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Corrosion and bulk phase reactions in CO_2 transport pipelines with impurities: review of recent published studies

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Abstract

A limited number of papers report experimental corrosion data in the presence of flue gas impurities like SO_x, NO_x and O_2. When SO_2, water and O_2 are present, sulphurous and/or sulphuric acid (H_2SO_3 and H_2SO_4) might form. The minimum water concentration required for acid formation is not known, but the presence of $FeSO_3$ and/or $FeSO_4$ on the corroded surface in some experiments indicate that the reactions occur at water concentrations far below the water solubility in pure CO_2-water systems.

The corrosiveness increases considerably when NO_x is present. NO_2 is highly soluble in water and reacts with water to produce nitric acid and NO under atmospheric conditions. The same type of reaction probably occurs in the dense phase CO_2 system. Experimental results indicate that the rust-like dusty products formed does not efficiently reduce the corrosion rate.

There is limited number of papers presenting data and discussing the effect of combined impurities on corrosion. When both, NO_2 and SO_2 are present, NO_2 catalyzes the oxidation of SO_2 to form sulphuric acid. In addition, in the presence of H_2S, elemental sulphur can form.

Such interactions between impurities are especially dangerous when network pipeline systems are considered and CO_2 streams from different sources and with different impurities are mixed. As a result two non-corrosive streams can become very corrosive if highly corrosive acids are formed as a result of the reaction between added impurities.

Keywords: CO₂ transport, impurities, CCS, pipeline corrosion, CO₂ specification

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1. Introduction

More than 5000 km of dense phase CO_2 pipelines have been or are in operation, mostly in the USA. No serious corrosion problems have been reported in the part of the system that has been exposed to reasonably dry and pure CO_2. Based on more than 40 years of experience, CO_2 transport is perceived to be a well-known technology and little attention has been paid to transport of CO_2 captured from fossil-fuelled power plants and other industrial sources that might give dense phase CO_2 containing impurities that have not been transported before.

The captured CO_2 stream might contain, depending on the type of capture technology (pre-combustion, oxy-fuel, or post-combustion), a number of flue gas impurities like SO_x, NO_x, O_2, CO, H_2S and H_2O.[1,2] There is limited knowledge about possible corrosion and bulk phase reactions when the CO_2 contains these impurities.[3,4] A fundamental understanding of which reactions are thermodynamically possible and kinetically favourable is necessary in order to define the safe operation window for CO_2 transport and the knowledge is required before new CO_2 pipelines are constructed or existing gas pipelines converted. A too conservative purity requirement will increase the costs associated with the CO_2 capture whereas too liberal may result in transport and storage problems.

The current understanding is that the majority of the pipelines will be constructed from carbon steel, typically X65 or X70 grades for high pressure service. Pure CO_2 is essentially non-corrosive to carbon steel, but carbonic acid will form if a free water phase is present. The reported carbon steel corrosion rates measured in the water phase are very high, 1-40 mm/year,[5,6,32,33] and even higher in the presence of impurities like O_2, SO_x or NO_x.[40,41]

Combination of impurities at levels that can lead to corrosion in the CO_2 pipeline has to be avoided. The target for CO_2 transport must be to avoid any free aqueous phase formation as well as solid formation. In the CCS value chain, CO_2 transport pipeline integrity has to be considered together with CO_2 storage demands.

The aim of this review is to compare existing literature on corrosion and bulk phase reaction data in dense phase CO_2 and to evaluate whether CCS CO_2 pipelines can be safely operated within the impurity limits recommended in the literature. Experimental challenges will also be addressed.

2. Present specifications of maximum impurity limit in CO_2 transport

The impurity content in a CO_2 stream will vary depending on capture technology, flue gas quality and optimization cases and it has been issued a number of different tentative CO_2 specifications.[1] The EDGAR (Energy Delta Gas Research) CO_2 purity project published recently a survey of the expected CO_2 purity for post-combustion, pre-combustion and oxyfuel, see Table 1.[7] New technologies that will be developed in the future can give other types and other levels of impurities. It is seen in Table 1 that the concentration of corrosive gasses (H_2S, NO_x, SO_x, O_2, H_2O) varies a lot depending on the capture process. This has to be taken into account in multi-source transport systems where different CO_2 streams have to be compatible.

