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Testing of CO₂ specifications with respect to corrosion and bulk phase reactions

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Abstract

Captured anthropogenic CO₂ contains impurities that might react and form solids and separate corrosive phases when the impurity concentrations exceed the limit where the impurity combination becomes thermodynamically unstable. A number of tentative CO₂ specifications and recommendations for the maximum acceptable impurity concentrations have been published. The recommendations include impurity combinations and impurity levels that are not found in the published CO₂ specifications for pipelines that are or have been in operation. The lack of field experience and the lack of published lab data that support these specifications are a concern.

The most referred recommendations have been challenged in the present work. Experiments were performed with dense phase CO₂ containing 300 ppmv water, 350 ppmv O₂, 100 ppmv SO₂, 100 ppmv NO₂ and 100 ppmv H₂S. The CO₂ and the impurities were continuously injected in the test autoclaves and the consumption rate of the impurities was measured. The experiments showed that the carbon steel corroded and that elemental sulfur formed together with a liquid phase containing sulfuric and nitric acid.

The paper discusses the experimental technique and the results obtained in four autoclave experiments. The paper also discusses how the lack of fundamental data and understanding makes it difficult to predict corrosion rates and define a safe operation window for transport of dense phase CO₂ originating from different sources with different contaminants.

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1. Introduction

Although dense phase CO₂ has been transported for more than 40 years, there is limited knowledge about possible corrosion and bulk phase reactions when the CO₂ contains flue gas impurities like SO_x, NO_x, O₂ and CO in addition to H₂O and H₂S. A number of CO₂ specifications and recommendations for maximum impurity concentrations have been published (see Table 1). The most referred CO₂ quality recommendation has been suggested in the DYNAMIS project^{1,2}. Other frequently referred CO₂ specifications have been presented by IPCC³ and Kinder Morgan.⁴ The National Energy Technology Laboratory (NETL) issued in 2012 and 2013 a Quality Guideline giving recommendations for the impurity limits to be used for conceptual design of carbon steel pipelines.^{5,6} The recommendations were based on a review of 55 CO₂ specifications found in the literature. A large variation in the reported impurity concentrations can be seen and that is reasonable as the impurities in the CCS/CCUS 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 CO₂ phase with an unknown effect on corrosion and cross chemical reactions in the bulk phase.

The justification for many of the proposed recommendations can be questioned as the reported^{8,9} CO₂ compositions presently transported in pipelines does not include flue gas impurities like for instance SO₂ and NO₂, and as concluded in a recent review¹¹ hardly any lab data were found supporting CO₂ specifications with these impurities.

A CO₂ composition (Table 1, last column) with impurity concentrations within the maximum ranges given in the DYNAMIS and NETL recommendations have been tested with respect to corrosion and bulk phase reactions. The experiments were performed in a rocking autoclave system in the dense phase CO₂ lab at IFE. The paper presents the results of four experiments performed at 100 bar CO₂ pressure, 25 or 45 °C, and with the following impurities: 300 ppmv water, 350 ppmv O₂, 100 ppmv SO₂, 100 ppmv NO₂ and 100 ppmv H₂S.

Table 1 Impurity concentrations reported in existing pipelines, CO₂ specifications recommended by Dynamis^{1,2} and NETL^{5,6} and the CO₂ specification tested in the present experiments.

	Impurity levels in existing pipelines ^{8,9}				Published CO ₂ recommendations ^{2,5,6}			IFE exp.
	Canyon Reef Carriers	Central Basin Pipeline	Cortez Pipeline	Weyburn	DYNAMIS ^{1,2}	NETL ^{5,6}	Literature review ⁵	
H ₂ O, ppmv	122	630	630	20	500	730 ⁵ / 500 ⁶	20-650	300
H ₂ S, ppmv	<260	<26	20	9000	200	100	20-13000	100
CO, ppmv	-	-	-	1000	2000	35	10-5000	
O ₂ , ppmv	-	<14	-	<70	<40000	40000 ⁵ / 10 ⁶	100-40000	350
NO _x , ppmv	-	-	-		100 ¹	100	20-2500	100
SO _x , ppmv	-	-	-		100 ¹	100	10-50000	100

2. Experimental

There are no recognized standards for corrosion testing in dense phase CO₂ with impurities. The main experimental challenge is impurity control. The volume of the corrosive phases that might form in a system with a few hundred ppmv of impurities is very small. The volume fraction will be < 10⁻⁴ (< one droplet per liter) and key issues are 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, particularly in stagnant experiments. In order to

get reliable data a dynamic test system with renewal of impurities and instant (continuous) analyses of the dissolved impurity concentrations is required.

