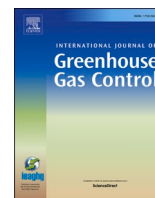


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journal homepage: [www.elsevier.com/locate/ijggc](http://www.elsevier.com/locate/ijggc)Experimental based CO<sub>2</sub> transport specification ensuring material integrityBjørn H. Morland<sup>\*</sup>, Arne Dugstad, Gaute Svenningsen

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## ABSTRACT

Material choice has a large impact on the total cost of the CO<sub>2</sub> transport system for carbon capture and storage (CCS). Cost-considerations make carbon steel the preferred candidate for long pipelines. As carbon steel will corrode if aqueous phases are present, it is important to control the CO<sub>2</sub> composition and operate the system such that formation of water containing phases is avoided.

There are many suggested specifications and recommendations for the type and concentration of impurities to be allowed in the CO<sub>2</sub> stream. The impurity limits were often set from a health, safety, and environmental point of view and are due to lack of knowledge not so much based on material integrity issues. This gap of knowledge makes it difficult to define a specification that will ensure safe operation and long-term integrity.

The present paper summarises the results of a large research project that systematically tested CO<sub>2</sub> with various combinations and concentrations of potentially reactive impurities (H<sub>2</sub>O, NO<sub>2</sub>, SO<sub>2</sub>, H<sub>2</sub>S, O<sub>2</sub>). It was clearly shown that many impurity combinations were basically inert, while other resulted in chemical reactions and some combinations even resulted in the formation of a separate aqueous phase that contained high concentrations of sulfuric and nitric acid as well as elemental sulphur. This aqueous phase was corrosive to carbon steel. Corrosion was also observed in certain situations even when a separate aqueous phase was not observed visually.

It is important to avoid precipitation of solid products since it may cause problems at the injection point and in the reservoir. The present work demonstrated that the types and combination of impurities that are present are important for the maximum impurity concentration that can be allowed before chemical reactions and corrosion occur. For the investigated conditions, 100 bar and 25 °C, the concentration limit for each impurity should be below 20 ppmv if NO<sub>2</sub>, SO<sub>2</sub>, H<sub>2</sub>S, O<sub>2</sub> are present together. The limits may be different at other temperatures and pressures.

## 1. Introduction

Carbon capture and storage (CCS) are one of the emerging solutions to reduce the emission of CO<sub>2</sub> to the atmosphere (IPCC, XXXX). To have any practical effect on the climate change, it must be scaled up significantly. It is foreseen numerous capture and storage sites that are connected through a CO<sub>2</sub> transportation network. Such a network will be a combination of ship, trailer, train and pipelines (IEA, XXXX). Carbon steel is a natural choice as construction material for the CO<sub>2</sub> transportation system since it has excellent strength, is relatively cheap and is readily available in large quantities. Carbon steel corrodes when exposed to CO<sub>2</sub> and water, therefore it is crucial that the transportation systems are operated in a manner that prevents formation of aqueous phases.

The different combustion and capturing techniques may introduce a

wide range of additional components that will be mixed into the CO<sub>2</sub> stream (Porter et al., 2015). These components are usually present at low concentrations (ppm-level) and are therefore referred to as impurities in the present paper. Impurity limits have been proposed in several published CO<sub>2</sub> specifications (de Visser et al., 2008, Herron and Myles, 2013, Harkin et al., 2017) during the last decades. Most of the initial CO<sub>2</sub> specifications were mainly based on health, safety, and environmental (HSE) concerns in case of accidental release of CO<sub>2</sub>. Chemical reactions that potentially could result in corrosion and production of solids were not addressed to the same extent due to lack of experience and experimental data. During the last decade, chemical reactions between impurities have received increased attention. Experimental work and field experience have shown that certain impurities are practically non-reactive while other impurities react and form corrosive phases (Dugstad et al., 2014). The impurities and the concentration must be

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monitored and controlled to maintain the integrity of a CO<sub>2</sub> transportation system.

The work presented in this paper originates from the Kjeller Dense phase CO<sub>2</sub> project, which aims to determine safe operation windows for CO<sub>2</sub> transport. Most of the results have been published (Dugstad et al., 2014, Dugstad et al., 2013, Dugstad et al., 2013, Dugstad et al., 2014, Morland, 2015, Morland et al., 2019, Morland et al., 2019, Morland et al., 2019, Dugstad et al., 2011). The project was started in 2011 and is currently in phase III (Carbon Capture, XXXX). Several experimental setups have been designed to mimic the transport system in a realistic manner. In particular, a system that continuously replenish and monitor impurities at low concentrations is important for the simulation of CO<sub>2</sub> transportation systems where impurities can react chemically.