There is not much published work on CO_2 transport with the various types of impurities expected from the different capture technologies. The widely accepted recommendation given by the Dynamis project[8,9] (Table 2) and the recent recommendation given by NETL (National Energy Technology Laboratory)[10,11] do not take fully into account the cross-reactions between impurities. The only cross-effects described in the Dynamis project are the H_2S and CH_4 impacts on water solubility. Interactions between impurities such as e.g. H_2O and NO_2 or SO_2 were not considered although suggested for follow-up work.[9] The justification for the given NO_x and SO_x concentrations was only based on health and safety risk in a release scenario.

Table 1. CO$_2$ purity table – EDGAR CO$_2$ purity project[7]

Gas component	Post-combustion	Pre-combustion				Oxyfuel
	Amine Scrubbing	Selexol IGGC	Rectisol IGCC	Amine scrubbing	Sour SEWGS	Oxyfuel + double flashing
CO$_2$	99.8-99.9	98.1-99.7	95-98.5	>97.2	> 99	97
H$_2$	-	1.5%	20ppm	<1%	<1%	-
O$_2$	150-300 ppm	-	-	-		1.2%
N$_2$	450-900 ppm (incl. Ar)	195 ppm	< 1% (stripping)	<1%	<1%	1.6% 150ppm NOx
Ar	See N2	178ppm	150 ppm	<1%	<1%	0.4%
Sulphur Comp.	10-20 ppm (SO$_2$ mostly)	2<H$_2$S<1700 ppm	0.2-20 ppm	H2S<200 ppm For 2-stage plant	<5000ppm to ppm level with H$_2$S stage	35 ppm SO$_2$
CO	10-20 ppm	100<CO<1300 ppm	400 ppm	<1%	<1%	-
CH$_4$	-	112ppm	100 ppm	<1%	<1%	-
MeOH	-		20-200ppm			
H$_2$O	100-600 ppm	376ppm	0.1-10 ppm	1.8	500 ppm	-

Table 2. Dynamis[8] and NETL[10,11] CO$_2$ purity recommendation

Component	Dynamis		NETL	
	Concentration	Limitation	Concentration	Literature*
H$_2$O	500 ppmv	Technical	350/500 ppmv	20-650
H$_2$S	200 ppmv	Health&Safety	100 ppmv	20-13000
CO	2000 ppmv	Health&Safety	35 ppmv	10-5000
O$_2$	Aquifer < 4 vol%, EOR 100 – 1000 ppmv	Technical	40000/10 ppmv	100-400000
SOx	100 ppmv	Health&Safety	100 ppmv	10-50000
NOx	100 ppmv	Health&Safety	100 ppmv	20-2500
CH4	Aquifer: <4 vol% EOR: <2 vol%	ENCAP proposed limit	4 vol%	0.01-4
N2	< 4 vol%	ENCAP proposed limit	4 vol%	0.01-7
Ar	< 4 vol%	ENCAP proposed limit	4 vol%	0.01-4
H2	< 4 vol%	To be minimized	4 vol%	0.01-4

* *Various literature data reported by NETL*

When impurity effects are discussed in the literature, the main focus has been on changes of physical properties of CO_2 mixture such as the critical pressure, density, viscosity and compressibility.[1,12-14] There is not much awareness of impurity interactions in the CO_2 streams (such as NOx, SOx, O_2, H_2S and H_2O) although potential interactions of H_2S and SO_2 which might undergo the catalyzed Claus reaction forming elemental sulphur were already suggested in an IEA report[15] in 2004. The formation of elemental sulphur can cause equipment blockages or plug reservoirs. Disproportionation reactions leading to the formation of nitric and sulphuric acid are also to be considered.

