25}$$

$$H_2S + 2NO_2 \rightarrow \frac{1}{2}SO_2 + 2NO + H_2O + \frac{1}{2}S \tag{26}$$

$$2NO + O_2 \rightarrow 2NO_2 \tag{27}$$

$$NO_2 + SO_2 + H_2O \rightarrow NO + H_2SO_4 \tag{28}$$

$$SO_2 + \frac{1}{2}O_2 + H_2O \rightarrow H_2SO_4 \tag{29}$$

$$2NO_2 + H_2O \rightarrow HNO_2 + HNO_3 \tag{30}$$

$$H_2S + H_2SO_4 \rightarrow S + SO_2 + 2H_2O \tag{31}$$

$$H_2S + HNO_3 \rightarrow 3S + 2NO + 4H_2O \tag{32}$$

$$SO_2 + H_2O \rightarrow H_2SO_3 \tag{33}$$

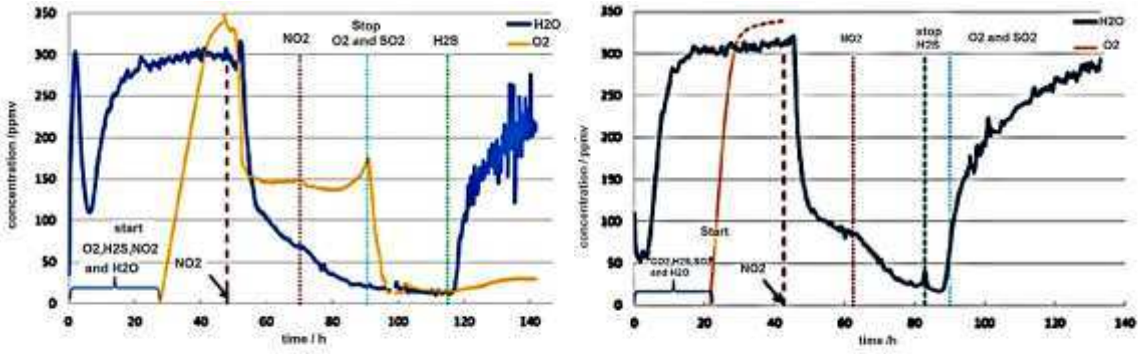
$$4NO_2 + O_2 + 2H_2O \rightarrow 4HNO_3 \tag{34}$$

Currently, no publically available models are available to predict which of these reactions are the most thermodynamically favourable, or provide information on the rates at which these reactions can occur.

To help understand the level of impurity consumption and the depletion of impurities within a dense phase CO_2 environments, Dugstad et al.[101] performed experiments using a rocking autoclave. The autoclave was continuously fed with CO_2 and impurities (water, H_2S, O_2, NO_2 and SO_2) causing the excess CO_2 mixture to be vented out. This vented CO_2 was analysed, enabling the reaction mechanisms consuming impurities to be identified. The setup implemented for impurity analysis consisted of a tuneable diode laser system for water measurement, an optical feedback cavity enhanced absorption spectroscopy laser for H_2S, O_2 and water analysis, a non-dispersive infrared/ultraviolet/visible photometer for NO_x and SO_x and gas chromatograph for H_2S and O_2 analysis.

From two initial tests performed in which impurity concentrations were fed into the autoclave over total periods of up to 133 to 147 hours, it was possible to propose some tentative mechanisms based on observed changes in impurities within the system (details of the exact impurities concentrations fed into the autoclave and the operating conditions are provided in Figure 10). Referring to analysis performed by Dugstad et al.[101], it was observed that when O_2, SO_2 and H_2S were injected all at the same time, no rapid cross-chemical reactions appeared to occur within the first few days. Consequently, although Reactions (24) and (25) (also known as the Claus process) could not be excluded, it was clear these reactions were slow as they could not be detected after 3-6 days. When NO_2 was introduced to the system, the level of water, SO_2 and NO increased immediately, whilst H_2S and NO_2 reduced, corroborating with the process proposed by Reaction (26). A few hours after the injection of NO_2, a decrease in SO_2 and NO were reported, linking in with any of Equations (27) to (30). When NO_2 injection ceased, an increase in SO_2 content was observed, suggesting that H_2SO_4 is formed preferentially by Reaction (28) and not (29), again supporting the catalytic effect of NO_2 on sulphuric acid formation through the lead chamber effect.