IFE uses an experimental set up where slim (ID 20-30 mm) autoclaves are rotated on a shaft inside a temperature controlled chamber (see Figure 1). A short description of the system is given below and more details can be found in reference 10. The temperature in the chamber can be varied from 0-50 °C. The rotating device can accommodate 5 long (2 m) and 4 short (0.6 m) autoclaves. The test specimens are mounted on small cylindrical racks that slide from one end to the other when the autoclave rotates. The cylindrical steel specimens (10 mm long, OD 10 mm, surface area 3.14 cm²) used in the present experiments were machined from ferritic-pearlitic X65 pipeline steel with the composition shown in Table 2. The sliding rack gives good mixing and disturbed flow around the test specimen, a feature that is important for the mobilization of tiny corrosive phases. The rack weight determines the maximum flow velocity. The autoclaves can be rotated continuously at various speeds or in steps according to a programmed sequence. The rotation speed was 3 revolutions per minute in the present experiments, corresponding to an average flow velocity of 0.2 m/s and a peak flow velocity around 1 m/s.

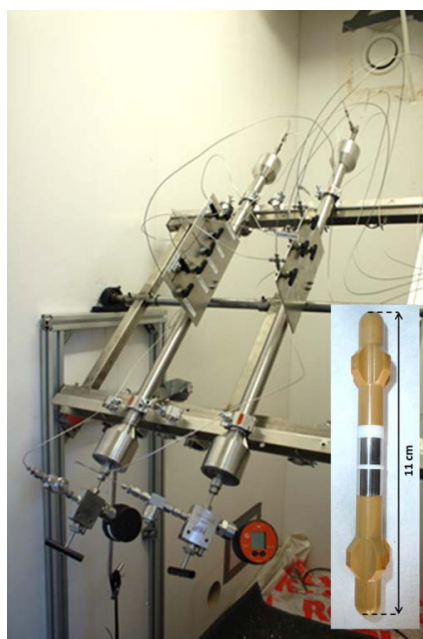


Figure 1 Hastelloy autoclaves with flexible injection and analysing lines. The autoclaves are mounted on a shaft that can be rotated.
Insert: cylindrical rack with specimen

Table 2. Element analysis (wt-%) of the exposed steel specimens

Steel	C	Si	Mn	S	P	Cr	Ni	V	Mo	Cu	Al	Sn	Nb
API 5L X65	0.08	0.25	1.54	0.001	0.019	0.04	0.05	0.095	0.01	0.02	0.038	0.001	0.043

The autoclave was continuously fed with CO₂ and impurities (H₂O, H₂S, O₂, NO₂ and SO₂) via three flexible capillary lines. Three lines were required as many of the impurities will react with each other if they are injected from the same reservoir. When the autoclaves are fed continuously with CO₂ and impurities the excess CO₂ must also be vented/drained continuously. Comparing the composition in the vented CO₂ and the feed makes it possible to:

- identify reactions that consume impurities (in the absence of corrosion specimens)
- measure the impurity concentrations at which separate corrosive aqueous phases are formed

- measure reaction rate of impurities by varying the impurity feed rate
- measure corrosion rates and identify corrosion mechanisms

There is no analyzing system that can measure all the injected impurities, and five separate state of the art analyzers were used to analyze the vented CO₂, i.e. a Tunable Diode Laser System (TDLS) for water analysis, a OFCEAS (Optical Feedback Cavity Enhanced Absorption Spectroscopy) laser for H₂S, O₂ and H₂O analysis, a NDIR/UV/VIS photometer for NO_x and SO_x analysis, a Gas chromatograph (GC) for H₂S analysis and a Zirconium oxide sensor for O₂ analysis when H₂S, SO_x and NO_x are not present.

Phase separation must be avoided in order to obtain representative samples and correct measurements of impurity concentrations. The sampling line and the pressure reduction valves are therefore heated in order to avoid water drop out at cold spots.

Four experiments were performed with the CO₂ composition given in the last column in Table 1. The autoclave was filled with dry CO₂ and pressurised to 100 bar before the impurity dosing was started. All the impurities were dosed from the beginning of the exposure in the first two experiments while the impurities were dosed at various times and intervals in the two last experiments.