When the acceptable water content is discussed the concentration is usually related to the solubility of water in pure CO_2 (Figure 1). The water solubility in dense phase CO_2 varies with temperature, pressure and the presence of other components as described in the Dynamis project.[8] A limited number of publications with solubility data[6,16-20] have been issued and a number of models for the pure water-CO_2 system[21-26] and systems contaminated with hydrocarbons[17,18,19, 24,27] have been developed based on these data.
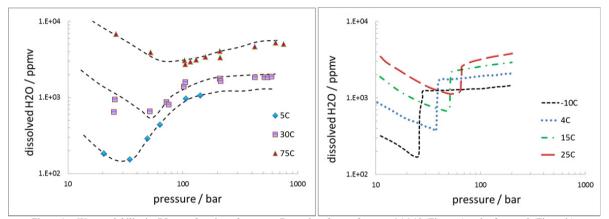

Figure 1.   Water solubility in CO_2 as a function of pressure. Data taken from references 6,16,18 (Figure a) and reference 8 (Figure b).

Precipitation of a water containing phase that will give corrosion is not expected in the pure CO_2-H_2O system as long as the water concentration is well below the reported solubility. The water solubility in the pure CO_2-system is higher than 1000 ppmv in the temperature range relevant for CO_2 transport (4-50 °C). It is expected that water can precipitate at much lower water content when impurities like amines, salt, glycol, SO_x and NO_x are present. These impurities can interact with water and form a mixed aqueous phase (e.g.H_2SO_4 or HNO_3) at a much lower water concentration than the solubility limits reported for pure CO_2.

3. Effect of impurities on corrosion in dense phase CO_2

3.1. $CO_2 - H_2O$ system

Water content below saturation

Based on experience from the USA, no corrosion problems have been reported in the part of the system that has been exposed to dry CO_2 only. The corrosion rate is insignificant when the water content is well below the solubility limit for the pure CO_2-H_2O system. Both field experiences[28-30] and most lab experiments[31-39] indicate this. The high corrosion rates measured by Thodla et al.[40] in CO_2 with 100 ppm water are questioned as the corrosion rate was measured electrochemically with a water droplet present on the electrode surface (challenges of experimental approach will be further discussed in chapter 4).

Chevron did some experimental work[37,38] in the 1970's and concluded: *"No evidence of pitting or general corrosion attack. Corrosion rates were less than 0.02 MPY (0.0005 mm/year)."* The water content in these experiments was 1000 ppmv, the H_2S concentration 800 ppmv and the temperature about 3 and 23 °C.

Corrosion has been reported in process systems where free water was present. Accumulation of water due to

insufficient drying and a leak at a low point due to water build up are reported from the start-up of the SACROC CO_2 injection project.[42]

Presence of free-water

Seiersten[6] measured the corrosion rates of X65 steel exposed 150 to 300 hours at 40°C in water equilibrated with CO_2 at different pressures. As seen in Figure 2, the corrosion rate decreases with CO_2 pressure. It was pointed out by Seiersten that the corrosion rates are high, 1-6 mm/year, but much lower than expected from models based on low-CO_2 partial pressure (<20bar) experiments. It was further reported by Seiersten and Kongshaug that 20 ppm CO_2 corrosion inhibitor can lower the corrosion rate to less than 0.1 mm/y at temperatures up to 30°C and CO_2 pressures up to 72 bar.[43,44] Continuous injection of corrosion inhibitors under normal operation with dry CO_2 is not likely. Inhibition, however, might be applied for corrosion mitigation during upset periods.
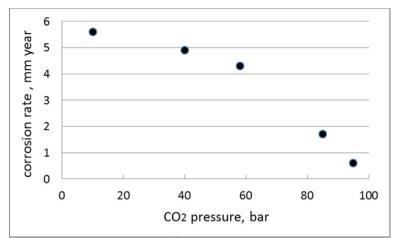