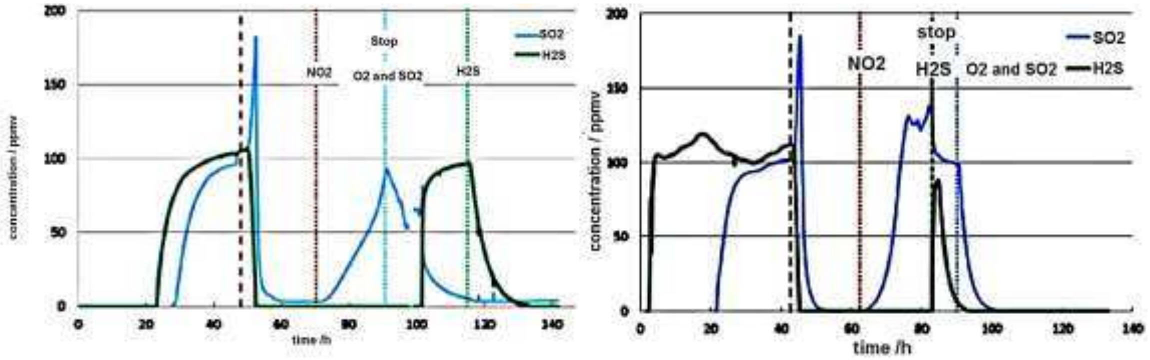
Changes in water and O_2 concentration



(a)

(b)

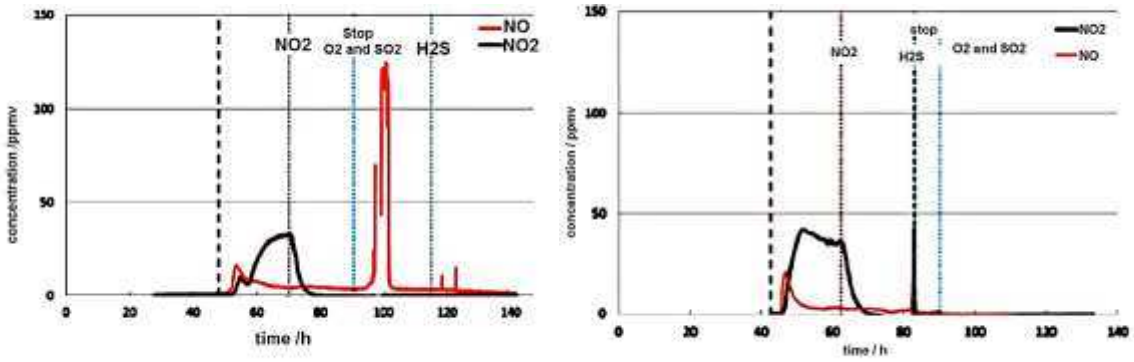
Changes in H_2S and SO_2 concentration



(c)

(d)

Changes in NO_2 concentration



(e)

(f)

Figure 10: Impurity concentrations in vented CO_2 experiments – adapted from the publication by Dugstad et al.[101]; The *left column* ((a), (c) and (e)) correspond to *one* test performed at 25°C for the following impurities concentration feed: 300 ppm H_2O (injected from 1-142 h), 100 ppm NO_2 (48-70 h), 100 ppm SO_2 (28-91 h), 350 O_2 (28-91 h) and H_2S (22-115 h); The *right column* ((b), (d), and (f)) corresponds to *one* test performed at 45°C for the following impurities concentration feed: 300 ppm H_2O

(injected from 1-133 h), 100 ppm NO_2 (43-63 h), 100 ppm SO_2 (22-90 h), 350 O_2 (22-90 h) and H_2S (2-84 h).

The initial research conducted by Dugstad et al[101] provides an interesting insight into the numerous reactions capable within complex mixtures of impure dense phase CO_2. This is even without considering any of the reaction processes which occur on the steel surface. The implementation of such a technique and an understanding of the likely reactions and their kinetics is pivotal to be able to determine the change in CO_2 stream chemistry along the length of pipelines and whether this increases or decreases the risk of corrosion.

7.7 Depressurisation, accumulation of impurities and fracture

When dense phase CO_2 is depressurised within a pipeline below the critical temperature, a two-phase gas/liquid system will form. Within this system, compounds will partition between the two phases and the concentration of impurities such as water, SO_2 and NO_2 will become more concentrated in the remaining liquid phase.[26] When the water solubility in a particular phase in exceeded, a third phase can also form. The accumulation of such impurities can increase the corrosivity of the liquid phase significantly.[102]

Very few experiments within the literature, other than the work of Dugstad et al.[102], focus on the level of corrosion potentially encountered as a result of depressurisaton and accumulation of impurities. Their research involved depressurisation experiments at 4 and 25°C in which autoclaves were vented via the gas phase. In order to ensure the corrosive phase reached the carbon steel test material, thin carbon steel foils were placed in the bottom of the autoclave to contact the sinking corrosive phase during depressurisation.

Dugstad and colleagues[102] found that when the system contained CO_2 and water only (488 and 1222 ppm), the corrosion rate recorded was below 0.1 mm/year. The introduction of 138 ppm SO_2 increased corrosion rates to just over 0.1 mm/year and covered the samples in a black deposit. Perhaps most interesting was that the experiment in the presence of 191 ppm NO_2 produced corrosion rates reaching 0.9 mm/year. It is important to note that these tests were closed system experiments and that the corrosion rate of the sample will have inevitably reduced over time as the impurities were consumed on the steel surface. Consequently, it could be argued that the value of 0.9 mm/year in the presence of NO_2 may have been substantially lower that the true corrosion rate for such a scenario.