3. Results

3.1. Experiment A and B (all impurities dosed from the beginning of the exposure)

Test conditions and results are summarised in Table 3. The replacement rate of CO₂ and impurities was about 0.2 autoclave volume per hour apart from the first few hours where the dosing rate was speeded up 2-3 times for some of the impurities. If no reactions took place in the autoclave, it would take less than 24 hours to reach an impurity concentration equal 95 % of that in the feed.

Figure 2 shows how the concentration of the impurities in the vented CO₂ changed with time. The H₂O, SO₂ and NO₂ concentration increased rapidly the first few hours, passed a maximum and then decreased. The maximum concentration was less than the feed concentration in experiment A (25 °C) while the concentration of H₂O and SO₂ were slightly higher for a few hours in experiment B (45 °C). The higher concentrations might be attributed to over dosage of the impurities or to reactions forming H₂O and SO₂. It should be noted that the dosed H₂S reacted immediately both at 25 and 45 °C and was not detected in the vented CO₂. It should also be noted that NO was not part of the feed, but formed in the autoclave. The SO₂ level stabilised at about 20 ppmv in the 25 °C experiment and became less than the detection limit after two days at 45 °C.

Table 3 Impurity concentrations in the feed. The numbers in the brackets indicate the time when the feed was started and stopped. All experiments were performed at 100 bar.

Experiment	Temp. °C	H ₂ O ppmv (h)	NO ₂ ppmv (h)	SO ₂ ppmv (h)	O ₂ ppmv (h)	H ₂ S ppmv (h)	Duration hour
A	25	300 (1-77)	100 (1-77)	100 (1-77)	350 (1-77)	100 (1-77)	77
B	45	300 (1-74)	100 (3-74)	100 (3-74)	350 (3-74)	100 (3-74)	74
C	25	300 (1-142)	100 (48-70)	100 (28-91)	350 (28-91)	100 (22-115)	147
D	45	300 (1-133)	100 (43-63)	100 (22-90)	350 (22-90)	100 (2-84)	133

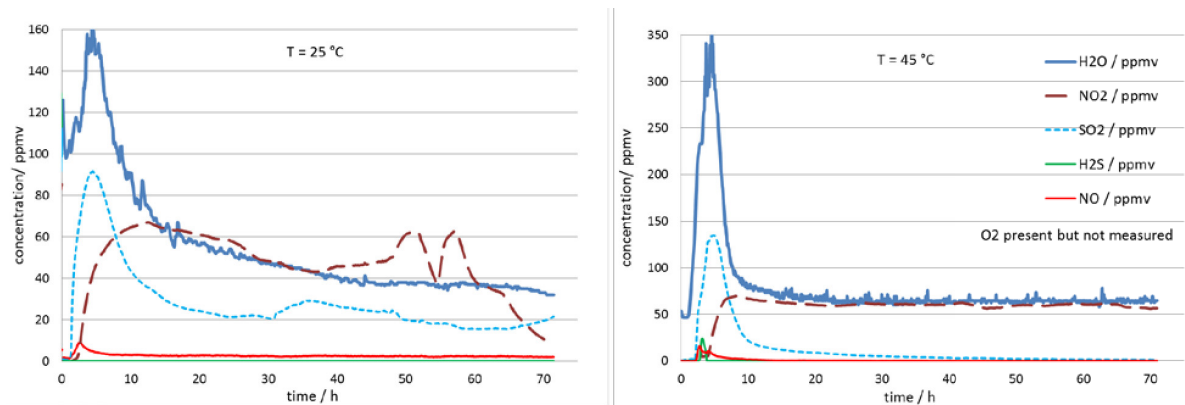


Figure 2 Measured impurity concentration in the vented CO₂ as a function of time. Exp A (right) and Exp. B (left).

A small liquid pool of greenish acids and yellowish elemental sulfur were found in the autoclave after the exposure (see Figure 3). Ion chromatography analysis indicated the presence of 8M H₂SO₄+0.4M HNO₃ at 25 °C and 7M H₂SO₄+0.2M HNO₃ at 45 °C. The carbon steel specimen and the specimen holder were also wetted by liquid droplets as seen in Figure 4. SEM image of the carbon steel surface (Figure 4, right) indicated that the steel was corroded underneath the droplets giving pitting attack. The corrosion film was composed of mainly iron and oxygen, but contained also small amounts of sulfur (< 1 wt%). The weight loss corrosion rate was less than 0.1 mm/y. A higher corrosion rate was expected due to the high concentration of acids in the liquid phase.