Figure 2. The average corrosion rate measured by Seiersten[6] during 150-300 hours exposure at 40ºC in water equilibrated with CO_2
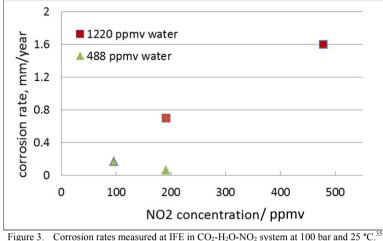
The risk of forming aqueous phases during pipeline decompression should also be considered. Below the critical temperature, depressurizing the CO_2 to less than the critical pressure results in a two phase gas/liquid system and impurities will partition between the two phases. The concentration of many impurities (H_2O, SO_2, NO_2) will increase in the remaining liquid CO_2 phase. If the water concentration in the liquid CO_2 phase exceeds the solubility, water will form a separate corrosive phase together with the other impurities.[76-78] As the corrosion rate in free water can be very high, a strategy for handling accidental water ingress is required.[36,78]

3.2. CO_2 - H_2O - NO_2 system

A limited number of papers report experimental data in the presence of flue gas impurities like SOx, NOx and O_2. The corrosiveness of the CO_2-H_2O system increases considerably when NO_2 is present. NO_2 is highly soluble in water and reacts with water to produce nitric acid and NO under atmospheric conditions. The same type of reaction probably occurs in the dense phase CO_2 system:

$$3\ NO_{2(g)} + H_2O_{(l)} = 2\ HNO_{3(aq)} + NO_{(g)} \tag{1}$$

As shown in Figure 3, a corrosion rate of 1.6 mm/year was measured in an IFE experiment performed with 1222 ppmv H_2O and 478 ppmv NO_2 and 0.7 mm/year in the experiments with 1222 ppmv H_2O and 190 ppmv NO_2.[35] The figure also shows results from experiments carried out with 488 ppmv water and the higher corrosion rate in the experiment with 96 ppmv NO_2 compared to the experiment with 191 ppmv NO_2 was attributed to the much shorter exposure time, 20 vs. 3 days. It was pointed out in this work that the measured corrosion rates probably would have been much higher if water and NO_2 were replenished at the same rate as they were consumed.[45,46]

Figure 3. Corrosion rates measured at IFE in CO_2-H_2O-NO_2 system at 100 bar and 25 °C.[35]

In dense phase CO_2 containing 1000 ppmv H_2O, 4.7 vol% O_2 and 100 ppmv NO Paschke et al[47] observed changes of the color of the specimen with longer exposure time, from uniform yellowish to brownish. Both Dugstad et al[35] and Paschke et al[47] suggested that nitric acid oxidizes Fe^{2+} and give a rust-like dusty product without protective properties.

Very high corrosion rate, 11.6 mm/year was reported by Ayello et al[40,41] in dense phase CO_2 containing 2440 ppmv water and 96 ppmv NO_2. This high corrosion rate cannot be explained only by the higher water content. The corrosion rate was measured with electrochemical technique where water was added directly on the electrode surface and it should be confirmed whether the water dissolved quickly enough not to give significant corrosion attack before equilibrium was achieved.

When mobility and reactivity of acids in supercritical CO_2 (60 °C, 120 bar) were investigated by Ruhl et al[48] it was found that nitric acid was very mobile and corrosive towards the carbon steel. Thickness measurements showed localized material losses on carbon steel specimens exposed in dense phase CO_2 in an autoclave where a few droplets of nitric acid was positioned in the bottom.

Sim et al.[49-51] performed corrosion experiments in supercritical CO_2 (76 bar, 50 °C) with varying concentrations of salts (NaCl, NaNO₃, Na₂SO₄), acid impurities (pH 4, HNO₃) and 10g/L water. The pit depth rate was the highest after exposure to HNO₃, 1-3 mm/y vs. 0.1-0.2 mm/y for salts. It was confirmed in other studies[50] that NO_3^- impurities show the highest impact on corrosion rates compared to H_2SO_4, Cl^- and SO_4^{2-} and that HNO_3 is approximately twice as corrosive when compared to H_2SO_4 and HCl.[51]

Cole et al.[52] studied the effect of contaminants like HCl, HNO₃ and SO_x on the pH of aqueous phases. In order to model the state and the chemistry of the two phase system (liquid CO_2 and water) with different contaminants, the software package OLI Stream Analyzer was employed. It was stated that contaminants such us HCl, HNO₃ and SO_3 will have dramatic effect on the pH of the aqueous phase even in small concentrations while the impact of SO_2 will be moderate.