In addition to the partitioning of phases, the expansion of CO_2 from a region of high pressure to a region of low pressure causes a decrease in system pressure due to the Joule-Thomson effect. A sudden accidental release from a CO_2 pipeline would cause rapid cooling and potential embrittlement of the steel structure.[103] This process can lead to fracture of the steel and the resulting cracks can then propagate along the pipeline. The problem is exacerbated further by the fact CO_2 exists as a two-phase mixture over a range of velocities, meaning that the pressure at the crack tip is maintained at a high level during propagation.[103] It is necessary to ensure that any propagating cracks are arrested.

7.8 Solid product formation

Various authors have reported the formation of solid products (believed to be elemental sulphur) in the bottom of autoclaves when performing experiments with complex mixtures of impurities.[76, 101] The formation mechanism for elemental sulphur is currently uncertain, although the formed acids within the system can potentially take part in the generation of elemental sulphur as shown previously in Reactions (31) and (32) with the Claus process (Reaction (24)) also becoming important. However, Brown et al.[76] also suggested that the H_2S-O_2 reaction has the potential to form elemental sulphur at very low H_2S and O_2 concentrations i.e. in the ppb range:

$$H_2S + O_2 \rightarrow S + H_2O \tag{35}$$

Currently, no information relating to Reaction (35) in dense phase CO_2 has been found. However, Brown et al.[76] stated that conversion of 100 ppm H_2S would produce in excess of 100 tons of sulphur per year for a 20" pipeline at a flow velocity of 1.5 m/s. Consequently, understanding sulphur formation and its associated mechanisms is crucial to ensure efficient and safe CO_2 transport.

Furthermore, in terms of the build-up of solid compounds, the presence of corrosion products on the pipe wall can also pose an issue and requires consideration. A 0.1 mm thick $FeCO_3$ corrosion product on a 100 km long 20" line would produce approximately 50 tons of solids[76], whilst $FeSO_3$/$FeSO_4$ would produce approximately 58 to 66 tons for the same thickness. A degree of understanding of the tenacity of the corrosion product to the inner wall may be required to understand the risks associated with corrosion product formation and build-up.

8 Stress corrosion cracking

Currently, corrosion research in CO_2 transport has focused on identifying corrosion rates during CO_2 transport. The risk of Stress Corrosion Cracking (SCC) has not been extensively investigated. A recent conference paper by Sandana et al.[104] explores the possibility of SCC in CO_2 transportation lines. The paper also highlights gaps in the current knowledge and provides some preliminary test results that indicate that SCC may be of concern. A summary of this review is provided here for completeness, but the reader is referred to the paper in question for a detailed discussion of the risk of SCC in CO_2 pipelines.

8.1 Effect of Carbon Monoxide

The presence of carbon monoxide (CO) is likely under pre-combustion processes. Sandana et al.[104] stated that cracking of carbon steels was observed in wet CO_2-CO environments in the 1970's. The interest generated in this area led to the first studies by Brown et al.[105] and Kowaka and Nagata[106] into SCC in CO_2-CO-H_2O systems. The aforementioned research indicated that the presence of water is critical for the incidence of cracking and that CO can promote trans-granular cracking in carbon steels. Brown et al.[105] showed that an increase in CO activity promoted faster crack growth and reduced the minimum initial stress required for SCC to occur. Interestingly, the results also indicated that the introduction of O_2 into the system resulted in an increase in SCC susceptibility. Unfortunately, the majority of this data is limited to partial pressures of CO_2 below 2.0 MPa, so the conditions are not particularly reflective of those likely to be encountered during CO_2 transport. Consequently, there is a requirement to explore the likelihood of SCC occurring in high pressure CO_2-CO-H_2O environments during upset conditions under which the dehydration process might fail, resulting in significant water presence in the pipeline.

8.2 Effect of Hydrogen Sulphide

Even though supercritical CO_2 lines have been in operation for approximately 40 years, there are few standards which relate to their design or construction.[107] ASME B31.4 is the standard which describes the design and construction requirements of supercritical CO_2 pipelines, although there is no mention of H_2S in the CO_2 or any requirement to consider the potential for cracking from H_2S.[107]

H_2S can be present as an impurity in both anthropogenic and natural sources of CO_2 and can result in both Sulphide Stress Corrosion Cracking (SSCC) and Hydrogen Induced Cracking (HIC). Although these threats and their associated mitigation techniques have been covered extensively by the oil and gas industry by ANSI/NACE MR0175/ISO 15156[108], CO_2 pipelines are not specifically covered by these standards and the threat of SSCC and HIC needs to be considered, particularly where the CO_2 source contains H_2S.[107]

8.3 Effect of bicarbonates, sulphates and nitrates

The risk of bicarbonate/carbonate internal SCC is unlikely given that there is no surface electrochemical polarisation to drive internal pipeline surface steel potential into the SCC critical range for initiation.[104] Furthermore, the intergranular SCC of low alloyed steels in bicarbonate/carbonate systems is usually referred to as high-pH SCC since it readily occurs in solution of pH 9-10.[104] The typically low pH encountered in the aqueous phase is expected to reduce the likelihood of SCC. It is also expected that relatively low concentrations of bicarbonates would be present in the aqueous phase, also minimising the risk of SCC.

