Carbon Dioxide Capture for Storage in Deep Geologic Formations – Results from the CO$_2$ Capture Project

Geologic Storage of Carbon Dioxide with Monitoring and Verification

Volume 2

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Carbon Dioxide Capture for Storage in Deep Geologic Formations – Results from the CO$_2$ Capture Project

Geologic Storage of Carbon Dioxide with Monitoring and Verification

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Chapter 16

MATERIALS SELECTION FOR CAPTURE, COMPRESSION, TRANSPORT AND INJECTION OF CO_2

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ABSTRACT

The principal alternative for long-distance transportation of CO_2 from source to storage site is in pipelines. To a large extent pipelines can be made in carbon steel as pure, dry CO_2 is essentially non-corrosive. More corrosion-resistant materials or corrosion inhibition must be considered when the CO_2 contains water that condenses out during transportation. This will occur where it is impossible to dry CO_2 to a dew point well below the ambient temperature. Water-saturated CO_2 is corrosive when water precipitates, but experiments show that corrosion rates at high CO_2 pressures in systems containing only water or water/MEG (monoethylene glycol) mixtures are considerably lower than predicted by corrosion models. This applies particularly at low temperatures that are typical for sub-sea pipelines in northern waters. In our previous study, it has been demonstrated that 20 ppm CO_2 corrosion inhibitor is sufficient to lower the corrosion rate below 0.1 mm/y at temperatures up to 30 °C and CO_2 pressures up to 72 bar.

The present study focuses on determining the corrosion rate as function of CO_2 pressure up to 80 bar. The results are compared to existing corrosion models that have been developed to cover a pressure range relevant for oil and gas transportation, i.e. pressures up to 20 bar. The objective of the present study was to verify or extend the use of corrosion models at CO_2 pressure above 20 bar. The experiments show that the models overestimate the corrosion rate when they are used above their CO_2 partial pressure input limit. At low temperature the models predict more than 10 times the measured corrosion rate. Furthermore, the results indicate that the corrosion rate has a maximum as function of CO_2 pressure at 40 and 50 °C. The maximum is at 30–50 bar depending on temperature.

Part of the present study was devoted to determine the solubility of water in CO_2 containing up to 5% CH_4 at high pressure. The results show that CH_4 lowers the water solubility and hence increases the risk of free water in liquid or supercritical CO_2.

INTRODUCTION

Choice of materials for transportation and storage of CO_2 is a critical issue although the oil industry has re-injected CO_2 for the purpose of enhanced oil recovery (EOR) for decades with little or no problems related to corrosion. Low alloy carbon steel pipelines have been used for transportation of liquid CO_2 at high pressure, but in all these cases, drying the CO_2 to less than 100 ppm water and thus removing free water in the pipeline has eliminated the corrosion risk. Drying the CO_2 increases the handling costs especially at offshore installations.

There are several alternatives for CO_2 transportation. Pipelines are the most realistic alternative to bring CO_2 from the source to the storage site. If the transportation distance is more than a few km, carbon steel will be the most cost-effective alternative. In some cases, it may also be practical to reuse old pipelines or co-feed the CO_2 in existing multiphase pipelines. The latter has already been considered in the North Sea [1].

Abbreviations: CR, corrosion rate; MEG, monoethylene glycol; LPR, linear polarization resistance.

More such cases will probably arise when the use of depleted oil fields or aquifers for final storage of CO_2 increases. When CO_2 is transported in existing pipelines from old platforms, it will be impossible or very costly to dry the CO_2 and avoid all free water in the pipeline.

The use of carbon steel either requires that the CO_2 is dried to eliminate free water in the pipeline or that corrosion caused by free water is inhibited. Reliable corrosion data and prediction models are needed in order to evaluate the inhibition and estimate corrosion allowance.

Carbon dioxide has been utilized for EOR for 30 years and there are more than 100 installations worldwide. Most of these use carbon steel pipelines for CO_2 transportation. Despite this, there are few thorough investigations on the corrosion of steels and other materials in CO_2 at pressures above 50 bar [2]. The reason is that there have been few problems with the recovery and transportation systems. The CO_2, in this case, is pure and is dried to a dew point well below the ambient temperature before transportation. At the Sleipner Field, wet CO_2 is injected into the Utsira aquifer. The transportation distance is short and the use of corrosion-resistant duplex steel is therefore cost effective.

Table 1 lists candidate steels for CO_2 processing and transport. It is evident from the table that little is known about the performance of steels in these environments. The transportation costs can be considerable when the CO_2 storage sites are located at some distance from the source. For a CO_2 storage scenario with a 200 km transport line, the transportation costs have been estimated to 20–40% of the total costs [3]. It is not known what the materials costs amount to, but the cost figures in Table 1 clearly show that carbon steel is the most attractive alternative for long pipelines and that 13% Cr steels can be considered for shorter lines. Earlier studies have indicated that the corrosion rate of pipeline steel in wet CO_2 is less than anticipated, and that some water wetting of the pipeline may be allowed for a limited period of time [4]. More data for the corrosion of pipeline steels will be needed to be able to specify CO_2 quality and set limits for trace chemicals and free water. It should also determine the possible extent to which carbon steels can be used with corrosion and hydrate inhibitors. Furthermore, little is known on the corrosion of 13% Cr steel in liquid or supercritical CO_2 with free water. It is a candidate material if water wetting is anticipated, especially for shorter pipelines.

TABLE 1
CORROSION RATES AND EXPERIENCES REPORTED IN THE LITERATURE FOR CANDIDATE STEELS FOR CO_2 PIPELINES AND PROCESS EQUIPMENT

Environment	Quantitative measurements or reported experience		
	Carbon steel	13% Cr steel	Duplex and other high-alloy steels
Dry pure CO_2	Good	–	Good
Wet pure CO_2	Some investigations indicate corrosion rate > 10 mm/y	Not investigated	Most are resistant; corrosion rate ~ 1 μm/y
Dry CO_2 with traces of chemicals from the separation process and hydrocarbons	Few investigations, probable limits for trace elements	Not investigated	Depending on the trace elements (stress corrosion cracking, SCC, must be considered)
Wet CO_2 with traces of chemicals from the separation process and hydrocarbons	Not investigated, corrosion rate probably high	Not investigated	Depending on the trace chemicals (SCC must be considered)
Cost factor for piping material	1	2	≥ 4

The table summarizes investigations at CO_2 pressure above 70 bar. A cost factor for piping materials (with carbon steel as 1) is indicated in the bottom row.