Numerous multi-impurity experiments have been performed to identify safe maximum impurity limits (operation windows). Such data can be used for establishing safe CO<sub>2</sub> specifications. It should be noted that the acceptable impurity limits may vary from project to project depending on the integrity management philosophy, design lifetime, corrosion allowance etc. In principle, slight corrosion or some chemical reactions could be allowed if the consequences are manageable from an operating perspective. The allowed impurity level will affect the need for purification of the CO<sub>2</sub> after capture as well as the acceptance of using carbon steel for line pipe transport and will therefore affect the overall cost for capture and transport.

## 2. Experimental

The experimental setup has been described in earlier publications (Dugstad et al., 2014, Dugstad et al., 2013, Dugstad et al., 2013, Dugstad et al., 2014, Morland, 2015, Morland et al., 2019, Morland et al., 2019, Morland et al., 2019, Dugstad et al., 2011), and only a brief description is given here. The setup consisted of three main parts: a multiple impurity injection system, a reaction chamber (various types of autoclaves) and an impurity analysis module. The injection module could continuously inject pure CO<sub>2</sub> and stock solution of pre-mixed CO<sub>2</sub> and impurities (one or two impurities in each stock solution) from up to 4 individual reservoirs. These stock solutions were made by weighing the impurity and the CO<sub>2</sub> in the reservoirs. A mixing ball inside the reservoir and rotation ensured homogeneity before use. The impurity

concentrations inside the reaction chamber were adjusted by varying the injection rate of each stock solution relative to the total injection rate (sum of stock solutions and pure CO<sub>2</sub>). Each reservoir had a separate tubing into the reaction chamber. In most of the experiments, the reaction chamber was equipped with a magnetic stirrer that ensured good mixing. Various types of autoclaves were used as reaction chambers and the most advanced was equipped with transparent windows. The analysing module consisted of several separate analysers that were connected in series and could measure the following impurities: H<sub>2</sub>O, O<sub>2</sub>, SO<sub>2</sub>, NO, NO<sub>2</sub>, N<sub>2</sub>O, H<sub>2</sub>S, CO, and COS. The detection limit of these analysers varied, but it was typically a lower detection limit (LOD) of 0.1 ppmv with repeatability of three times the LOD. The setup was rigged to measure the concentrations both upstream and downstream the reaction chamber, a feature that made it possible to quantify consumption and formation of impurities. Most of the experiments were conducted at 100 bar and 25 °C (simulation of typical CO<sub>2</sub> transportation pipeline conditions), but a few experiments were also carried out at low pressure and low temperature (simulation of typical ship/bulk transport condition (Suzuki et al., 2013)). The total exposure time varied but it was mostly in the range of 20 – 50 days. Table 1 gives a summary of the experimental work discussed in the paper.

## 3. Results and discussion

Previous experimental studies have shown that certain impurity combinations are practically inert, while other combinations result in chemical reactions and corrosion. The number of experiments and published papers is large and the summary in Table 1 is included to provide a quick overview. The concentrations that result in chemical reactions and corrosion vary strongly with the combination of impurities that are present together. Thus, the possible impurity combinations (and therefore also impurity concentration limits) are in principle endless, but several impurity mixtures have been verified experimentally to not result in corrosion or formation of a separate aqueous phase (see Table 2). The experimental testing was carried out over a period of more than 10 years, and several improvements were made on both equipment and test approach during this period. The simplest type of experiment was carried out in a closed autoclave with no replenishment of the impurities (NRI). This type of experiment could be used to identify if corrosion took place or not, but since the reactants would be depleted in

**Table 1**  
Summary of experimental test conditions and results.

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

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

**Table 2**

Verified impurity concentration (VIC) for CO<sub>2</sub> transport based on experimental testing at 25 °C and 100 bar. Numbers in brackets are verified based on experiments with only chemical analyses but not visual observation.

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

\* Precipitation of liquid water must be avoided. The water solubility varies with temperature and pressure. Check the temperature and pressure profile for the transportation system to identify the point with lowest solubility.

\*\* These impurities might be increased, since it was the water concentration that was controlled/ramped up until corrosion occurred.

case of a reaction it was difficult to establish a realistic corrosion rate and to identify the reactions that took place. Experiments with continuous impurity injection (SI) were introduced later. Hence, the problem with impurity depletion was avoided. The continuous injection and bleed-off of CO<sub>2</sub> made it possible to analyse the impurity content, and chemical reactions could be identified by comparing inlet and outlet concentrations. Ramping of the water content (RW) was a type of test where the other impurities were kept constant, and water was increased in steps until corrosion was observed. In some experiments, the injection of the different impurities was started in a consecutive manner (ISI). This approach made it possible to identify the impurity that caused onset of chemical reactions or corrosion, and through a series of ISI experiments, it was possible to establish acceptable impurity limits for various CO<sub>2</sub> blends. Visual observation (camera and autoclave with transparent windows) was used to determine if and when corrosion occurred during an experiment.