The stainless steel specimen was less attacked than the carbon steel specimen and the weight loss corrosion rate was below the detection limit (< 0.01 mm/y). The corrosion products were blade-like and contained more sulfur (5- 10 wt%) than the products found on the carbon steel.

A high concentration (> 1000 mg/l) of Ni, Mo and Cr was dissolved in the greenish liquid indicating that the Hastelloy C autoclave was attacked during the exposure.

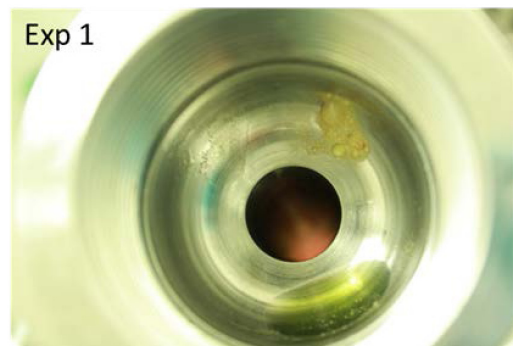


Figure 3 Liquid acids and elemental sulfur formed in the experiment A (25 °C)

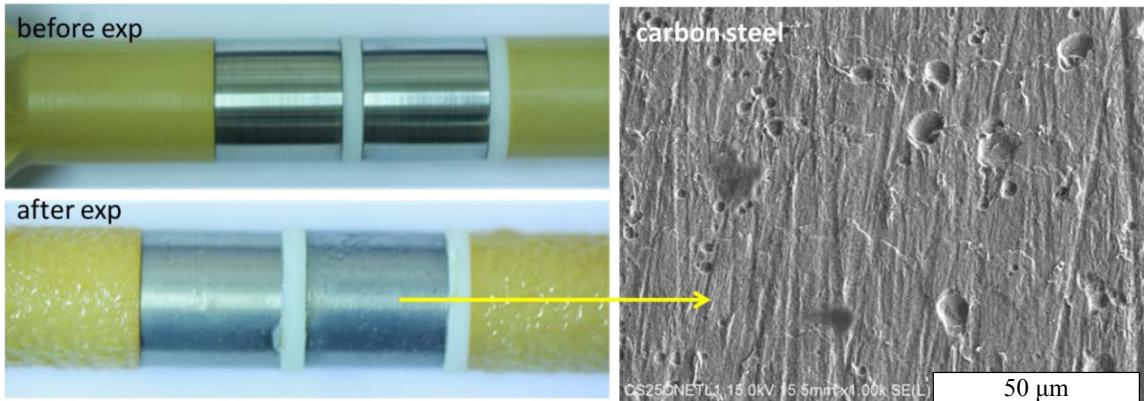


Figure 4 Left: The cylindrical specimen rack before and after exposure in experiment A.
Right: SEM image showing the C-steel surface after the exposure

3.2. Experiment C and D (impurities introduced at various times)

A lot of cross chemical reactions took place in experiment A and B and it was not possible to identify which of the impurities that reacted with each other and which impurities that were required to start the reactions. In order to get more information about the reaction mechanisms, the impurities were introduced at various times in experiment C and D. The injection periods are indicated in brackets in Table 3 and with vertical lines in Figure 5.

Water was injected all the time in both experiments. Introduction of O_2 and SO_2 after about 25 hours and H_2S after 22 (Exp C) and 2 (Exp D) hours respectively did not affect the water concentration and the H_2S , O_2 and SO_2 concentrations increased as expected indicating that cross chemical reactions did not take place at significant rates. Rapid changes in all concentrations were observed when NO_2 was added after about 45 hours. In both experiments the SO_2 peaked for a short period before the concentration of SO_2 and H_2S were reduced to almost zero. The SO_2 concentration increased again when the NO_2 feed was turned off after 70 (Exp C) and 63 (Exp D) hours respectively, but the H_2S concentration remained low until the O_2 and SO_2 injection was stopped after about 90 hours.

Small amounts of NO formed shortly after the NO_2 injection started and large peaks were seen about 25 hours after the NO_2 injection had stopped. The peaking seems to be related to the H_2S concentration that also increased sharply at the same time. The NO peak was most pronounced at 25 °C.

The water concentration increased again and approached the feeding concentration when the injection of the other impurities was stopped. Elemental sulfur and a blackish acidic liquid phase were found when the autoclave was opened.

The weight loss corrosion rates of the carbon steel specimens were about 0.04 mm/y in both experiment C and D. No stainless steel specimens were exposed.