The possibility of free water will determine the materials selection and thus costs. Depending on its origin, CO_2 for injection will contain other substances that may reduce the water solubility in the fluid. CO_2 separated from natural gas may for instance contain up to 5% CH_4. While the solubility of water in pure CO_2 (liquid or supercritical) is well known as function of pressure and temperature, few data are available for the effect of trace chemicals on solubility. It is known, e.g. that CH_4 lowers the solubility of water substantially, but the solubility as function of composition has only been measured for a few compositions and the applicable pressure and temperature range is not extensive [5]. The data available are therefore inadequate for use as design parameter for CO_2 injection pipelines and there is a need of accurate solubility limits in actual mixtures.

Project Objectives
The objective of the study was to establish a basis for materials selection for the processes of CO_2 capture, compression, transportation, and injection. The project was coordinated with the CCP Transportation project run by Reinertsen Engineering and SINTEF. The sub-goals were:

1. To quantify the amount of water that can be dissolved in CO_2-NGL (max 5%) mixtures at 50–500 bara and temperatures up to 30 °C. The effect of trace components from the separation process will also be addressed.
2. To provide the data needed by the Reinertsen/SINTEF project in the development of the guidelines to be used for cost-effective development of CO_2 transportation systems.
3. To determine the corrosion rate of carbon, temperature and pressure and to clarify if it is possible to extend the use of carbon steels with corrosion inhibitors.

EXPERIMENTAL

Water Solubility in CO_2 and in Mixtures of CO_2 and CH_4
The experiments were based on the use of tritium-labeled water. The water phase was allowed to equilibrate with a gaseous or liquid CO_2 phase at a given temperature. Samples of the gas phase were washed out with water to pick up the tritium-labeled water in the gas phase and the resulting water was analyzed for tritium.

The experimental apparatus shown in Figure 1 is a modification of the one described by Song and Kobayashi [5]. It consists of a titanium grade 2 autoclave with gas inlet and outlet and a sampling cylinder in stainless steel AISI 316L. The volume of the autoclave is 1000 mL. The autoclave is completely submerged in a thermostatic bath. The water in the bath circulates continuously and is controlled to ± 1 °C. The autoclave and the sampling system can be evacuated to 0.1 bar.

Tritium-labeled water was obtained from the nuclear reactor at IFE, Kjeller. It was thinned 10 times to obtain an activity of 6 Mbq (Mega Becquerel) in the test solution.

Experiments were started by filling the autoclave with 100 mL tritium-labeled water. The autoclave was evacuated and the gas or fluid phase was added through the bottom inlet and bubbled through the water phase. Measurements on CH_4 and CO_2 mixtures were carried out by adding CH_4 and let it equilibrate with the water phase at the correct partial pressure before CO_2 was added and the pressure was stabilized at the correct total pressure. In this way, it was easy to obtain correct gas mixtures and avoid uncertainty due to the high solubility of CO_2 in the water phase. Liquid CO_2 was be pumped in for high-pressure studies.

The autoclave was decoupled after filling and shaken in the thermostatic bath before it was coupled to the sampling system. It was equilibrated for 4–24 h before sampling started. The sampling system was thoroughly dried and evacuated before sampling began.

The volume of the sampling cylinder was 150 mL and before sampling, it was filled with ca. 100 mL distilled water. The water content was accurately determined by weighing. The cylinder was evacuated before sampling. The pressure change in the autoclave during the operation was less than 1 bar.
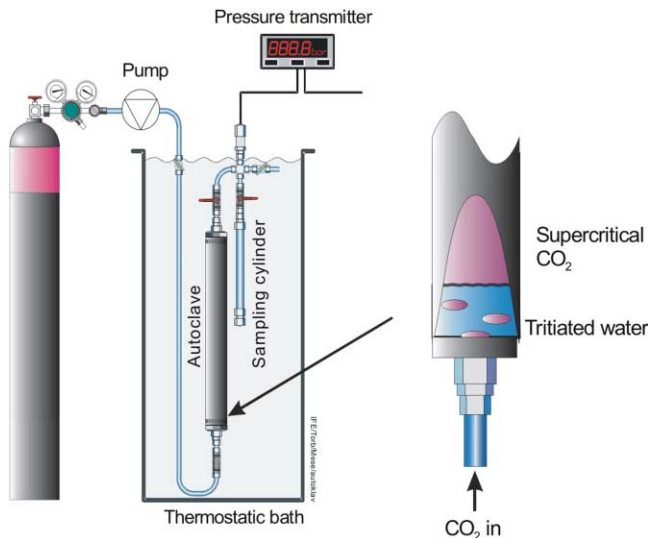
Figure 1: Apparatus for measurements of water solubility in liquid/gaseous CO_2.

The sample amount was determined by weighing and the sampling cylinder was thoroughly shaken before the tritium content of the water was measured. The analysis was carried out on a Quantulus low background level liquid scintillation counter. The analysis samples were diluted 1 to 10 by a low-level tritium Ultra Gold scintillation liquid.

Set-Up for Studies of Corrosion of Carbon Steel in CO_2 and CO_2-Saturated Water

The experimental equipment is shown in Figure 2. It consists of an autoclave with a circulation pump. All exposed materials are made of Hastelloy C. The autoclave has both a cooling and heating system. It can be operated from 0 to 100 °C and is certified for a pressure of 80 bar. The total volume of the autoclave is 8.9 L. The autoclave can be evacuated with a pressure-driven vacuum pump. When both water and liquid CO_2 are added, there is a phase separation with the water phase at the bottom. Corrosion coupons can be inserted both in the CO_2 phase at the top of the autoclave and in the CO_2-saturated water phase at the bottom. In most of the present experiments, there were corrosion coupons in the water phase only.

The test specimens were machined from X65 low-carbon steel. The composition of this steel is given in Table 2. The specimens were ground with 1000 mesh SiC paper wetted with isopropanol, cleaned with technical acetone in ultrasonic bath and flushed with ethanol. The specimens were blow dried before they were mounted on the specimen holder.