The corrosion rates given in Table 1 might deviate from the rates expected in the field as the exposure time, volume to surface ratios, flow conditions and replenishment rates will be different. Corrosion rates are also expected to vary around the pipeline circumference, particularly if strong acids are present.

The brackets in row 5 in Table 2 indicates acceptable concentration based on an ISI experiment, meaning that no reaction was detected with chemical analyses. A brief discussion of how the limits in Table 2 were established is given in the following subchapters, but it is recommended to visit the referenced papers for more details.

### 3.1. CO<sub>2</sub> with water and one or two impurities

The water solubility in CO<sub>2</sub> varies strongly with pressure and temperature. When water is the only impurity, the water concentration limit for corrosion to occur can be set slightly below the saturation limit of the system (Morland et al., 2017). For systems that might experience local temperatures below 10 °C there is a risk for hydrate or ice formation (Morland, 2015) and the lowest acceptable water concentration for such systems can be lower than for corrosion and therefore determine the water limit. Condensation of water in CO<sub>2</sub> system with carbon steel present will give corrosion (Choi et al., 2010, Hua et al., 2015, Dugstad

et al., 2011) and must be avoided.

CO<sub>2</sub> with water, SO<sub>2</sub> and O<sub>2</sub> has shown slight corrosion (<10 µm/y), but only if the water concentration is 1900 ppmv or higher (Morland et al., 2019). The limits are given in row 2 and 3 in Table 2.

CO<sub>2</sub> with only water and NO<sub>2</sub> was noncorrosive for water content up to 250 ppmv (row 4 in Table 2). Slight surface discolouration was observed for 350 ppmv of water, but the effect stopped after the whole coupon had been covered with surface product. Severe corrosion was observed for higher water contents (670 ppmv). The results are shown in Fig. 1 (Exp05). In this experiment, the NO<sub>2</sub> concentration was fixed while water was increased stepwise until corrosion occurred. It is possible that the NO<sub>2</sub> limit could be increased to more than 70 ppmv if the water content is kept low, but this needs to be verified experimentally. Higher concentration of NO<sub>2</sub> was tested in Exp06 and Exp07, but the water content (490 and 1220 ppmv) was already above the safe limit found in Exp05 (250 ppmv), and the corrosion rate was higher than acceptable.

Experiments have shown that O<sub>2</sub> and H<sub>2</sub>S can react and form elemental sulphur and water (Dugstad et al., 2014). The reaction was kinetically slow, but in the presence of certain iron oxides the reactions went to almost full completion. Since iron oxides may be present inside carbon steel pipelines (flash rust, mill scale etc), it can presently not be concluded that this reaction will not take place in a CO<sub>2</sub> transport pipeline. However, if the H<sub>2</sub>S content is kept below a certain threshold that corresponds to the solubility of elemental sulphur (Morland et al., 2017), the risk of accumulation of solid elemental sulphur should be eliminated.

### 3.2. CO<sub>2</sub> with water and three impurities

The verified impurity composition in row 5 and 6 (Table 2) are based on visual observation of the steel surfaces during the first period of the exposures in Exp14 – Exp20. In these periods with only water and three impurities present, there were no visual signs of corrosion for up to 100 h (confirmed by photographs), and it is therefore assumed that no (or insignificant) corrosion took place and that the concentrations should be considered safe. However, one more impurity was added later in these experiments and created a corrosive condition. Therefore, only visual observations (several thousand pictures) were available for the non-corrosive period (water and three impurities).

Row 6 in Table 2 is based on the start-up period of Exp20, where no changes on the carbon steel coupon were observed in the initial period (50 h) with water, SO<sub>2</sub>, O<sub>2</sub> and NO<sub>2</sub>. It is possible that some of these limits could be relaxed somewhat, but the water content should not be increased above 200 ppmv due to the result in Exp05, and the concentration of SO<sub>2</sub> should be maximum 60 ppmv due to the observed levels of total sulphur (SO<sub>2</sub> + H<sub>2</sub>S < 60 ppmv) in conjunction with acid reaction (see Chapter 3.3).