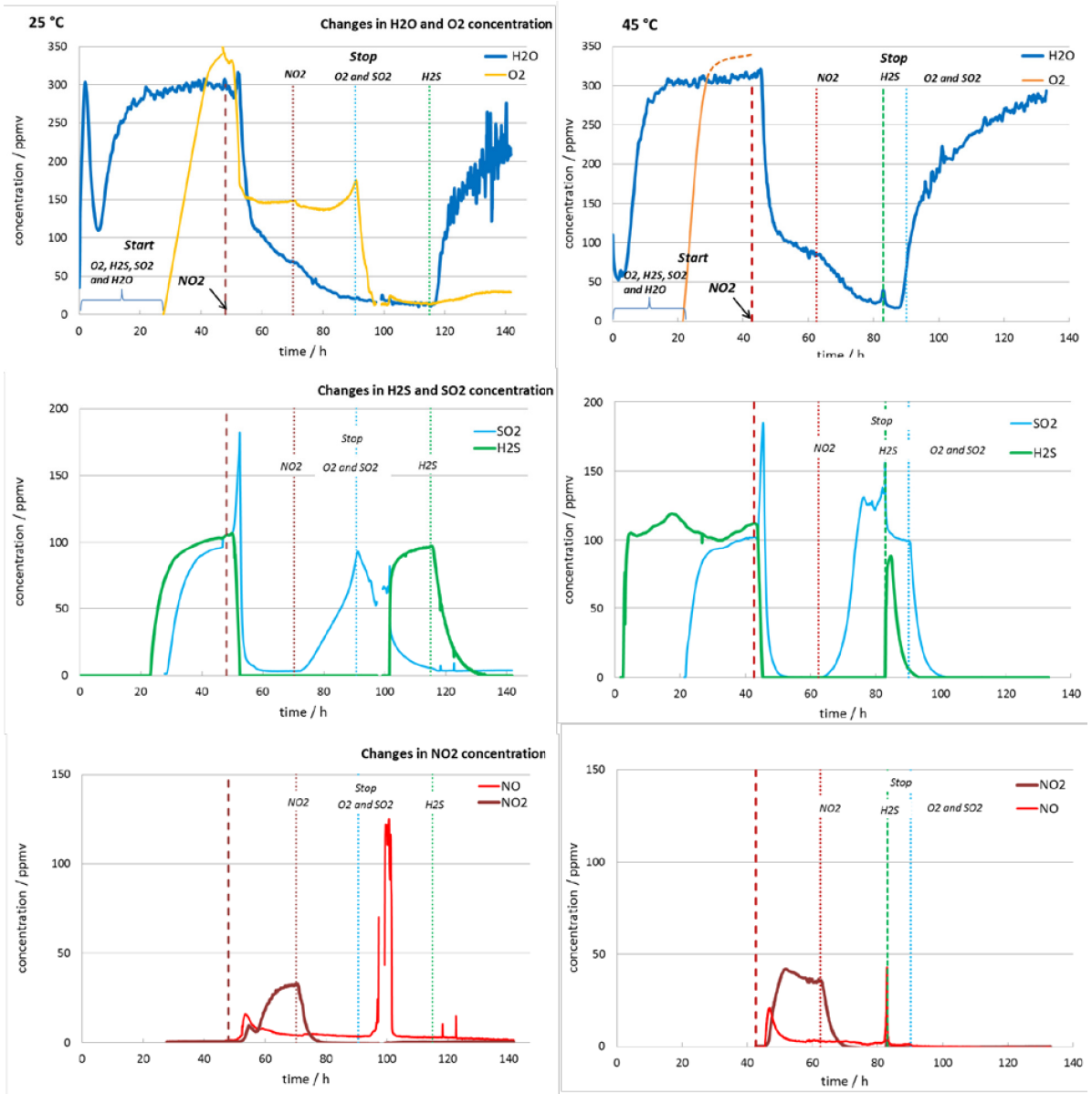
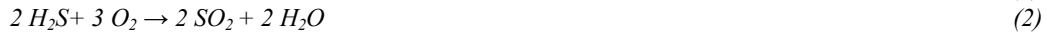


Figure 5 Impurity concentrations in the vented CO₂ in experiment C (left) and experiment D (right).