The test solutions were prepared from technical or analytical grade chemicals and distilled water. Some of the experiments were performed with MEG as hydrate-preventing agent. When MEG was applied, the concentration was always 50% by weight in the aqueous phase. The solutions were deaerated by CO_2 bubbling for at least 4 h. Oxygen was removed from the autoclave by repeated evacuation and CO_2 flushing. The test solution was transferred to the autoclave by vacuum suction. The autoclave was not filled completely; a 0.3 L gas cap was left to ensure CO_2 gas/liquid equilibrium. For experiments below/above room temperature the test solution was cooled/heated to the experimental temperature before the CO_2 was let in. To obtain pressures above the saturation pressure of CO_2 at room temperature ($\sim$58 bar), the test solution was saturated with liquid CO_2 at 15 °C. The autoclave was then heated to the experimental temperature, and the experimental pressure was obtained by venting off CO_2 during heating. The experiments were typically run for 5–7 days.
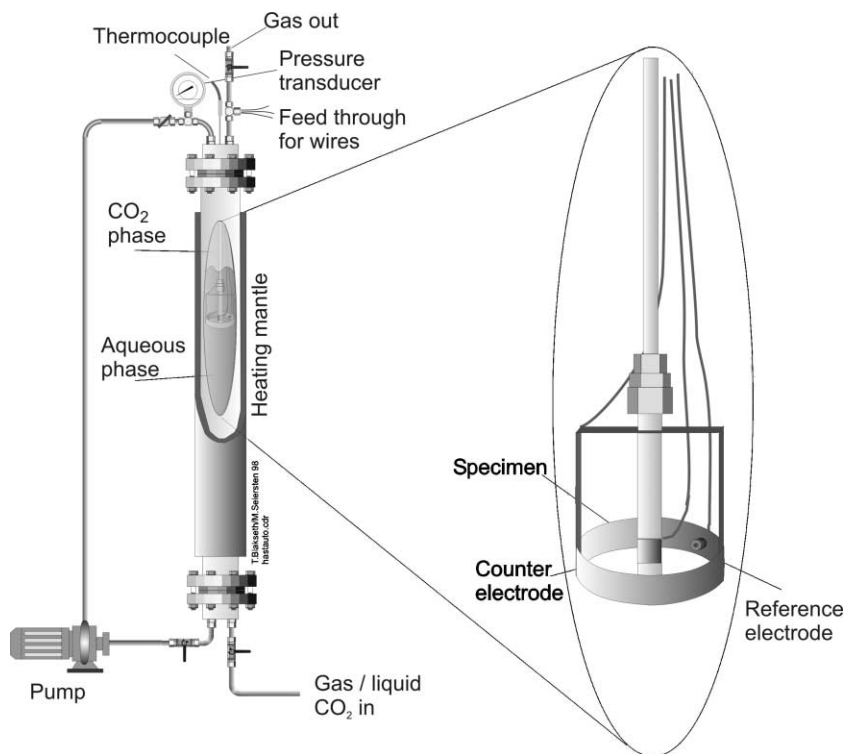
Figure 2: Schematic illustration of the test autoclave used for corrosion experiments.

TABLE 2
ELEMENT ANALYSIS (WT%) FOR THE CARBON STEEL USED IN THE TESTS

Steel	C	Si	Mn	S	P	Cr	Ni	V	Mo	Cu	Al	Sn	Nb
#57	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 measurements are at 100 bara.

The corrosion rate was measured by the linear polarization resistance (LPR) technique in the three-electrode configuration. The specimens were small cylinders with surface area of 3.14 cm^2. The counter electrode was a Pt-foil mounted around the specimen. The reference electrode was a 1 mm Ag rod mounted in a PTFE bar in the counter electrode. Even though the electrode was anodized in 0.1 M HCl before each experiment, it did not remain stable during the experiments. A new agar-based Ag/AgCl reference electrode was therefore constructed (Figure 3) and used in the late experiments (CCP_K11–K20). The electrode was made with standard Swagelock fittings, and was composed of an Ag rod covered with AgCl, 3 M KCl in agar and a porous ceramic plug. The electrode was placed in the bypass line. Even this electrode did not provide sufficient stability and it had to be regenerated before each experiment following a procedure described in Ref. [6].
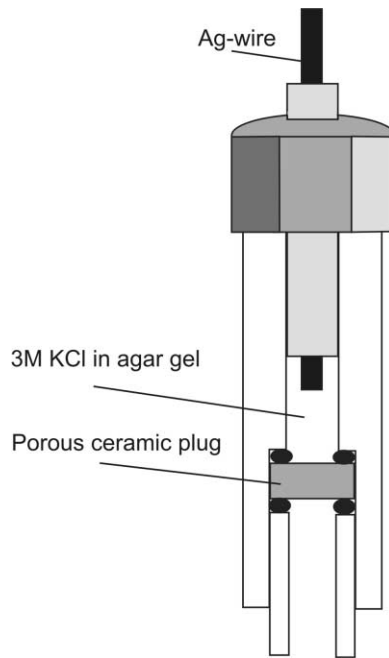
Figure 3: Schematic representation of the Ag/AgCl reference electrode.

RESULTS AND DISCUSSION

Water Solubility in CO_2 and in Mixtures of CO_2 and CH_4
Verification test
A series of experiments was carried out to verify the experimental set-up. The test condition of 25 °C and 100 bar was chosen, as this was the parameter set where most data could be found in the literature. An additional series was carried at 36.5 °C and 100 bar to study the effect of temperature on the time needed to reach equilibrium. The results are given in Table 3. The results show that 8 h are needed to reach equilibrium at 25 °C, while equilibrium is obtained after 2 h at 36 °C.

Measurements on mixtures of CO_2 and CH_4
A series of experiments was conducted to measure the solubility of water in pure CO_2 and in mixtures of CO_2 and CH_4. The CH_4 concentration of the mixtures was 5%. Figure 4 gives the results at 25 °C. The spread in the measured values is considerable, but that is also the case for literature data. Measurements at 14 °C were not successful, as equilibrium could not be established in a reasonable time. The conclusion from these experiments is that the method is best suited for high-density CO_2 fluids and that it is difficult to obtain reliable results for gaseous CO_2. The reason is that it is more difficult to sample the gaseous phase as only small temperature gradient leads to water condensation in the tubing and the valves.

Corrosion of Carbon Steel in CO_2 and CO_2-Saturated Water
Previous work
Pure, dry CO_2 is essentially non-corrosive. Experimental studies indicate this [10–12] and, in addition, field experience shows few problems with transportation of high-pressure dry CO_2 in carbon steel pipelines [13–15]. More than 3000 km of pipelines carrying CO_2 are in operation worldwide, most of these in the USA.

