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Summary

Equipment for measurements of water solubility in CO_2 fluids have been set up and successfully tested with liquid CO_2 at 25 and 36 °C. The results have shown that it is difficult to obtain equilibrium between a water phase and gaseous CO_2 at low temperature. The problems can probably be solved by equilibrating for longer time and by applying more vigorous shaking during the experiments.

An experimental set-up for corrosion studies in liquid water/glycol solutions as well as in CO_2 with high water content has been constructed and utilised in corrosion studies. The results show that the corrosion rates are manageable at temperatures lower than 30 °C and that it is possible to obtain corrosion rates that are lower than 0.1 mm/y with corrosion inhibitors.

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Contents

1. Introduction

It is a high priority issue in political, scientific, and industrial circles as "how to limit or decrease emissions of carbon dioxide due to its role in global atmospheric greenhouse warming" [1]. A wide range of technologies is being investigated that are able to capture, compress, transport, and inject CO_2. Unless the captured CO_2 can be used for enhanced oil recovery or other processes where CO_2 can be utilised to increase product value, CO_2 removal will represent a substantial cost [2,3].

The costs will depend on the process and duty select, but considerable expenditure cut can be achieved by proper materials and process selection. Corrosion will be a major concern in materials selection for process equipment for sequestration, transportation and injection and water play a key role especially for pipelines. If the drying is insufficient, water may precipitate in a transportation line, and it will be very corrosive due to the high CO_2 pressure. CO_2 for deposition may contain trace elements from the separation process in addition to nitrogen and hydrocarbons. The corrosivity of the trace components has to be evaluated. They may also have indirect effect on corrosion as they may enhance water precipitation from liquid CO_2 in the same way as hydrocarbons and N_2.

Carbon dioxide has been utilised for enhanced oil recovery for nearly 30 years and there is more than 100 installations all over the World. Several of these have pipelines in carbon steel 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 [4]. 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. In that case, the transportation distance is short and the use of corrosion resistant duplex steel could be justified. The table below summarises experience with some candidate materials for CO_2 injection equipment. It also shows the lack of experience with materials in environments that can be expected in process, transport, and injection systems for CO_2 deposition. A cost factor for piping materials is also indicated.

Table 1 *Corrosion rates and experiences reported in the literature for candidate steels for CO₂ pipelines and process equipment. The table summarises investigations at CO₂ pressure above 70 bar. A cost factor for piping materials is indicated in the bottom row.*

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 ~1μm/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 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 (stress corrosion cracking must be considered)
Cost factor for piping material	1	2	≥4

It is evident from the table above that little is known about the performance of candidate steels for CO_2 processing and transport. For injections areas located at some distance from the source, transportation costs are considerable. For a CO_2 sequestration scenario with a 200 km transport line, the transportation costs have been estimated to 20-40% of the total costs 2. It is not known what the materials costs amounts to, but the cost figures in the table above clearly show that carbon steel is the most attractive for long pipelines and that 13%Cr steels can be considered for shorter lines. Introductory studies have shown that the corrosion rate of pipeline steel in wet CO_2 is less than anticipated, and that some wetting of the pipeline may be allowed for a limited period 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 be clarified if it is possible to extend the use of carbon steels with corrosion inhibitors. This will be in solutions with glycol or other hydrate preventers. Furthermore, little is known on the corrosion of 13%Cr steel in CO_2 with free water. Several 13%Cr steels are candidate materials if water wetting is anticipated, especially for shorter pipelines.

Apart from cost considerations, the possibility of free water will determine the materials selection. 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, little has been done on effect of trace chemicals. As an example, it is known 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 pressure and temperature range that has been covered are not extensive [5]. The number of data points is too few to be used as design parameter for CO_2 injection pipelines and accurate determination of the solubility limit in the actual mixtures is required.

1.1.　Project objectives

The objective of the project is to establish a basis for materials selection for CO_2 capture, compression, transportation, and injection. The project will be closely coordinated with the CCP Transportation project run by SINTEF and Reinertsen Engineering (SINTEF/Reinertsen project). The sub-goals will be:

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 elements from the separation process will also be addressed.
2. To deliver the data needed by the SINTEF/Reinertsen project in the development of the tool (nomogram) to be used for cost effective development of CO_2 transportation systems.
3. To determine the corrosion rate of carbon, 13%-chromium, and duplex steels in liquid/supercritical CO_2 as function of water content, temperature and pressure and to clarify if it is possible to extend the use of carbon steels with corrosion inhibitors.