### 3.3. CO<sub>2</sub> with water and four impurities–H<sub>2</sub>S, SO<sub>2</sub>, O<sub>2</sub> and NO<sub>2</sub>

The first series of multi-impurity experiments in KDC was carried out with about 100 ppmv of H<sub>2</sub>S, SO<sub>2</sub>, and NO<sub>2</sub>, and with 300 ppmv water and 350 ppmv O<sub>2</sub> injected at the same time (Exp12 – Exp15) (Dugstad et al., 2014). This composition agreed with the CO<sub>2</sub> specifications that were available at the time (de Visser et al., 2008, Herron and Myles, 2013). The experiments provided several interesting observations. Firstly, some impurity combinations were practically inert, as the ISI experiments revealed. Secondly, certain impurity combinations resulted in chemical reactions leading to formation of elemental sulphur and a secondary phase containing strong acids (sulphuric and nitric acid) and water, hereafter referred to as “aqueous phase” to clearly distinguish it from liquid or supercritical CO<sub>2</sub>. Chemical reactions occurred both at 25 °C (Exp12, Exp14) and at 45 °C (Exp13, Exp15), with essentially the same observations.

Going into details of all experiments is outside the scope of this

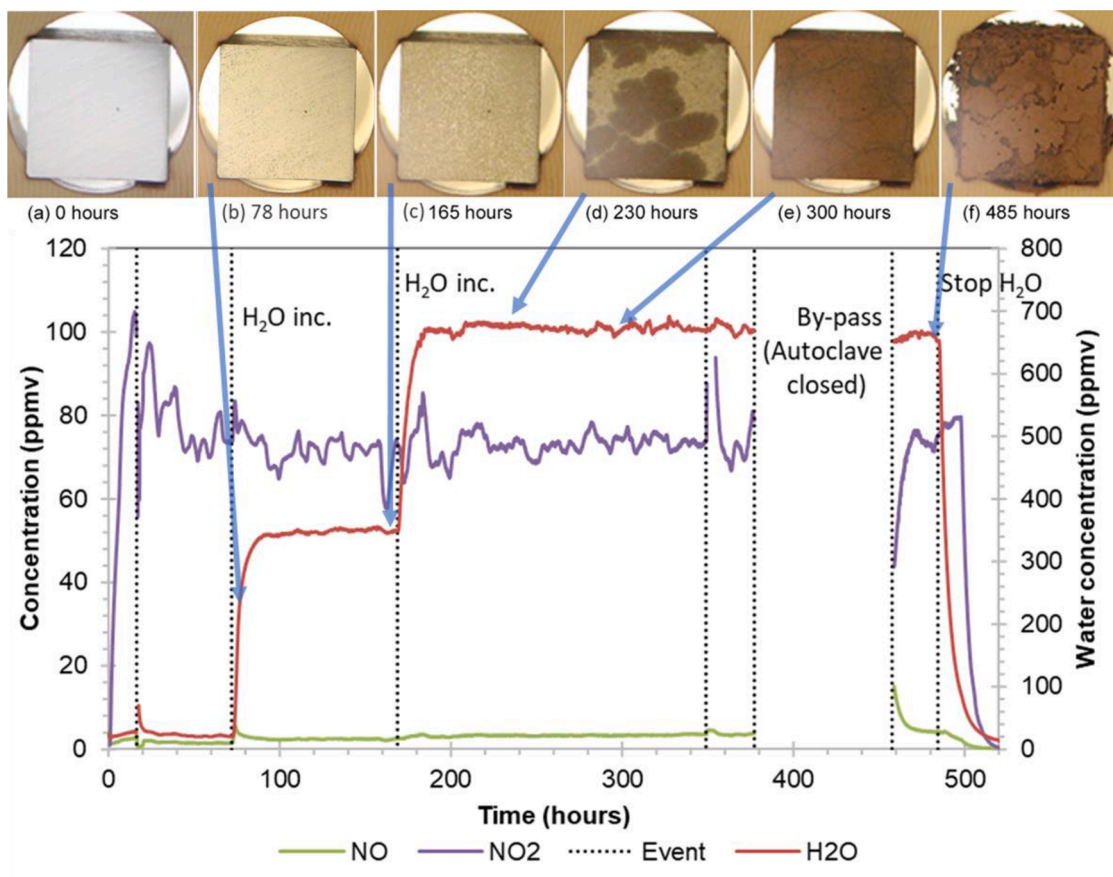


Fig. 1. Results from Exp05 showing the increase in corrosion with increasing water concentration (Morland et al., 2019). Small fluctuations in the water and NO<sub>2</sub> content are related to minute diurnal temperature changes in the lab.