TABLE 3
WATER SOLUBILITY IN PURE CO2 AT 100–103 BAR

Temperature (°C)	Mole fraction water in CO_2/ppm ($X \times 10^6$)	Comments
25	2743	Equilibrium time 2 h
25	2909	Equilibrium time 4 h
25	3381	Equilibrium time 8 h
36.5	4145	Equilibrium time 2 h
36.5	4312	Equilibrium time 4 h
36.5	4199	Equilibrium time 8 h
25	3539	101 bar, Data from Wiebe and Gaddy [7]
25	3374	103 bar, Data from Song and Kobayashi [5]
25	3270	101 bar, Data from King et al. [8]
25	3360	101 bar, Data from Dewan [9]
35	4070	101 bar, Data from King et al. [8]

Designation: API 5L X65, microstructure: ferrite–perlite.
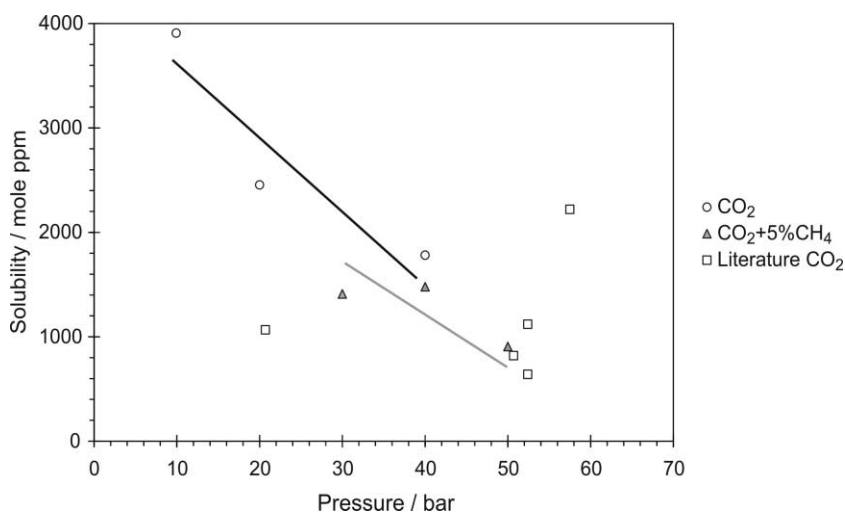
Figure 4: Water solubility in pure CO_2 and in a 5% CH_4 in CO_2 mixture at 25 °C as function of pressure.

CO_2 in the presence of water, however, will form carbonic acid which is corrosive. The impact of CO_2 corrosion on carbon steel has been studied extensively at pressures relevant for oil and gas transport (up to 20 bar). At higher pressures experimental data are sparse. Studies of CO_2 corrosion of carbon steel conducted at 170 °C and 100 bar CO_2 for 200 days [10] and at 50 °C and 240 bar CO_2 for 24 h [16] provide qualitative evidence for corrosive attacks on carbon steel. In both these cases CO_2 contains water just above the solubility limit. A study conducted in a 0.8 L autoclave filled with 1.0 M NaCl solution at 80 °C and CO_2 pressures up to 50 bar [16] showed that the pH change of the test solution, during the experiments introduced by the corrosion process, affects the corrosion rates at high CO_2 pressures. Experiments performed under "floating pH" conditions showed small differences in corrosion rates at 5 and 50 bar CO_2, whereas experiments performed at constant pH showed 1.5–3 times higher corrosion rate at 50 bar than at 5 bar. For instance, the corrosion rate at pH 3.5 was about 10 mm/y at 5 bar and 15 mm/y at 50 bar.

Generally, the corrosion rates decreased with increasing pH, and the experiments performed under "floating pH" conditions gave the lowest corrosion rates (~ 2.5 mm/y). Formation of a protective carbonate scale under "floating pH" conditions explains this observation. Within the project "Large Scale CO_2 Transportation and Deep Ocean Storage" sponsored by US Department of Energy (DOE) and performed by McDermott International, corrosion experiments were conducted in a high-pressure autoclave at conditions simulating deep ocean environment (i.e. 300 bar and 2 °C) [18]. Corrosion rates on carbon steel were measured by LPR for 0–30% CO_2 in sea water. The relevant DOE report has not been made public.

Reported field experiences with wet CO_2 at high pressures are also sparse. Accumulation of corrosion products due to insufficient drying and a leak at a low point due to water build up are reported from the start up of one CO_2 pipeline [19]. Failures of carbon steel pipe fittings with high-pressure CO_2 line tapping were reported in a urea plant. The CO_2 pressure in the pipeline was 156 bar and the temperature was 104 °C [20].

Experimental results
Table 4 summarizes the corrosion rate for the experiments CCP_K1–K21. The reported rates are the average rates during the last 24 h of the experiments. In systems containing 50 wt% MEG, experiments were run at three different temperatures 5, 25 and 50 °C, respectively.

TABLE 4
CORROSION RATES FOR THE EXPERIMENTS CCP_K1–K21

Eksp. No.	Temperature (°C)	MEG concentration (wt%)	CO_2 pressure (bar)	NaCl (g/kg)	Precorrosion	Average corrosion rate (mm/y)
CCP_K1	5	50	44	10		0.1
CCP_K2	5	50	5	10		0.04
CCP_K3	25[a]	50	1–58	10		2.3
CCP_K4	25[a]	0	58	10		2.4
CCP_K5	25[a]	50	58	10		2.3
CCP_K6	25[a]	90	58	10		0.2
CCP_K7	25[a]	50	30	10		1.3
CCP_K8	5	50	10	10		0.06
CCP_K9	5	50	20	10		0.075
CCP_K10	5	50	1–44	10		0.045
CCP_K11	25	50	64	10	yes	0.6
CCP_K12	25	0	64	10	yes	3.6
CCP_K13	50	50	1	10		1.5
CCP_K14	50	50	10	10		2.3
CCP_K15	50	50	30	10		2.7
CCP_K16	50	50	55	10		2.5
CCP_K17	50	50	80–64	10		1.7
CCP_K18	50	0	80–63	10		4.6
CCP_K19	50	0	40	10		6.9
CCP_K20	50	0	20	10		4.3
CCP_K21	50	0	5–60	10		2.3

The reported corrosion rates are the average of the last 24 h.
[a] Temperature control failed, and the actual temperature was slightly higher than 25 °C.