In the first project period (2001-2002), the project will be concentrated on task one and two.

1.2.   Equipment build-up

Two experimental equipments have been set up in the project. One is for the measurement of water solubility in CO_2 mixtures and one is for the measurement on corrosion. Both are described in detail in this report together with results of preliminary experiments.

2. Water solubility measurements

2.1.   Experimental procedure for water solubility measurements

The experiments are based on the use of tritium labelled water. The water phase is allowed to equilibrate with a gaseous or liquid CO_2 phase at temperature. Samples of the gas phase is washed out with water to pick up the tritium labelled water in the gas phase and the resulting water is analysed for tritium.

The experimental apparatus shown in Figure 1 is a modification of the one described by Song and Kobayashi[6]. It consist 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 within ±0.1 ºC. The autoclave and the sampling system can be evacuated to 0.1 bar.

Tritium labelled water was obtained from the experimental reactor at Kjeller. It was thinned 10 times to obtain an activity of 6 Mbq (Mega bequerel) in the test solution.

A series of experiments is started by filling the autoclave with 100 ml tritium labelled water. The autoclave is then evacuated and the gas or fluid phase is added through the bottom inlet and bobbled through the water phase. Measurements on CH_4 and CO_2 mixtures are carried out by adding CH_4 and let it equilibrate with the water phase at the correct partial pressure before CO_2 is added and the pressure is stabilised at the correct total pressure. In this way, it is easier to obtain correct gas mixtures and avoid uncertainty due to the high solubility of CO_2 in the water phase. Liquid CO_2 can be pumped in for high pressure studies.
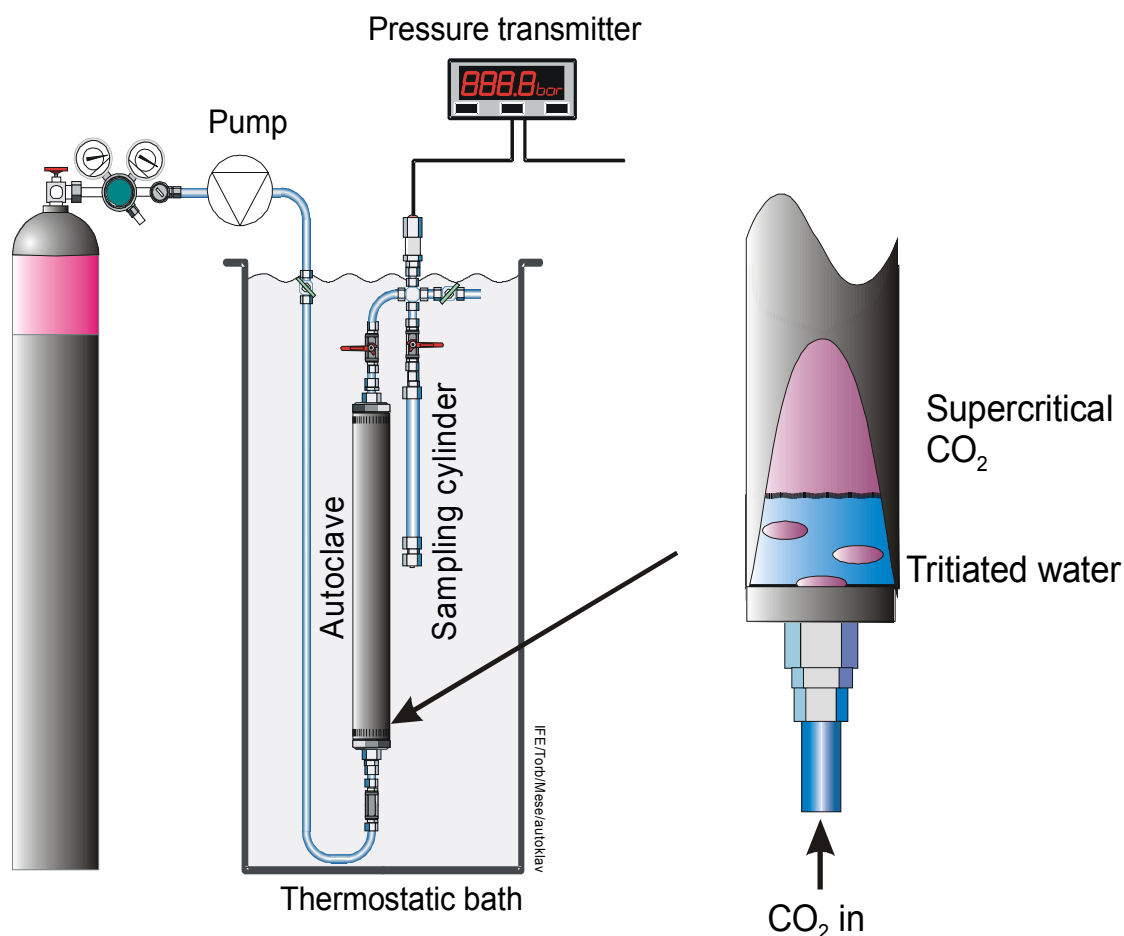
Figure 1   Apparatus for measurements of water solubility in liquid/gaseous CO_2.