4. Discussion

4.1. Reaction mechanisms and formation of corrosive phases

There is a number of possible cross chemical reactions that might form sulfuric/sulfurous acid, nitric acid and elemental sulfur when water and SO₂, NO, NO₂, O₂ and H₂S are present:



Presently, there is no publically available model that can predict which of the reactions that are thermodynamically and kinetically possible and favourable under the present test conditions. Experiment A and B showed that the impurities reacted and the concentration of all the impurities were reduced during the exposure. The reduction is not only due to chemical reactions that consume the impurities, but is also attributed to different partitioning of impurities in the CO₂ phase and the acidic aqueous phase. When for instance an acidic phase is formed, water will tend to go to this phase and dilute it until the water activity matches the water activity in the CO₂ phase. That means that the water solubility becomes much lower than in the pure water-CO₂ system. The dissolved water concentration was about 40 ppmv in experiment A (25 °C) and 60 ppmv in experiment B (45 °C) after 3 days exposure. These concentrations are more than one order of magnitude less than the water solubility in the pure water-CO₂ system.

It is too early to draw firm conclusions on the reaction mechanisms from the limited number of experiments that were performed in the present project. Some tentative mechanisms are proposed based on the observed changes (Figure 5) in the impurity concentrations when the impurity injection was started and stopped in experiment C and D:

- When H₂S, O₂ and SO₂ were injected at the same time, the measurements indicated no rapid cross chemical reactions. Reactions known from the Claus process (eq. 1 and 2) cannot be excluded, but the kinetics was apparently too slow to be registered under the present test conditions. The duration of the experiments was a few days only.
- When NO₂ was added, the concentration of water, SO₂ and NO increased immediately for a short period while NO₂ and H₂S decreased. The formation of SO₂ and NO fit with Eq. 3.
- A decreasing concentration of SO₂ and NO were measured a few hours after the NO₂ had started. Possible reactions are suggested in Eq.4-7. The presence of both sulfuric and nitric acid was confirmed with ion chromatography after the exposure and it is assumed that the acid formation started shortly after NO₂ was introduced. When the NO₂ injection was stopped, the SO₂ concentration increased indicating that H₂SO₄ is preferentially formed via the reaction in Eq.5 and not Eq.6.
- A large amount of sulfur formed in the experiments. The formation mechanism is uncertain. The formed acids can take part as indicated in Eq. 9 and 10, but it is also a possibility that Eq. 2 became important with time although it was not a fast reaction in the first part of the exposure.

4.2. Safe operation window

Thousands of pipelines will be required to fulfil the Blue Map scenario.¹² The only economical choice is to use carbon steel. Pure CO₂ is essentially non-corrosive to carbon steel, but in the presence of an aqueous phase corrosion rates of 1–40 mm/year have been reported depending on temperature, pressure and flow velocity.^{13,14,15}

Avoiding the formation of corrosive phases and solids in the pipeline is essential for safe operation of the CO₂ transport network. The present experiments show that the impurity concentrations given in the CO₂ specifications suggested by Dynamis, NETL and IPCC are too high as elemental sulfur and sulfuric and nitric acids were formed.

If the carbon steel surface is wetted by a water containing phase it is not a question whether corrosion takes place, but how rapidly. The weight loss corrosion rates measured in the present experiments were less than 0.1 mm/y. The test duration was short, 3–4 days only. It is also uncertain when the steel wall became wetted and the actual corrosion rates towards the end of the exposures might therefore be much higher than the average measured corrosion rates.

In order to predict corrosion rate in future pipelines, there is a strong need to better understand how the water and impurity content affects the formation of separate corrosive phases and how the amount of corrosive phases impact the corrosion rate.

5. Conclusions

Impurity control is a challenge in corrosion experiments with dense phase CO₂. When the impurities react giving corrosive acidic phases, solid corrosion products and other type of solids (sulfur) the impurities are consumed and must be replenished. Therefore laboratory tests need to be performed in dynamic test systems where precise high pressure dosing systems and analytical instrumentation are used to control the impurity levels.

The justification for the proposed CO₂ specifications recommended by Dynamis and NETL was questioned in the present work as apparently none of the reported CO₂ compositions transported in pipelines include flue gas impurities, and hardly any published lab data are found supporting the suggested CO₂ specifications. Experiments carried out with CO₂ containing 300 ppmv water, 350 ppmv O₂, 100 ppmv SO₂, 100 ppmv NO₂ and 100 ppmv H₂S showed that cross chemical reaction took place and that both elemental sulfur and sulfuric and nitric acids were formed.

The present lack of relevant corrosion data from the lab and the field makes corrosion predictions difficult. In order to predict the corrosion rate in 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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