Depressurization of the pipeline will increase the concentration of NO_2 in the remaining liquid phase and this will steadily increase the corrosivity of the system. Dugstad et al[77,78] performed corrosion experiments during depressurization of an autoclave filled with dense phase CO_2 containing 190 ppmv NO_2 and 490 ppmv H_2O. A carbon steel foil got a rusty layer of corrosion product and the corrosion rate was ~1mm/year.

3.3. $CO_2 - H_2O - SO_2$ system

In the presence of water, SO_2 and O_2 sulphurous and/or sulphuric acid (H_2SO_3 and H_2SO_4) might form.[53,54] The minimum water concentration required for acid formation is not known, but the presence of $FeSO_3$ and/or $FeSO_4$ on the corroded surface in some experiments indicate that the reactions occur at water concentrations far below the

water solubility in the pure CO_2-water systems.[45,46,55,56] It is still not clear if SOx reacts with water in the bulk and forms acid or a thin layer of water is formed on the pipeline surface first and then reacts with SOx.

A survey of experiments performed with low amount of water, SO_2 and O_2 are shown in Table 3. Low corrosion rates were reported by Dugstad et al[45,57] when experiments were performed at low water content and low SO_2 concentration. Mostly spot type attacks were observed. Since the attacks were localised covering less than 10% of the surface, it was reasonable to assume that the local corrosion can be at least 5-10 times higher than the average rate.

Higher corrosion rates, up to 1.5 mm/year, were measured by Xiang[54,58-60] and this can be attributed to higher water (saturated solution in most of the experiments) and SO_2 concentration. Xiang studied the influence of temperature, time, SO_2 and H_2O concentration. Very low corrosion rate was observed when the water content was lower than 50% of the relative humidity in the pure H_2O-CO_2 system. The corrosion rate was decreasing with time indicating the formation of a protective layer or depletion of impurities with time.

Corrosion rates as high as 3-4 mm/y were reported when 1% SO_2 was present in supercritical CO_2 with 650 ppmv water.[61,63] The corrosion rate decreased to 0.03 mm/y at a SO_2 level of 0.1%.[55] It was stated that a concentration of SO_2 less than 0.1% did not lead to significant corrosion of carbon steel. However, in high pressure liquid CO_2 conditions with 650 ppmv of water and 0.05% SO_2, localized attacks were seen with a rate of about 2.4 mm/y.[55] The corrosion rate obtained by Choi et al [61,63] is much higher than that reported by Xiang et al[54,58-60] and can be explained by different exposure time, 1 vs. 12 days.

Table 3. Corrosion rates measured in dense phase CO_2 containing water, SO_2 and/or O_2.

H_2O ppmv	SO_2 ppmv	O_2 ppmv	T °C	P bar	Time days	CR mm/y	Reference
488	344	-	25	100	14	<0.005 (spots)	Dugstad[45, 46,56]
1220	344	-	25	100	14	0.02 (spots)	Dugstad[45, 46,56]
488	1000	100	25	100	7	0.01	Dugstad[45, 46,56]
488	200	100	25	100	7	<0.01	Dugstad[45, 46,56]
650	1%	-	50	80	1	3.48	Choi[63]
650	1%	4%	50	80	1	3.7	Choi[63]
650	0.1%	-	50	80	1	0.03	Farelas[55,]
650	0.05%	-	50	80	1	0.05	Farelas[55]
650	0.1%	-	25	80	1	6.8 (localized CR)	Farelas[62]
3310 (sat)	1%	-	50	80	1	5.6	Choi[63]
3310 (sat)	1%	4%	50	80	1	7	Choi[63]
Saturated	1.4%	0.1%	50	100	12	0.8	Xiang[58]
Saturated	0.2%	0.1%	50	100	12	0.15	Xiang[58]
saturated	2%	0.01%	50	100	5	1.5	Xiang[54,58-60]
RH 50%	2%	0.01%	50	100	5	0.04	Xiang[58,54,59,60]