Figures 5 and 6 illustrate the pressure dependence of the corrosion rates at the different temperatures. At 5 °C the corrosion rates increase with increasing pressure, and the maximum rate is 0.1 mm/y at 44 bar. Increasing the temperature to 25 °C results in a large increase in the corrosion rate (0.1 mm/y at 5 °C to 2.3 mm/y at 25 °C). Also at this temperature there seems to be an increase in corrosion rates with increasing

pressure. However, just two experiments are performed at this temperature. Increasing the temperature further to 50 °C has only a limited effect on the corrosion rates (2.3 mm/y at 25 °C to 2.7 mm/y at 50 °C). In contrast to the behavior at the 5 and 25 °C, the corrosion rates do not increase with increasing pressure. Instead the corrosion rate reaches a maximum of 2.7 mm/y at 30 bar (Figure 6). A similar behavior with respect to the influence of pressure increase on the corrosion rates is observed in systems containing only water at 50 °C (Figure 7). Here the corrosion rate has a maximum of 6.9 mm/y at 40 bar. Similar behavior of decreasing corrosion rates with increasing pressure has also been reported previously at 40 °C [21].
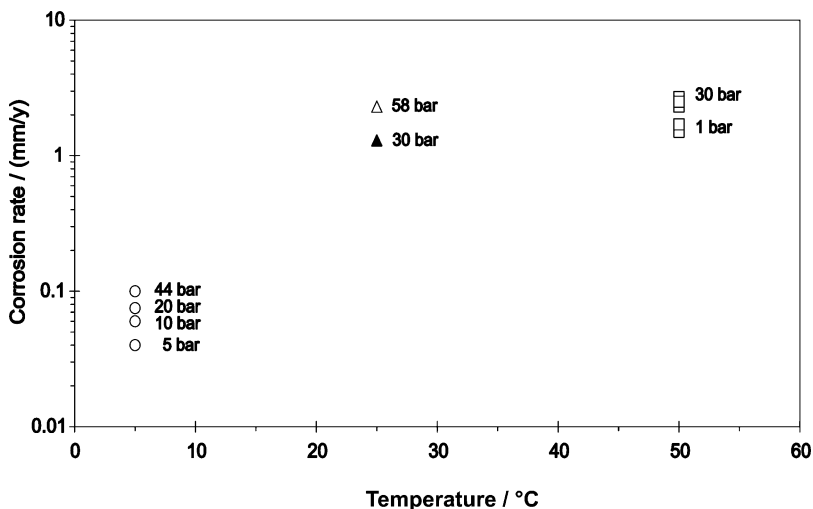
Figure 5: Pressure dependence of the final corrosion rates for experiments performed at 5, 25 and 50 °C, 50 wt% MEG, 10 g/L NaCl, semi-stagnant conditions, floating pH.
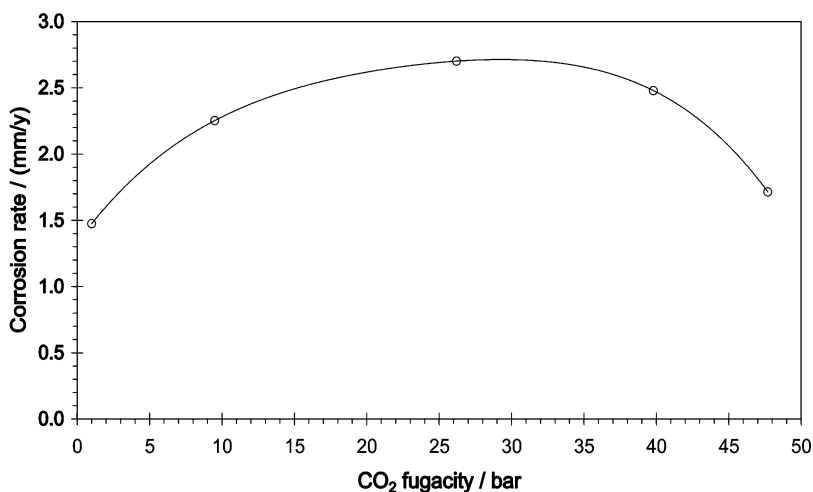
Figure 6: Final corrosion rates in 50 wt% MEG solution (10 g/L NaCl) at 50 °C as a function of CO_2 fugacity at semi-stagnant conditions with floating pH.
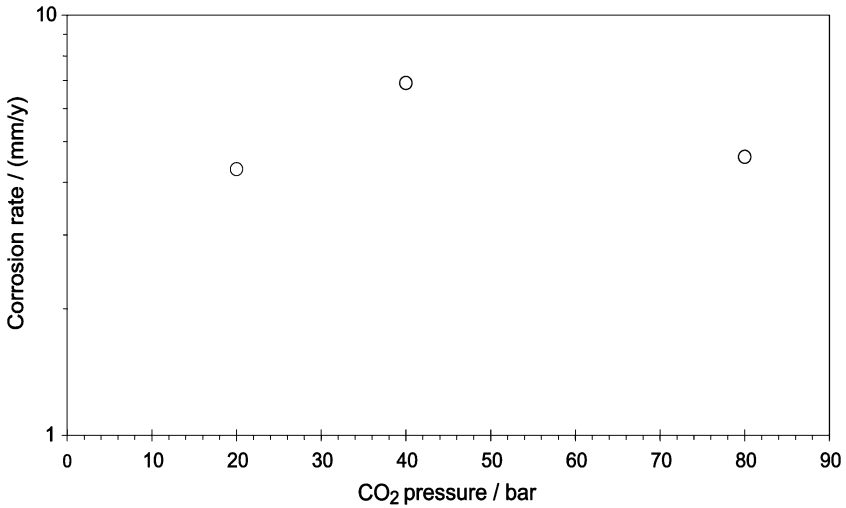
**Figure 7:** Final corrosion rates in water (10 g/L NaCl) at 50 °C as a function of CO_2 pressure fugacity at semi-stagnant conditions with floating pH.