In terms of SO_x and NO_x, it is important to consider the potential effects these impurities may have on the SCC mechanisms in CO_2 pipelines. The presence of nitrates, sulphates and even sulphide films may have the ability to promote SCC.

Nitrates are known to cause SCC of carbon steel on their own, with the susceptibility to cracking increasing with the concentration of nitrates and temperature.[104] The occurrence of SCC becomes significant at temperatures above 70°C due to the rapid formation of an Fe_3O_4 film[104]. Whether this process is capable of occurring at lower temperatures is unknown, but the risk is thought to be low.[104]

8.4 Quantifying the risk of SCC and HIC in supercritical CO_2 pipelines

From an extensive review of the literature, it appears that there are no studies relating to SCC or HIC of pipeline steels when exposed to supercritical CO_2 containing H_2S. Clarification is required as to whether SCC or HIC can even occur under these conditions and whether the threshold conditions established for H_2S to avoid cracking in oil and gas service would be applicable to supercritical CO_2 pipelines.[107]

The risk of HIC and SCC are dependent upon the presence of an aqueous phase within the pipeline. In the presence of such a phase, SCC is obviously a potential risk. When H_2S and other impurities are present in the CO_2 stream, the rapid and catastrophic nature of SCC makes its consideration essential. In contrast, HIC is generally a much slower cracking mechanisms, but still requires attention.

Although there are currently no regulatory requirements to design and construct dense phase CO_2 pipelines to resist SCC and HIC, it is essential to mitigate their risk of occurrence. Furthermore, because these processes are reliant upon the presence of a significant aqueous phase (which would only effectively be present during upset conditions i.e. failure of the dehydration system) it is perhaps prudent to determine the requirement for SCC and HIC resistance based on the frequency and duration of upset conditions as well as how these materials behave during long term exposure to an aqueous phase.[104]

Until SCC and HIC tests are performed in supercritical CO_2 in the presence of impurities such as NO_x, SO_x and H_2S, it is impossible to be confident that SCC and/or HIC are not potential risks for dense phase CO_2 pipelines.

As a final note, the expected low pH (~pH of 3 without impurities in CO_2 stream) of the aqueous phase within the pipeline has the potential to cause significant hydrogen adsorption and permeation. Although CO_2 is less aggressive than H_2S in enhancing the adsorption of hydrogen in steels, it still contributes to the adsorption process.[107] There is also the possibility for hydrogen to accumulate within traps and remain after water has been removed. Therefore, periodic upsets could result in significant accumulation of hydrogen, leading to HIC at a later stage.[107]

9 Issues associated with closed system laboratory experiments, replicating field conditions and defining a safe operating window

Currently, no reliable prediction models are available for anthropogenic dense phase CO_2 transport.[103] Although numerous corrosion prediction models for CO_2 corrosion in oil and gas environments exist, extending the models to pressures and conditions typical of CCS could pose challenging. The models would be unable to account for the additional anthropogenic impurities expected from flue gases such as NO_x and SO_2.

One model has recently been proposed within the literature for supercritical CO_2-SO_2-O_2-H_2O environments.[109] The details of the model by Xiang et al.[109] are beyond the scope of this review, however it was established using a combination of standard CO_2 models and an atmospheric corrosion model and is yet to be correlated or verified by field data.

In order to develop a reliable and uniformly acceptable corrosion model, researcher and stakeholders must develop a standardised methodology for the evaluation of materials in dense phase CO_2 transport environments. Currently, no standards exist in relation to performing laboratory experiments to replicate the conditions encountered in the field. The absence of a standard methodology for performing laboratory corrosion experiments has produced results which may be of limited use in terms of selecting materials or identifying safe conditions for CO_2 transport.[103] There are a number of issues and/or limitations associated with performing laboratory experiments which represent field conditions and the following main aspects are discussed within this section:

- replicating dynamic conditions
- addition of impurities prior to pressurisation
- consumption of impurities during testing
- application of electrochemical techniques in dense phase CO_2

9.1 Replicating dynamic conditions

It has been suggested in literature that the presence of flow within the system is capable of reducing the extent of water condensing onto the steel surface and subsequently minimising the level of corrosion.[81, 83]

In terms of supporting the theory, the work of Farelas et al.[83] demonstrated that the presence of flow (1000 rpm sample rotation speed) reduced corrosion rates of X65 steel by around an order of magnitude in specific dense phase CO_2 environments. Farelas et al.[83] performed tests at 8.0 MPa in both liquid (25°C) and supercritical (50°C) conditions with the addition of 650 ppm water and 0.008 MPa (0.1 %) SO_2. General corrosion rates reduced as a result of the transition from static to dynamic from 0.03 to 0.02 mm/year in supercritical conditions and from 0.1 to 0.01 mm/year in liquid CO_2.