paper, but the result of ISI Exp14 is used here as an example (see Fig. 2). In the initial period (0 to 50 h), injection of H<sub>2</sub>O, H<sub>2</sub>S, SO<sub>2</sub> and O<sub>2</sub> was started consecutively. Analysis of the exhaust CO<sub>2</sub> showed that each impurity reached its target concentration and reactions were not observed. Shortly after the injection of the fourth impurity (NO<sub>2</sub>) was started at 50 h, H<sub>2</sub>S was completely consumed (dropping rapidly towards zero). At the same time, the SO<sub>2</sub> content started to increase above the injection level until it reached a peak value and then decreased

rapidly to very low values. NO<sub>2</sub> was detected 5 h after the injection started, however at much lower values than what was injected. More than 50% of the injected O<sub>2</sub> was consumed by the chemical reactions. Elemental sulphur and an aqueous phase containing sulfuric acid and some nitric acid were found inside the autoclave after the experiment was terminated. If it is assumed that almost all the SO<sub>2</sub> reacts to sulfuric acid (as was observed in the experiments), it corresponds to the formation of about 0.5 kg sulfuric acid per ton CO<sub>2</sub>. The presence of such

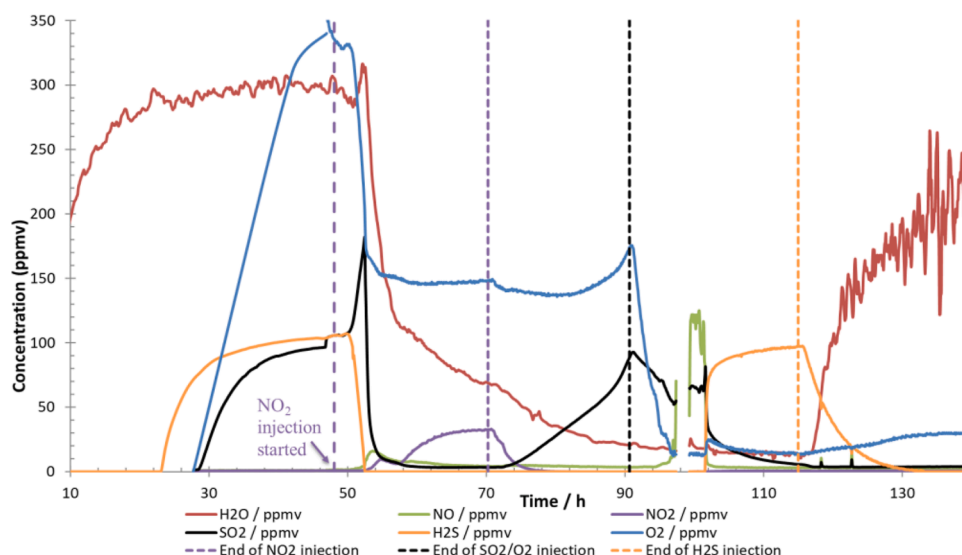


Fig. 2. Impurity content of exhaust CO<sub>2</sub> from Exp14 (Dugstad et al., 2014).

amounts of strong acids will lead to corrosion of carbon steel and is not acceptable from a material point of view. Hence more experiments were performed to find some limits where acid formation does not take place.

Further experimental work focused on the effect of reducing the impurity content in CO<sub>2</sub> when water and the four impurities SO<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>S and NO<sub>2</sub> were present together (Morland et al., 2019, Morland et al., 2019). These experiments provided better insight into the processes that take place. It was shown that many of the reactions observed in the first experiments did also take place at lower impurity concentrations from 5 through 35 ppmv for SO<sub>2</sub>, H<sub>2</sub>S, and NO<sub>2</sub> (O<sub>2</sub> had higher concentration for stoichiometric reasons) but formation of a separate aqueous phase was only observed at the highest impurity content of 35 ppmv (Exp17). This indicates that there is a threshold (impurity content limit) that needs to be exceeded for a separate acid phase to form. An experimental campaign to determine the solubility of sulphuric and nitric acid was therefore carried out (phase II of the KDC project). It was shown that the solubility of these acids varied with temperature and pressure (Morland et al., 2019), as shown in Fig. 3. Furthermore, it was shown that the solubility of HNO<sub>3</sub> in CO<sub>2</sub> is 100 - 1000 times higher than the solubility of H<sub>2</sub>SO<sub>4</sub> (on molar basis). This means that in situations where these acids are formed, most of the HNO<sub>3</sub> will remain dissolved in the CO<sub>2</sub> bulk phase, while almost all of the H<sub>2</sub>SO<sub>4</sub> will precipitate and form a separate aqueous phase (sulphuric acid is known to be hygroscopic (Greenewalt, 1926)).