Similar to NO_2, SO_2 will also partition to the remaining liquid phase during pipeline depressurization. Dugstad et al.[77,78] performed corrosion experiments during depressurization of an autoclave filled with dense phase CO_2 containing 140 ppmv SO_2 and 1220 ppmv H_2O. The exposed carbon steel foil got a black layer of corrosion products and the corrosion rate was ~0.1mm/year. Sulphuric acid which is not very mobile[48], but very hydroscopic, will absorb water from the surrounding CO_2 phase. As concentrated (ca 70-80 mass %) sulphuric acid is less corrosive than diluted one[66], corrosion rate can increase with time.

3.4. $CO_2 – H_2O – $**$SO_2$**$ – $**$NO_2$**$ and CO_2 – H_2O – $**$SO_2$**$ – $**$NO_2$**$ – $**$H_2S$**$ system

A synergistic corrosive effect of SO_2 and NO_2 dependent on relative humidity is observed in atmospheric corrosion.[64,65] It is assumed that NO_2 increases the rate of SO_2 oxidation to sulphate and acts as oxygen carrying agent. A similar phenomena was recently observed in the multi impurity system $H_2O – O_2 – SO_2 – NO_2$ in dense phase CO_2.[47]

Screening experiments, at ambient pressure and at constant flow of CO_2 were presented by Ruhl et al[67,68] (see Table 4). Experiments were performed with different water content, at different temperatures and with different steels (carbon steels, chromium containing steels and corrosion resistant steels). The water content was measured with a dew point meter. Visible condensation occurred at 5 °C at both 1000 and 8000 ppmv water and corrosion products containing $FeSO_3 \cdot 3H_2O$ and $FeSO_4 \cdot 4H_2O$ (rozenite) were detected.[67] The condensed phase contained sulphuric acid and a 10 times lower concentration of nitric acid.

Paschke et al[47] and Rutters et al[69] reported that carbon steel specimen (L360NB) exposed to CO_2 containing 1000 ppmv H_2O and 4.7 vol% O_2 at 110 bar and 60 °C did not show sign of corrosion, neither after addition of 50 ppmv CO nor 70 ppmv SO_2. However, significant corrosion occurred after addition of 100 ppmv NO. Different kinetics for the different acid formation reactions were suggested. It was concluded that NO seems to be oxidized to NO_2 and form nitric acid whereas oxidation of SO_2 to SO_3 is kinetically hindered at such low temperatures and formation of sulphuric acid is hindered indirectly too. When both SO_2 and NO were present, sulphur was found in the oxide layer. The authors explained the phenomena with the catalytic behaviour of nitrogen oxides on sulphuric acid formation (lead chamber effect):

$$NO_2 + SO_2 + H_2O = NO + H_2SO_4 \qquad\qquad (2)$$

Yevtushenko et al[70] performed corrosion experiments in a circulating (but not refilling) CO_2 environment within the COORAL project. Experiments were performed in a loop consisting of a compressor, flow meter and two autoclaves with CO_2 containing H_2O, SO_2, NO_2, CO and O_2 (see Table 4). Mass loss corrosion rate of 30 μm/year was calculated for carbon steel (L360NB) and 40 μm/year for only iron. Pitting was observed for X20Cr13 and X46Cr13 steel. EDS analyses of the corrosion films formed on carbon steel and iron consisted of iron, sulphur and oxygen.