9.2 Addition of impurities prior to pressurisation

Numerous studies have been conducted in autoclaves where water is introduced into the autoclave followed by SO_x, NO_x, H_2S etc. before pressurisation.[3, 23, 70-72, 78, 81, 110] It is theoretically possible for the water to initially react with SO_x and NO_x to produce sulphuric and nitric acid before the system is pressurised. It could be argued that such an approach does not produce an accurate representation of CO_2 transport conditions.

9.3 Consumption of impurities

Perhaps the main issue associated with closed loop/system testing is the depletion of impurities within the system over the course of the experiment. The rate of consumption of impurities is dependent upon the corrosion rate of the sample, the steel surface area to fluid volume ratio and the bulk/surface corrosion mechanisms.[76] The actual level of consumption by corrosion in NO_2/SO_2 experiments was measured by the Institute for Energy (IFE).[76] They found that the level of impurity consumption was much greater than that expected from solely the corrosion rate of the sample. A large part of the impurities were reported to become ‘non-active’ in the system. This was believed to be a combination of immobilisation of the corrosive phase and reactions in the bulk fluid.[76]

With only a small part of the impurity consumption being attributed to corrosion, it could be questioned whether the corrosion rates recorded in such systems reflect a worst case scenario. These results support the requirement for a dynamic tests system whereby the impurity levels are continuously monitored and dosed precisely to maintain a constant stream composition.

9.4 Application of electrochemical techniques in dense phase CO_2

Real-time *in-situ* measurements of corrosion rates of materials exposed in impure dense phase CO_2 would enable instantaneous measurements of corrosion rates which can be linked to the formation of protective corrosion products, increased sensitivity for low corrosion rates and potentially an understanding for how depletion in impurities related to the observed decline in steel corrosion rate.[111] The issue associated with performing electrochemical measurements in dense phase CO_2 are its low conductivity, even when saturated with water vapour.

Previous attempts to perform electrochemical measurements in dense phase CO_2 where conducted by Thodla et al.[23] and Ayello et al..[110] A flush mounted probe was used with the electrodes mounted in an electrically insulated material with the cross-section exposed as the active surface. When the probe was polished, a flat surface was presented for condensation to occur on. A probe of this design, however, requires a certain degree of surface wetting, to enable conductivity between all electrodes (in this case, a three-electrode cell was implemented). Such a process can be intermittent and unreliable during long term testing. To overcome this issue, Thodla et al.[23] and Ayello et al.[110] administered water droplets to the steel surface *in-situ* at high pressure to maintain conductivity. However, such a thick water film may not be wholly representative of the films encountered in a CO_2 pipeline.

Recently, however, Beck et al.[111] produced a novel design involving the use of a three electrode flush mounted probe coated with an ion conducting polymer. Wetting of the polymer by moisture in the dense phase CO_2 enables sufficient electrolyte conductivity to perform electrochemical measurements without administering water directly onto the steel surface.

10 Material selection for CO_2 transport

Information pertaining to the assessment of the corrosion behaviour of corrosion resistant alloys (CRAs) in conditions similar to those encountered in CO_2 transport (i.e. dense phase CO_2) is relatively sparse in the literature. It is the opinion of some authors that the use of CRAs (stainless steels) may be capable of mitigating the corrosion risk during dense phase CO_2 transport.[112, 113] Although this is most likely impractical from an economic perspective for long distance pipelines, caution still needs to be exercised if these materials are considered as the pH of the aqueous phase could potentially become low enough to dissolve the passive film on some of these materials, causing extensive pitting corrosion or localised attack. This statement is supported by the work of Yevtushenko et al.[99, 100] who evaluated the performance of X20Cr13 and X46Cr13 in a circulating impure dense phase

CO_2 system. Corrosion experiments performed at 10.0 MPa and 60℃ in the presence of 1000 ppm water, 70 ppm SO_2, 100 ppm NO_x, 750 ppm CO and 8100 ppm O_2 produced severe pitting corrosion of X20Cr13 and slight pitting of X46Cr13.

Choi et al.[4] also reviewed the corrosion behaviour of X65 steel in comparison to 13Cr in water-saturated CO_2 in 24 hour experiments at 8.0 MPa CO_2 and 50℃ in the presence of 1% SO_2 and 4% O_2. They recorded a corrosion rate of 7 mm/year for both X65 and 13Cr, indicating that the CRA produced no beneficial effect in the form of corrosion mitigation.

To reinforce these observations, experiments performed by Dugstad et al.[101] at 10.0 MPa and 25℃ in the presence of 300 ppm water, 100 ppm NO_2, 100 ppm SO_2, 350 ppm O_2 and 100 ppm H_2S for 147 hours produced signs of corrosion attack on the Hastelloy autoclave used for the corrosion experiment, indicating the level of corrosivity of the aqueous phase which can be produced in such systems.