Two experiments were run for corrosion at low pressure (1 bar) for a period of 24 h (CCP_K11 and K12). These experiments can be compared with almost identical experiment runs without the low-pressure period, see Figure 8. In the system containing 50 wt% MEG the corrosion rate is lower than in a similar experiment without a low-pressure period (0.6 mm/y compared to 2.3 mm/y). On the other hand, in the system containing water only, the corrosion rate is highest in the experiments with a low-pressure period (2.4 mm/y compared to 3.6 mm/y). From these data it seems that in water only precorrosion at low pressure might "activate" the carbon steel and give a higher corrosion rate at high pressure, but the data are too sparse to draw any firm conclusion.
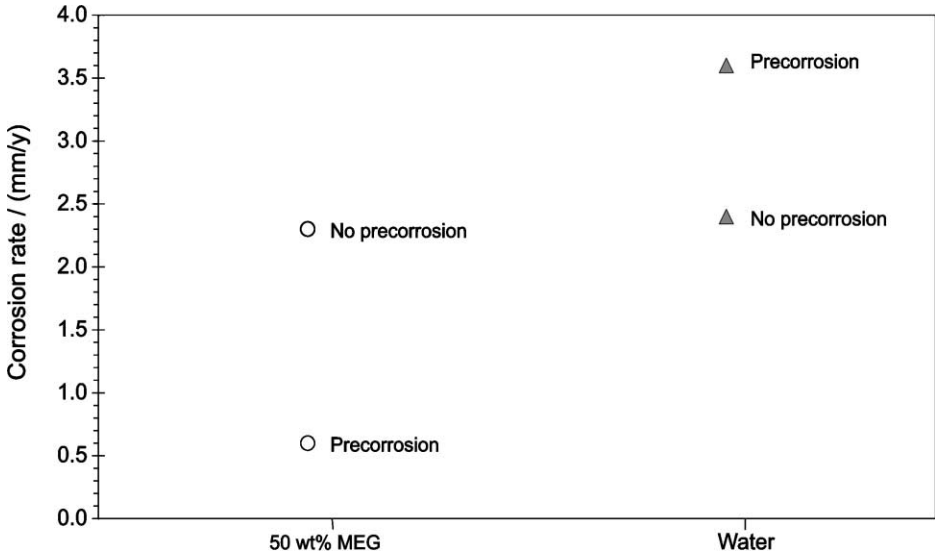
Figure 8: The effect of a precorrosion period at low pressure in systems with and without MEG at 25 °C.

In an actual high-pressure pipeline, MEG or another hydrate inhibitor will be injected to prevent hydrate formation if a temperature of less than 15–20 °C is expected. From studies conducted at lower CO_2 pressures, it is well known that MEG, in addition to preventing hydrates, reduces CO_2 corrosion [22]. In the 50 wt% MEG solution in water applied in this work, the corrosion rate is reported to reduce by a factor of 0.33 [23]. In two experiments conducted at 25 °C (Table 4, CCP_K4 and K5) under the same experimental conditions, but with and without MEG, respectively, the corrosion rates are almost the same. But at 50 °C (Table 4, CCP_K17 and K18) the correction factor of 0.33 fits the data very well. It is difficult to draw clear conclusions from these data on the inhibiting effect of MEG at high CO_2 pressures.

Corrosion coupons mounted in the CO_2 phase at the top of the autoclave did not show any signs of corrosion attacks.

Measured corrosion rates compared to model predictions
There exist a number of corrosion prediction models that can be used to assess CO_2 corrosion rates (Table 5) [24]. However, they have been developed to cover a pressure range relevant for oil and gas transportation, i.e. pressures up to 20 bar. When CO_2 pressure above 10 bar is used as input in these models, they tend to predict corrosion rates that are higher than the experimental rates that are reported in this study (Figures 9–12). Some of the models do not have an MEG correction factor incorporated, and the corrosion rates predicted in 50 wt% MEG solutions are obtained by multiplying corrosion rates predicted in pure water systems with a factor of 0.33 [23]. It should also be noted that not all models are applicable at temperatures below 20 °C.

TABLE 5
SURVEY OF PREDICTION MODELS FOR CO_2 CORROSION WITH APPLICATION LIMITS

Model	Developed by	T (°C)		P (bar)	pCO₂ (bar)		pH	
		Min	Max	Max	Min	Max	Min	Max
de Waard[a]	de Waard and coworkers (Shell, IFE), published	0	140			10		
HYDROCOR	Shell	0	150	200		20		
Cassandra 98[b]	BP		140	200		10		
NORSOK[c]	Hydro, Saga, Statoil (IFE data)	20	150	1000		10	3.5	6.5
CORMED[d]	Elf		120					
LIPUCOR	Total	20	150	250		50		
KSC model[e]	IFE (JIP)	5	150	200	0.1	20	3.5	7
Tulsa model[f]	University of Tulsa	38	116			17		
PREDICT[g]	InterCorr International	20	200			100	2.5	7
Ohio model[h]	Corrosion in Multiphase Systems Center at Ohio University	10	110	20				
SweetCor[i]	Shell	5	121		0.2	170		

[a] None of the de Waard papers give application limits. Maximum values in nomogram shown.
[b] Accepts input outside these values but displays a warning.
[c] Wall shear stress between 1 and 150 Pa. Will be extended down to 5 °C.
[d] CORMED accepts higher temperatures and ionic strengths but displays a warning, as the pH calculation becomes uncertain. The corrosion risk prediction is still valid.
[e] Flow velocity between 0.2 and 30 m/s.
[f] Recommends these limits, but accepts input outside these values.
[g] PREDICT does not give any limits, either in the software or in the manual.
[h] Minimum 10% water cut. Can be used at higher pressures with fugacity coefficient input.
[i] Analysis of CO_2 corrosion by managing a large database of corrosion data from laboratory experiments and field data.