An aqueous phase containing high concentrations of sulphuric and nitric acid was found in Exp17. The H<sub>2</sub>SO<sub>4</sub> content in the aqueous phase was about ten times higher than the HNO<sub>3</sub> content, further supporting the acid solubility measurements. Based on the experimental results, it was estimated that a CO<sub>2</sub> stream containing 35 ppmv of SO<sub>2</sub>, H<sub>2</sub>S, and NO<sub>2</sub>, together with 90 ppmv H<sub>2</sub>O and 70 ppmv O<sub>2</sub>, would produce 0.13 kg sulphuric acid per ton of CO<sub>2</sub>. The corrosion rate found in this experiment was only 0.07 mm/y, but higher corrosion rates could potentially occur if the acids are diluted by absorption of water from the CO<sub>2</sub> bulk phase (sulphuric acid is used as a desiccant and is less corrosive at high concentrations). It is further assumed that the corrosion rate will vary depending on the steel surface area to aqueous phase volume ratio.

Exp18 through Exp20 (Morland et al., 2019) were performed without corrosion coupons to study the chemical reactions without influence of corrosion processes. It was shown that NO<sub>2</sub> is a strong oxidant that reacts readily with H<sub>2</sub>S to form SO<sub>2</sub>, water and NO (reaction 1). O<sub>2</sub> and NO react to re-create NO<sub>2</sub> (reaction 1), which may react again (reaction 1). Thus, the reaction may proceed until all H<sub>2</sub>S is consumed or until all O<sub>2</sub> and NO<sub>2</sub> have reacted.



Sulfuric acid formed through the (simplified) chemical reaction:



It should be noted that the nitrogen dioxide acts as an oxidiser, both in reaction 1 and in reaction 3. If O<sub>2</sub> is present it will react with NO and convert it back to NO<sub>2</sub>. In practice this indicates that only a few ppmv of NO<sub>2</sub> (or NO) is needed to drive reaction 1 and 3 as long as O<sub>2</sub> is present. The only NO<sub>2</sub> sink is either formation of nitric acid or conversion to NO (in absence of O<sub>2</sub>). Simulations have later shown that oxidation of H<sub>2</sub>SO<sub>3</sub> to H<sub>2</sub>SO<sub>4</sub> by O<sub>2</sub> are too slow (Rütters et al., 2021) while the observed reactions occurred within seconds and supports the reaction route 1 to 3 instead of a oxidation of SO<sub>2</sub> to SO<sub>3</sub>.

The solubility of nitric acid in CO<sub>2</sub> is quite high, about 2100 ppmv (100 bar, 25 °C) (Morland et al., 2019), and most of the nitric acid would therefore remain dissolved and follow the CO<sub>2</sub> stream. Some nitric acid was found in the liquid phase deposit inside the autoclave (Dugstad et al., 2014, Dugstad et al., 2014, Morland et al., 2019, Morland et al., 2018), but it was far less than the amount of sulfuric acid. The reaction to nitric acid is believed to occur in the aqueous phase, see reaction 4. Thus, the amount of nitric acid depends on the amount of water that is present as aqueous phase. Experiments with low water content will have less water that is able to react after reaction 3 has taken place, thus further suggesting why the amount of nitric acid was so low.



Experiments Exp18 (details not shown) and Exp19 (Fig. 4) demonstrated clearly that 5 and 10 ppmv of H<sub>2</sub>S, SO<sub>2</sub>, NO<sub>2</sub>, and O<sub>2</sub>, did not result in formation of a separate aqueous phase (or elemental sulphur) even if H<sub>2</sub>S still was oxidized to SO<sub>2</sub> (reaction 1, 2 and 3). The NO signal comes from reaction 1. This suggests that these impurity concentrations probably can be accepted from an integrity point of view as long as both the reactants and the reaction products remain fully dissolved in the bulk CO<sub>2</sub> phase. Row 7 in Table 2 was based on this assumption. In Exp17 and Exp20, it was observed that formation of a separate aqueous phase started when the SO<sub>2</sub> content reach about 60 ppmv. This was used as a threshold for formation of the separate aqueous phase at 100 bar and 25 °C. It is important to note that the SO<sub>2</sub> produced by oxidation of H<sub>2</sub>S (reaction 1) comes in addition to the SO<sub>2</sub> already present in the CO<sub>2</sub> stream. Thus, as a conservative approach, it is suggested that the sum of SO<sub>2</sub> and H<sub>2</sub>S should be well below the threshold of 60 ppmv. A total sum of 40 ppmv of H<sub>2</sub>S + SO<sub>2</sub> was suggested as maximum limits to include some conservatism.