In light of the previous paragraphs, it must be noted that the effectiveness of CRAs will be heavily dependent upon the level and type of contaminants within the system and how they influence the pH of the aqueous phase formed on the pipe wall. For example, if 'appreciable' levels of nitric acid were to be present in the aqueous phase, it is unlikely that CRAs will offer any significant benefit in terms of mitigating corrosion as the protective passive film will not be stable under the conditions in the aqueous phase due to the low pH. However, if the impurity is H_2S or O_2, or a purely CO_2-H_2O system is considered with a high water content, then CRAs *may* be able to mitigate the effects of corrosion. The question then becomes whether the construction of pipelines using CRAs is economically feasible, and this is unlikely to be the case.

In summary, it is possible that CRAs and low Cr-bearing steels could offer superior corrosion protection compared to carbon steels for pipeline or downhole tubing materials whilst still remaining an economic alternative. However, this will be heavily dependent upon the type and level of impurities in the system and the conditions of the aqueous phase. The results of Yevtushenko et al.[99, 100], Choi et al.[4] and Dugstad et al.[101] all demonstrate that considerable corrosion can take place even on CRAs if specific impurities are present at high enough concentrations (namely SO_2 and NO_2). However, in contrast, other research by Choi et al.[97] has suggested that under the correct environmental conditions (CO_2-H_2O-H_2S), even 1Cr and 3Cr bearing steel are capable of reducing corrosion rates to acceptable levels when carbon steel is unable to perform, enabling a wider tolerance on impurity contents. The decision to move to a more 'corrosion resistant' material is one that should not be taken lightly and should be supported by experimental work under appropriate conditions to determine the level of effectiveness.

11 Corrosion inhibition in CO_2 transport

11.1 Potential of neutralising amines

It is evident that sufficient drying of the dense phase CO_2 is capable of preventing the breakout of free water and excessive corrosion rates. However, this contributes towards an increase in handling costs, particularly for offshore installations. Although the application of CRAs such as 13Cr are an option, they are expensive and appear to have little corrosion resistance to SO_2/NO_2 environments.[103] Therefore, the use of corrosion inhibitors may be the most appropriate corrosion mitigation technique for such instances.

Neutralising amines, in particular, offer themselves as a potential option to help prevent the corrosion caused by strong acids in systems where water condenses onto a metallic surface. Regrettably, the selection of an appropriate neutralising amine usually involves making compromising choices amongst their properties. For example, each amine possesses unique properties which dictate their ability to evaporate, to form liquid/solid salts, along with how quickly/readily they partition into the first drops of water, which condense onto a steel surface.[114] There is no one amine which exhibits all the desirable properties required, meaning that the compounds need to be carefully selected to perform the best form of corrosion inhibition. A number of properties require consideration when selecting an appropriate amine corrosion inhibitor. These include boiling point, the effect of excess amine, the vapour-liquid equilibrium, the base strength and potential salt formation.

A review of corrosion inhibitors would not be appropriate in this article given that no one inhibitor is universally applicable and usually a cocktail of chemicals are administered to control degradation of metals. Furthermore, although corrosion inhibitors have been reviewed extensively for oil and gas environments, there is a significant difference between the operating conditions, the dominant phase and the level and type of contaminants compared to CO_2 transport. Limited research exists in which inhibitors have been reviewed in dense-phase CO_2 with low water contents and this difference in operating conditions and environment may render an inhibitor ineffective for such an application, even if it performs well in a system where the aqueous phase dominates. Exceptions include the work of Turgoose[115] and a recent presentation by Dugstad at a National Association of Corrosion Engineers Technology Exchange Group Session[116], although the inhibitor chemistries were not disclosed in these publications.

Currently, little or no information exists on chemical inhibitors which have been evaluated in environments containing flue gas impurities. If inhibitors are to be developed for CO_2 transport upset conditions, it is imperative they are evaluated in conditions which reflect those which they will be used in as accurately as possible to ensure they are compatible with any anticipated impurities.

11.2 Environmental concerns in corrosion inhibition

One of the additional concerns with the application of corrosion inhibition for CO_2 pipeline materials is that any impurities or components added to the CO_2 stream will be injected into the chosen storage site if left untreated. Consequently, it is imperative that any unsuitable components are removed from the stream prior to injection, or that the residual concentration and environmental properties of the chemical are such that they do not adversely affect the environment where they are injected.

As well as providing sufficient levels of chemical inhibition, any components chosen should be non-toxic with high biodegradability and reduced bioaccumulation.[117] Whether a chemical is environmentally acceptable or not is usually determined by the national regulations of a particular country. In terms of the North Sea where numerous potential sequestration sites exist, this location is well regarded as having stringent criteria regarding chemical requirements compared with the rest of the world.