A partial explanation for the low experimental rates compared to model predictions is that the models are developed for flowing conditions. Although water solution in the autoclave is continuously pumped from the bottom to the top, the flow rate at the specimen site is low. Based on flow loop experiments at lower CO_2 pressures, it is expected that the corrosion rate may increase by a factor $2-3$, at normal pipeline flow rates. A discrepancy in the order of 10 is difficult to explain as a flow factor as long as the solution is undersaturated with iron.
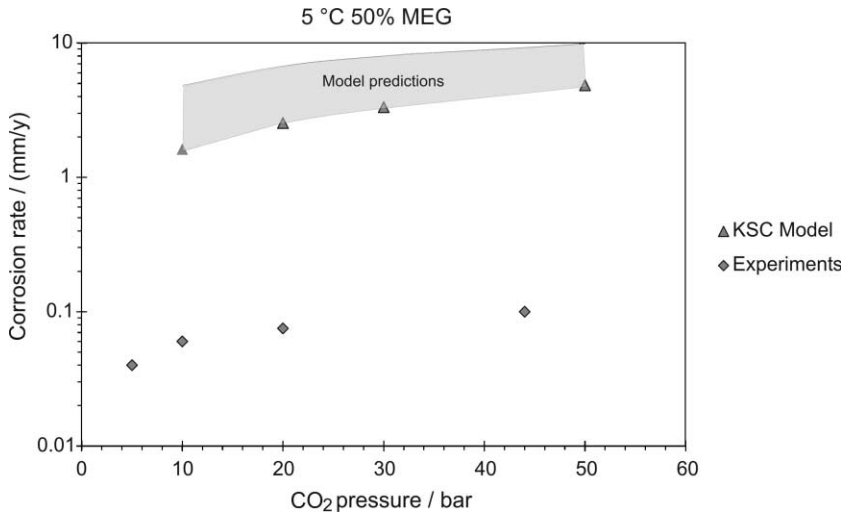
Figure 9: Experimental corrosion rates compared to model predictions in 50 wt% MEG solutions at 5 °C. The model predictions fall in the shaded area and only the values calculated by the KSC model are shown.
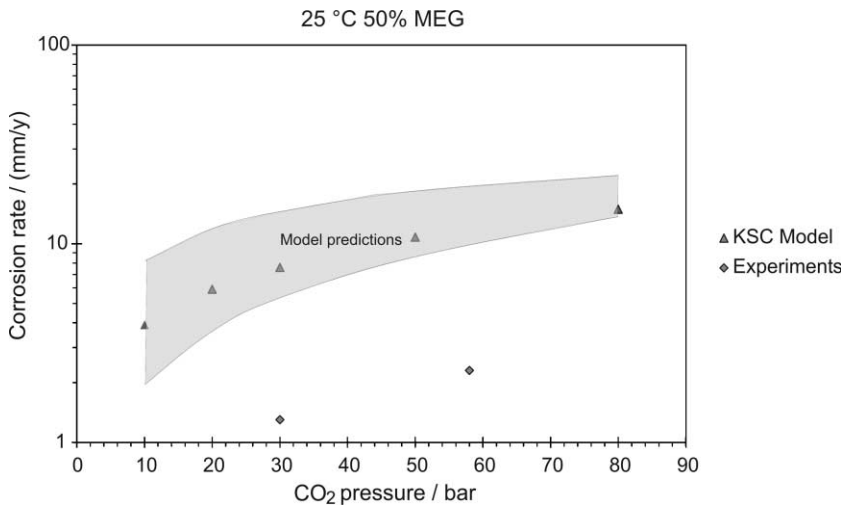
Figure 10: Experimental corrosion rates compared to model predictions in 50 wt% MEG solutions at 25 °C. The model predictions fall in the shaded area and only the values calculated by the KSC model are shown.
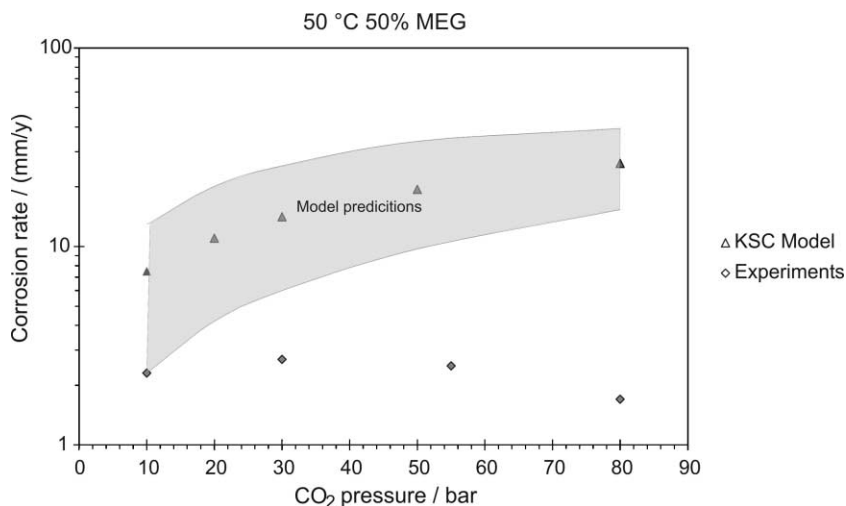
Figure 11: Experimental corrosion rates compared to model predictions in 50 wt% MEG solutions at 50 °C. The model predictions fall in the shaded area and only the values calculated by the KSC model are shown.
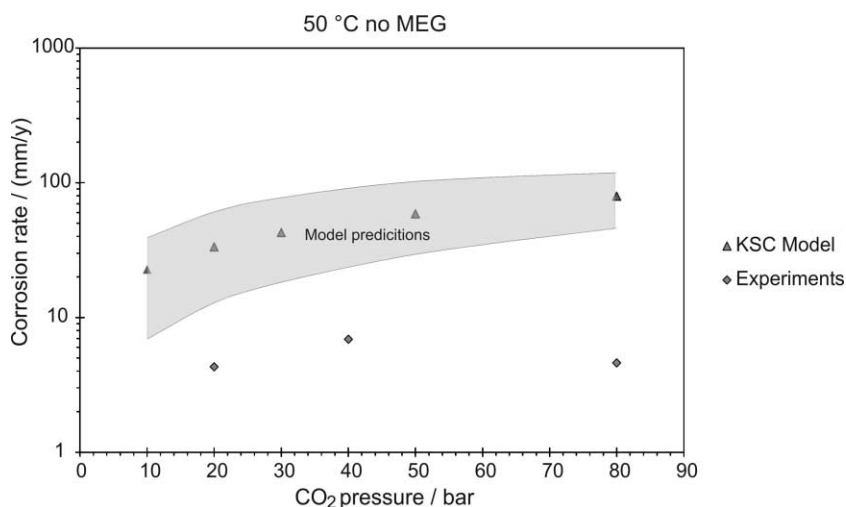

Figure 12: Experimental corrosion rates compared to model predictions in water at 50 °C. The model predictions fall in the shaded area and only the values calculated by the KSC model are shown.

A possible explanation for the large inconsistency between experimental and model values could be the formation of a protective $FeCO_3$ film at higher pressures. However, the pH in these experiments will be in the area 3–3.5, and thus the iron solubility limit will be above 200 ppm. Such iron concentrations were not reached in these experiments. The iron concentration at the end of the experiments was in the range

10–100 ppm. Examination of the specimens after the tests showed only patches covered by corrosion products, too thin to be analyzed. It is thus unlikely that $FeCO_3$ films cause the low corrosion rates. Another possible explanation for the low corrosion rates is that there is a change in the CO_2 corrosion mechanism at high pressures. This will be explored further in forthcoming experiments with a more reliable reference electrode.