The water limit in row 7 in Table 2 is based on previously published work (Morland et al., 2019). Exp18 with 5 ppmv SO<sub>2</sub> had a water

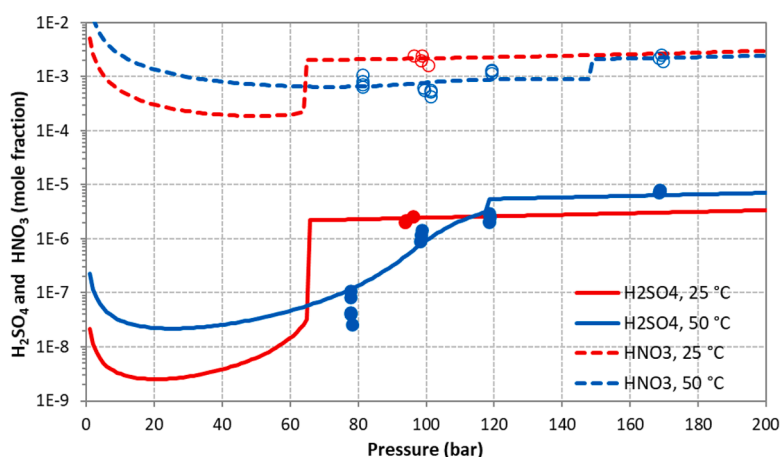


Fig. 3. Comparison of calculated and experimental solubilities of sulfuric acid (solid lines, solid symbols) and nitric acid (dashed lines, hollow symbols) in CO<sub>2</sub>. The lines show the OLI MSE model calculations whereas the symbols denote the experimental data (Morland et al., 2019).

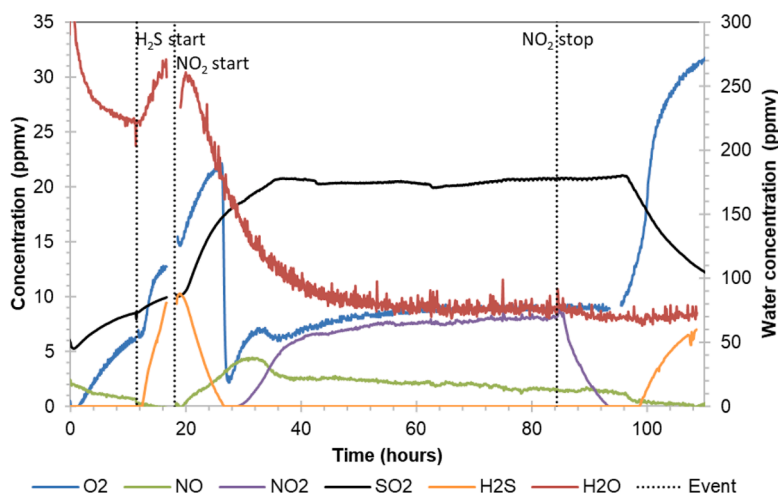


Fig. 4. Measured impurities in Exp19 (Morland et al., 2019).

concentration of 100 ppmv. No liquid phase was observed, suggesting that this water level was safe. In Exp05, which was carried out with only  $\text{NO}_2$  and water (Morland et al., 2019), corrosion was observed when the water level exceeded 300 ppmv (but not at 250 ppmv), see Fig. 1. Thus, these experiments indicate that a safe water content should be between 250 ppmv and 300 ppmv, and a 200 ppmv limit was suggested to include some conservatism.

Presence of  $\text{O}_2$  allows oxidation of  $\text{NO}$  to  $\text{NO}_2$  to proceed until all  $\text{O}_2$  has been consumed or all  $\text{NO}$  has been converted to  $\text{NO}_2$ . Thus, the 20 ppmv limit for  $\text{O}_2$  could be debated. Complete conversion of 20 ppmv  $\text{H}_2\text{S}$  demands (according to reaction 1) either 30 ppmv of  $\text{O}_2$  (and minute amount of  $\text{NO}_2$ ) or 20 ppmv  $\text{O}_2$  and 20 ppmv  $\text{NO}_2$ . Hence, the reactivity of  $\text{NO}_2$  is neutralised with the values given in row 7 and there is no excess  $\text{NO}_2$  for oxidizing  $\text{SO}_2$  to sulfuric acid. This provides additional safety, particularly since the potential  $\text{SO}_2$  content will be lower than the threshold value of 60 ppmv total sulphur species ( $\text{H}_2\text{S} + \text{SO}_2$ ). Further increase of the  $\text{O}_2$  limit could possibly be acceptable, but then there will be  $\text{NO}_2$  present in the  $\text{CO}_2$  stream and this could initiate unwanted corrosion or formation of liquid or solids.