12 Knowledge gaps

Reflecting on the previous Chapters within this review, it is evident that knowledge gaps still exist in the literature which if left unaddressed, will cast ambiguity over the long term safety and efficiency of dense phase CO_2 transport via carbon steel pipelines. Figure 11 highlights the different areas where research attention should be directed based on this review. In the opinion of the authors, there are four key areas from Figure 11 which require significant attention. These are listed below and outlined in the following section:

i. Predicting the thermo-physical properties of the CO_2 stream
ii. Understanding the mechanisms of localised corrosion
iii. Understanding upset conditions and elucidating NO_x reaction mechanisms
iv. Determining bulk phase reactions and kinetics

It is important to stress that other areas exist in addition to the aforementioned, however, the four listed here are regarded as priority areas.

12.1 Predicting the thermo-physical properties of the CO_2 stream

One of the key requirements for safe transport is to understand the thermo-physical properties of the process fluid being transported and how this is influenced by the presence of impurities. In addition is important to understand how the impurities within the system segregate into the aqueous phase, so that the chemistry can be accurately related to the extent of degradation observed within the system. Accurately determining the role of impurities in influencing the physical properties of the CO_2 stream (density, viscosity), the solubility of water in impure CO_2 and the conditions in the aqueous phase is essential if the corrosion processes are to be understood and if accurate prediction of corrosion rates is to be made possible.

12.2 Understanding the mechanisms of localised corrosion

Understanding the relationship between the species present in the CO_2 stream, the corrosion products formed on the steel surface and how this is related to the ability of pits to initiate and propagate is important to determine whether localised corrosion is a true threat to pipeline integrity. Most importantly it is essential to establish a robust methodology/standard for simulating dense phase CO_2 transport in laboratory experiments and to overcome the issues previously identified in this review (depletion of impurities and change in bulk phase chemistry with time in particular).

12.3 Understanding upset conditions and elucidating NO_x reaction mechanisms

One aspect which has resulted in failures in past CO_2 lines was caused by free standing water in the system. It is important to understand the effects of 'upset' conditions within the system which can cause extremely high degradation rates. This will enable operators to understand the potential risk and extent of damage cause in the event of water ingress into the system. Furthermore, the limited number of experiments with NO_x (even under normal service conditions) have shown that this particular component has the ability to be particularly aggressive, resulting in very fast corrosion kinetics. Further study of this component and its potentially synergistic behaviour with other compounds in the CO_2 stream (particularly through the lead chamber effect) is required to understand the corrosion processes and define the safe stream compositions for transport.

12.4 Determining bulk phase reactions and kinetics

Studies have indicated that in multi-impurity systems, the bulk phase composition can change over time and consequently, along the length of a pipeline. A better understanding of potential bulk phase reactions is required to determine whether the CO_2 stream exhibits any change in its corrosive nature along the length of a pipeline. This is an important area of research as will impact the corrosion management strategy significantly in long distance pipelines.