A long-term experiment (186 days) has been described by Yevtushenko et al in reference 71. Three different types of steel (CrMo, C, 13Cr) were exposed to impure supercritical CO_2 at 60 °C and 100 bar. The experiment was performed in the loop described previously. The fluid was changed every third day of the exposure, but the concentrations of the impurities in the CO_2 were not confirmed by any analytical method. The corrosion rate of the carbon steel decreased with exposure time. It was concluded that corrosion products precipitated out as a protective layer.[71]

In reference 72 the authors analyzed the condensed phase that precipitated from impure CO_2 and performed electrochemical measurements at ambient pressure in a liquid with the same composition as measured in the condensed phase, i.e. 2.5% H_2O, 1.8% O_2, 220 ppm SO_2 and 1000 ppm NO_2. The measured corrosion rate was 0.6 mm/y after 14 days exposure in H_2SO_4 and 1.5 mm/y after 14 days exposure in H_2SO_4 and HNO_3.[72] The corrosion rates are very high and much higher than compared to the corrosion rates measured at dense phase conditions. It can be questioned if all the condensed phase that is produced in dense phase CO_2 reached the corrosion sample and if there is other inhibiting factor like e.g. nickel presence in the condensed fluid.

Dugstad et al[73,79] described experiments performed in dense phase CO_2 containing H_2O, H_2S, NO_2, SO_2 and O_2 (see Table 4). The experiments were performed in a rocking autoclave with continuous dosage of CO_2 and impurities. The concentrations of impurities were continuously measured during the exposure. Different analytical techniques were applied: tunable diode laser system for water measurements, non-dispersive, infrared, ultraviolet, visible photometer for NOx and SOx and gas chromatograph for H_2S and O_2 analysis. Impurities were dosed continuously to the autoclave with 3 separate dosing lines as many impurities cannot be premixed.

Table 4.   Experiments performed with mixed impurities

Reference	Pressure bar	Temperature °C	Flow	H_2O ppmv	SO_2 ppmv	NO_2 ppmv	H_2S ppmv	O_2 ppmv	CO ppmv	Exposure time, days	CR, mm/y	Observations
Dugstad [45, 46]	100	25	rotated autoclave 3 rpm	488	138	191				7	0.017	Lower CR comparing to CO_2-H_2O-NO_2 system
Ruhl [67,68]	ambient	5, 30, 60, 170	continuous flow of humid gas with impurities	1000, 8000	220	1000		1.8%	750	25	not given	condensation at 5 °C, $FeSO_3$/$FeSO_4$ detected
Paschke [47] Rutters [69]	110	60	static	1000	70	100 ppmv NO		4.7%	50	7	0.015-0.073	XRD: α-FeO(OH) EDS: O, Fe, S
Yevtushenko [70]	100	60	loop, not refilled	1000	70	100		8100	750	7	0.03	EDS: Fe, O, S
Yevtushenko [71]	100	60	loop, batch every 3rd day	1000	70	100		8100	750	7 186	0.025 0.003	CR decreases with exposure time
Yevtushenko [72]	ambient	5	static		0.11M H_2SO_4	0.018M HNO_3				14	1.5	electrochemical test in simulated condensate
Dugstad [73]	100	25	rocking autoclave with continuous dosage of impurities	122	69	96	130	275		10	0.034	EDS: sulphur formation IC: H_2SO_4 and HNO_3
Dugstad [79]	100	25, 45	rocking autoclave with continuous dosage of impurities	300	100	100	100	350	-	6	0.04	acids and sulphur formation

The concentration of the impurities decreased significantly during the experiment as new phases were formed. Ion chromatography analysis indicated formation of sulphuric and nitric acid. EDS analyses confirmed formation of elemental sulphur grains. Although the mechanism of sulphur formation is uncertain, it was suggested that formed acids take part in the sulphur formation reaction according to the equations:

$$H_2S + H_2SO_4 = S + SO_2 + 2 H_2O \tag{3}$$
and
$$3H_2S + 2HNO_3 = 3S + 2 NO + 4 H_2O \tag{4}$$

Experiments done within the COORAL project[47,69,70,71] and at IFE[73,79] confirmed that reactions between impurities can occur at ppm level and that multi-impurity systems with impurity concentrations less than the concentrations suggested in the Dynamis[8] and NETL[10,11] recommendations are corrosive.