It should be noted that the experimental data in Table 1 were mostly obtained at 25 °C and 100 bar, which is typical conditions for pipeline transport of  $\text{CO}_2$ . The limits will most likely be different at other conditions, and as such the verified impurity concentrations in Table 2 are not applicable for all pressures and temperatures. For example, one experiment carried out at ship condition (-25 °C) resulted in formation of aqueous liquid even if the sum of  $\text{SO}_2$  and  $\text{H}_2\text{S}$  was less than 55 ppmv (Tjelta et al., 2020). This was most likely related to much lower acid solubility, which may lead to an increased amount of condensed acids. Most likely the concentration limits for onset of formation of an aqueous phase is also lower, but this should be investigated further.

### 3.4. Relaxation of the impurity levels and way forward

The VIC in row 7 (Table 2) is conservative but it is based on repeated number of laboratory experiments that were carried out in a controlled manner. It has been experimentally verified that below the proposed impurity limits there is no risk of condensation of acid and unacceptable corrosion for the given temperature and pressure condition (25 °C and 100 bar). This work has also shown that it is almost impossible to give a “universal”  $\text{CO}_2$  specification that always is safe and valid under all possible conditions.

The pressure and temperature will vary during operation and upsets as well as their short and longer impact need to be included when identifying a safe  $\text{CO}_2$  limit for a project.

However, defining the safe limits cannot only be based on whether

chemical reactions do occur or not. Slight acid formation might be tolerated in the field, as long as it is at an acceptably low level. Such an evaluation is further complicated by the need to quantify the amount of corrosive species (e.g. strong acids), the concentration in the aqueous phase, and how large steel surface area the corrosive phases is spread over. For example, continuous precipitation of acids at a fixed small area is much more serious than if the same amount of acid is uniformly spread over the whole internal surface a long pipeline.

The experimental work has shown that the limits are strongly dependent on which impurities are present together. The easiest way to “relax” some limits is therefore to reduce the number of impurities. Especially, removal of  $\text{NO}_2$  will make it possible to increase most of the other impurities. The experience from the laboratory testing strongly supports that new  $\text{CO}_2$  compositions should be verified experimentally. Inclusion of “new” (not yet tested) impurities should also be carried out in multi-impurity tests.  $\text{NH}_3$ ,  $\text{CO}$  and  $\text{HCN}$  are examples of impurities that might be present at significant concentrations. Sulphur containing species could in principle react and contribute to the total  $\text{SO}_2$  level and should be particularly focused on (e.g. mercaptans, thiols, carbon disulphide or carbonyl sulphide).

## 4. Conclusion

It has been experimentally verified that some  $\text{CO}_2$  blends can result in chemical reactions, formation of a separate aqueous phase and severe corrosion, while other  $\text{CO}_2$  blends are practically inert. Some  $\text{CO}_2$  blends that do undergo chemical reactions but do not cause corrosion or formation of aqueous or solid phases have also been identified.

In sum, the large number of experiments has shown that it is not possible to conclude on a “universal”  $\text{CO}_2$  specification allowing a large number of impurities to be present simultaneously. The concentration limits of such a specification would be very low, and in order to relax the limits some impurities need to be removed. The strong oxidation agent  $\text{NO}_2$  drives most of the reactions and its complete removal would make room for higher limits for other impurities like  $\text{SO}_2$ ,  $\text{H}_2\text{S}$  and  $\text{O}_2$ .

Impurity limits for several combinations of impurities are given in Table 2, but they have only been verified for 100 bar and 25 °C (typical  $\text{CO}_2$  transport pipeline condition). Most likely the limits will be different for other temperatures and pressures (cf. downhole or ship transport).

Presence of 35 ppmv of  $\text{SO}_2$ ,  $\text{O}_2$ ,  $\text{H}_2\text{S}$  and  $\text{NO}_2$  resulted in formation of a separate aqueous phase that contained sulfuric and nitric acid, acids that are highly corrosive. If either  $\text{H}_2\text{S}$  or particularly  $\text{NO}_2$  was removed, these reactions did not occur.

## CRedit authorship contribution statement

**Bjørn H. Morland:** Conceptualization, Methodology, Formal analysis, Writing – review & editing, Visualization. **Arne Dugstad:** Conceptualization, Investigation, Writing – original draft, Writing – review & editing, Visualization, Project administration, Funding acquisition. **Gaute Svenningsen:** Conceptualization, Formal analysis, Data curation, Writing – original draft, Writing – review & editing, Visualization, Project administration, Funding acquisition.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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