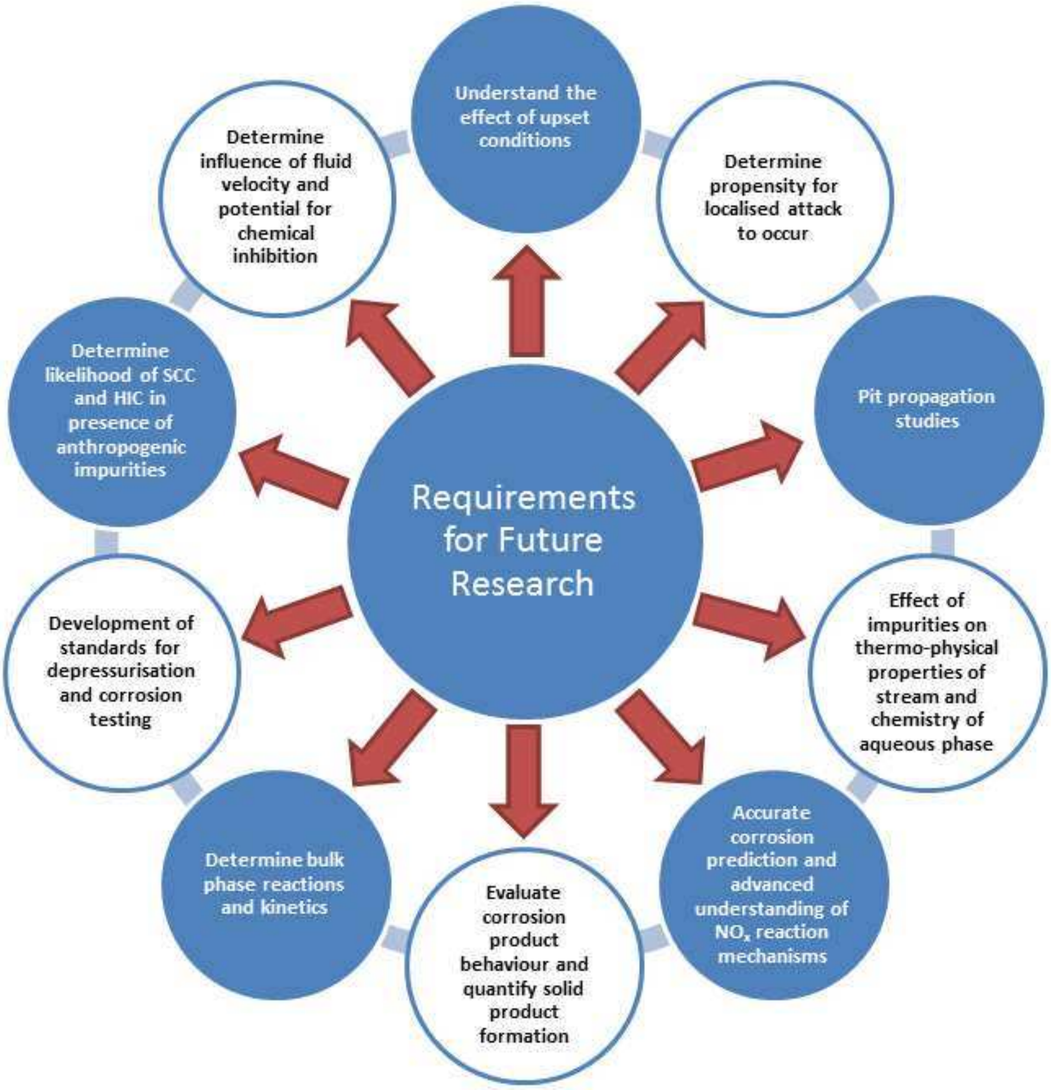


Figure 11: Knowledge gaps identified in the field of dense phase CO_2 transport

13 Conclusions

The most economically viable option for the transport of large quantities of dense phase CO_2 is a dedicated carbon steel pipeline network. Such extensive networks may potentially operate in densely populated areas and will only be permitted if the transportation process is safe and does not present a risk to the local population.

There is currently limited industry experience in handling anthropogenic CO_2 worldwide and no general consensus currently exists on the exact CO_2 stream composition required to ensure the safe transport of CO_2, although some tentative suggestions have been proposed by researchers and pipeline operators. It is essential to have in place a set of technical specifications/requirements for CO_2 processing and purification, enabling the CCS cycle to operate at a minimised cost.

Although tentative guidelines exist in the literature for the CO_2 stream quality, experiments have confirmed that reactions between impurities can occur at ppm level and that multi-impurity systems with impurity concentrations less than the recommended concentrations suggested by DYNAMIS, Alstom, IPCC etc. are corrosive towards carbon steel and result in the formation of nitric/sulphuric acids which are able to lower the critical water content at which general and localised corrosion is initially observed.

The distinct lack of corrosion data from both laboratory experiments and the field where anthropogenic CO_2 is transported makes accurate corrosion prediction challenging. This is particularly true for impurities such as NO_x and H_2S, for which there is a lack of understanding in the general/localised corrosion behaviour, mechanisms and corrosion product formation in dense phase systems. Furthermore, chemical reactions are not just limited to those which occur at the electrolyte-steel interface. Numerous reactions are capable in the bulk phase between H_2S, NO, NO_2, SO_2, O_2 and water. To better understand the corrosion rates in pipelines, there is a requirement to fully understand these reaction processes, the formation of separate corrosive phases and how these influence material degradation to define the safe operating window for CO_2 transport.

The risk of SCC and HIC to occur is dependent upon the presence of an aqueous phase. Although there are no regulatory requirements to construct dense phase CO_2 pipelines to resist SCC or HIC, it is essential to prevent such mechanisms from occurring. Until SCC and HIC tests are performed in supercritical CO_2 in the presence of impurities such as NO_x, SO_x and H_2S, it is impossible to be confident that SCC and/or HIC are not potential risks for dense phase CO_2 pipelines.

Various experimental challenges exist in replicating the conditions encountered during CO_2 transport, particularly for closed system tests with ppm-range concentrations. These include depletion of impurities through reactions with the steel surface, but also reactions in the bulk fluid resulting in the formation of acid phases, or solid products such as elemental sulphur. Furthermore, no standards exist for corrosion experiments in dense phase impure CO_2. An ideal laboratory experiment would involve a dynamic tests system whereby the impurity levels are continuously monitored and dosed/vented precisely to maintain a constant stream composition.

Based on the literature relating to material selection, alternate materials other than carbon steels (such as corrosion resistant alloys) for long-distance dense phase CO_2 pipelines are unlikely given their associated costs. Furthermore, research suggests that the corrosivity of the aqueous phase is too severe even for these materials when impurities such as SO_2 and NO_2 are present in appreciable concentrations.

The application of corrosion inhibitors through continuous injection is an alternative option to CRAs for long distance dense phase CO_2 pipelines. It is also possible that inhibitors could be applied exclusively in the event of ‘upset’ conditions (i.e. failure of dehydration system) to mitigate significant levels of corrosion. However, in such instances the environmental properties of the chemical used needs to be carefully considered if there is no intention to remove the inhibitor prior to injection.

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