Inhibiting corrosion of carbon steel at high CO_2 pressures
The possibility of inhibiting CO_2 corrosion at high CO_2 pressures has been studied earlier [1]. Figure 13 summarizes the findings at 30 °C and 72 bar CO_2. Adding 20 ppm film-forming inhibitor in addition to MEG decreases the corrosion rate markedly and the corrosion rate soon drops below the target value: 0.1 mm/y. In these experiments, 14 g/L NaOH was added to decrease the acidity. This does not have a beneficial effect on the inhibited corrosion rate as it decreases slower and does not reach the same low value as without NaOH.
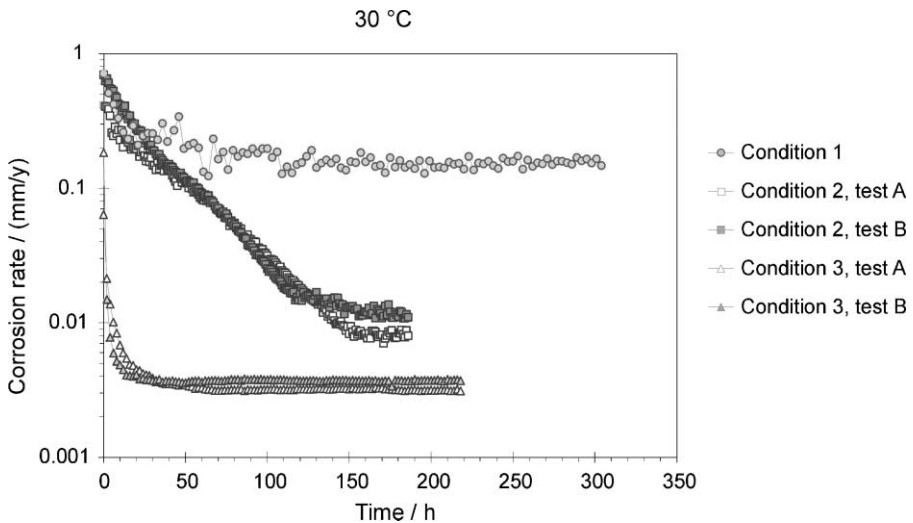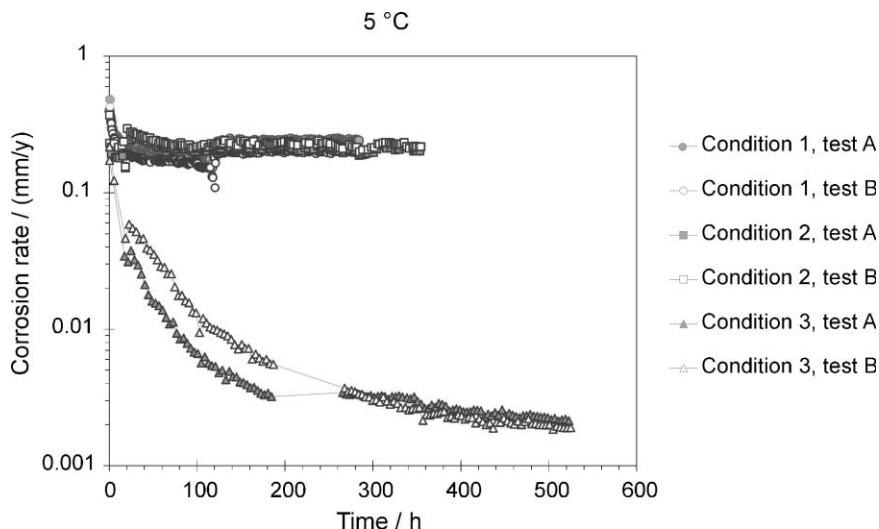

Figure 13: Corrosion rate as function of time at 30 °C and 72 bar CO_2 in a 1% NaCl solution without MEG. In some of the experiments 14 g/L NaOH was added in order to decrease the acidity. The inhibitor concentration was 20 ppm. Results from an earlier study [1]. The test conditions were as follows: Condition 1: no additions; Condition 2: both NaOH and corrosion inhibitor added; Condition 3: only corrosion inhibitor added.

Similar experiments were performed at 15 and 5 °C in the same study. The results were the same, i.e. adding 20 ppm CO_2 corrosion inhibitor reduced the corrosion rate substantially. Figure 14 shows the results at 5 °C and 44 bar CO_2. The corrosion rate without inhibitor is 0.2–0.3 mm/y independent of NaOH addition. Adding 20 ppm inhibitor to the solution lowers, also in this case, the corrosion rate well below 0.01 mm/y.

CONCLUSIONS

The literature survey and experiments performed in this study show that dry CO_2 and CO_2 that is not saturated with water is non-corrosive to carbon steel at transportation pipeline operation conditions.

Figure 14: Corrosion rate as function of time at 5 °C and 44 bar CO_2 in a 1% NaCl solution without MEG. In some of the experiments 14 g/L NaOH was added in order to decrease the acidity. The inhibitor concentration was 20 ppm. Results from an earlier study [1]. The test conditions were as follows: Condition 1: no additions, CO_2 pressure 35 bar; Condition 2: only NaOH added, CO_2 pressure 44 bar; Condition 3: NaOH and corrosion inhibitor added, CO_2 pressure 44 bar.

CO_2 with water content above saturation is corrosive when water precipitates, but the experiments show that the corrosion rates at high CO_2 pressures in systems containing only water and that containing water/MEG mixtures are considerably lower than predicted by existing corrosion models. This applies especially at low temperatures typical for sub-sea pipelines in northern waters. In a previous study it was demonstrated that 20 ppm CO_2 corrosion inhibitor is sufficient to lower the corrosion rate below 0.1 mm/y at temperatures up to 30 °C and CO_2 pressures up to 72 bar [1].

More work is needed in order to understand the apparent change in corrosion mechanism at high CO_2 partial pressure. It should also be emphasized that the present investigations have been performed at non-flowing conditions in autoclaves with gentle agitation. Before the results can be utilized for pipeline designs, the effect of flow should be investigated in flow loop experiments.

RECOMMENDATIONS

For the transportation of CO_2 in carbon steel pipelines it is recommended that more work be conducted in the following areas.

1. Verification of water solubility as function of temperature and pressure for actual fluid compositions. For corrosion evaluations this information will be needed to be able to predict the amount of water precipitation, if any. This information is also necessary in order to optimize compression cycles and water removal during compression.
2. Determination of corrosion risks at realistic flowing rates with actual fluid composition should be made. The effect of flowing conditions should be investigated before the corrosion results are utilized for design. This should also include inhibitor evaluation. The consequences of other fluid components than

CO_2 should also be explored, especially the effect of H_2S in reducing conditions or sulfur or nitrogen oxides at oxidizing conditions.

3. More work on the mechanisms of CO_2 corrosion at high CO_2 partial pressures will be needed in order to extend present corrosion models.

When stainless steels are used it will be necessary to evaluate the corrosion risks if the fluids are more aggressive than pure CO_2. In addition, the integrity of steels with sealants (such as might be used in abandoned wells) requires special experiments.

ACKNOWLEDGEMENTS

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