4. Experimental challenges

No standards exist for corrosion experiments in dense phase CO_2 with impurities. The data published in the literature have been obtained from experiments performed in stationary and dynamic autoclave and loop systems. The main experimental challenge has been impurity control. The volume fraction of the corrosive phase that can form in a system with a few hundred ppmv of impurities is very small, less than 10^{-4}. The consumption of the impurities during the exposure and to which degree the corrosive phase actually reaches the exposed steel specimens in the autoclave experiments become critical issues. The consumption rate of impurities (H_2O, SO_2, NO_2) due to corrosion depends on the corrosion rate, the steel surface to dense phase CO_2 volume ratio and the corrosion mechanism. A large part of the impurities can become "non-active" during the exposure as the corrosive phase can be trapped in dead legs or wet the autoclave walls preferentially.

Many studies have been performed in autoclaves where the water was added first, then followed by the other impurities (e.g. SOx, NOx) before the system was pressurized with CO_2 .[40,41,45,46,55,61] It cannot be excluded that part of the water reacted with the added impurities and formed H_2SO_4 and HNO_3 before the system was pressurised. In such cases, it can be argued that the observed corrosion is an experimental artefact and not representative for the real system.

In some of the experiments the corrosion rates were measured with an electrochemical technique where water droplets were present on the electrode surface.[40,41] Corrosion rate measurements under such conditions cannot be related to the corrosion in CO_2 containing low concentration of water, but rather corrosion rates measured in CO_2-saturated water. An electrochemical technique was successfully used by Beck et al[74] for corrosion studies in dense phase CO_2 with ≥ 2000 ppmv water present in the system when Nafion-coated electrodes were used. At higher water concentration the membrane could be saturated with water and enable electrochemical measurement.

The experimental observations support the need for a dynamic test system with renewal of impurities and instant (continuous) analyses of the dissolved impurity concentrations. Such dynamic tests are required in order to define acceptable CO_2 specifications with confidence. To our knowledge only 3 dynamic systems used for corrosion studies in dense phase CO_2 are described in the literature. The first system was developed at BAM in Germany within the COORAL project.[71] This system can replace impurities at intervals, but has no online systems for continuous measurements of the impurity levels. The second system was built at the Cranfield University in UK within the MATTRAN project[75] but so far there are no public data available from corrosion studies in dense phase CO2 with impurities in the ranges suggested in the DYNAMIS or NETL tables. The third system that was developed at IFE in Norway has capabilities for continuous injection of impurities and an online system for continuous analyses of impurity concentration in the test environment.[73]

Strong acids can form in multi impurity systems and corrosion of the equipment becomes an issue. Corrosion of CRA can release alloying elements that might affect the corrosion rate of the exposed carbon steel due to formation of inhibiting nickel or chromium layers.[72]

5. Conclusion

Although dense phase CO_2 has been transported for more than 30 years, there is limited knowledge about corrosion and bulk phase reactions when the CO_2 contains flue gas impurities like SOx, NOx, O_2, and CO, in addition to H_2O and H_2S. A number of tentative CO_2 specifications and recommendations for maximum acceptable impurity concentrations have been published i.e. Dynamis and NETL. A large variation in the reported impurity concentrations is seen, and that is reasonable as the impurities in the CO_2 stream will depend on the fuel type, the energy conversion process (post-combustion, pre-combustion, or oxyfuel) and the capture process. In addition, with new capturing technologies, new compounds (impurities) can be formed and higher concentrations of impurities can follow the CO_2 phase.

The justification for the proposed CO_2 specifications can be questioned as very little published lab data are found supporting the suggested compositions. The present lack of relevant corrosion data from the lab and the field makes corrosion predictions difficult. In order to predict corrosion rates and safe operation windows for future pipelines, there is a strong need to better understand the mechanisms for the formation of separate corrosive phases and how the amount of corrosive phases impact the corrosion rate.

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