The autoclave is decoupled after filling and shaken in the thermostatic bath before it is couplet to the sampling system. It is equilibrated for 4-24 hours before sampling starts. The sampling system is thoroughly dried and evacuated before sampling begins.

The volume of the sampling cylinder is 150 ml and before sampling it is filled with ca. 100 ml distilled water. The water content is accurately determined by weighing. The cylinder is evacuated before sampling. The pressure change in the autoclave during the operation is less than 1 bar.

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

2.2. Results

Verification test

A series of experiments was carried out to verify the experimental set-up. The test conditions of 25 ℃ and 100 bar was chosen as this is one of the parameter sets with most literature values. An additional series was carried at 36.5 ℃ and 100 bar to study the effect of temperature on the time needed to reach equilibrium. The results are given in Table 2. The results show that 8 hours are needed to reach equilibrium at 25 ℃, while equilibrium is obtained after 2 hours at 36 ℃.

Table 2   Water solubility in pure CO_2 at 100-103 bara.

Temperature / ℃	Mole fraction water in CO_2 / ppm (X * 10^6)	Comments
25	2743	Equilibrium time 2 hours
25	2909	Equilibrium time 4 hours
25	3381	Equilibrium time 8 hours
36.5	4145	Equilibrium time 2 hours
36.5	4312	Equilibrium time 4 hours
36.5	4199	Equilibrium time 8 hours
25	3539	101 bar, Data from Wiebe[7]
25	3374	103 bar, Data from Song6
25	3270	101 bar, Data from King[8]
25	3360	101 bar, Data from Dewan[9]
35	4070	101 bar, Data from King8

Results of introductory experiments

The first experimental matrix covers needs in the SINTEF/Reinertsen project. It is given together with the first results in Table 3. The scatter in the results is larger than expected, and the results do not follow the expected trends as illustrated in Figure 4. The reason is probably that the specimens have not equilibrated properly. Some results are higher than expected, this is most likely caused by water droplets in the gas samples. These are problems which are regarded as easily solvable and experiments underway seem to be more consistent and reproducible.

Table 3   Measured water solubilities in CO_2 and CO_2-CH_4 mixtures

| No	Temperature °C	Total pressure bar	CO_2 press bar	CH_4 press bar	Molfraction H_2O *10^6 (ppm)
CCP_1_1	20	10	10	0	2166
CCP_1_2	4	10	10	0	474
CCP_1_3	14	10	10	0	2226
CCP_1_4	25	10	10	0	2656
CCP_1_5	4	20	20	0	1019
CCP_1_6	14	20	20	0	560
CCP_1_7	30	20	20	0	1924
CCP_1_8	14	40	40	0	300
CCP_1_9	20	40	40	0	351
CCP_1_10	30	40	40	0	961
CCP_1_11	25	15	14.25	0.75	4076
CCP_1_12	25	30	28.5	1.5	3015
CCP_1_13	25	45	42.75	2.25	1177
CCP_1_14	25	60	57	3	914
CCP_1_15	14	15	14.25	0.75	915
CCP_1_16	14	30	28.5	1.5	570
CCP_1_17	14	40	38	2	219
CCP_1_18	14	50	47.5	2.5	474
CCP_1_19	25	30	28.5	1.5	930
CCP_1_20	25	40	38	2	3483
CCP_1_21	25	55	52.25	2.75	1012
CCP_1_22	5	15	14.25	0.75	1819
CCP_1_23	5	40	38	2	769
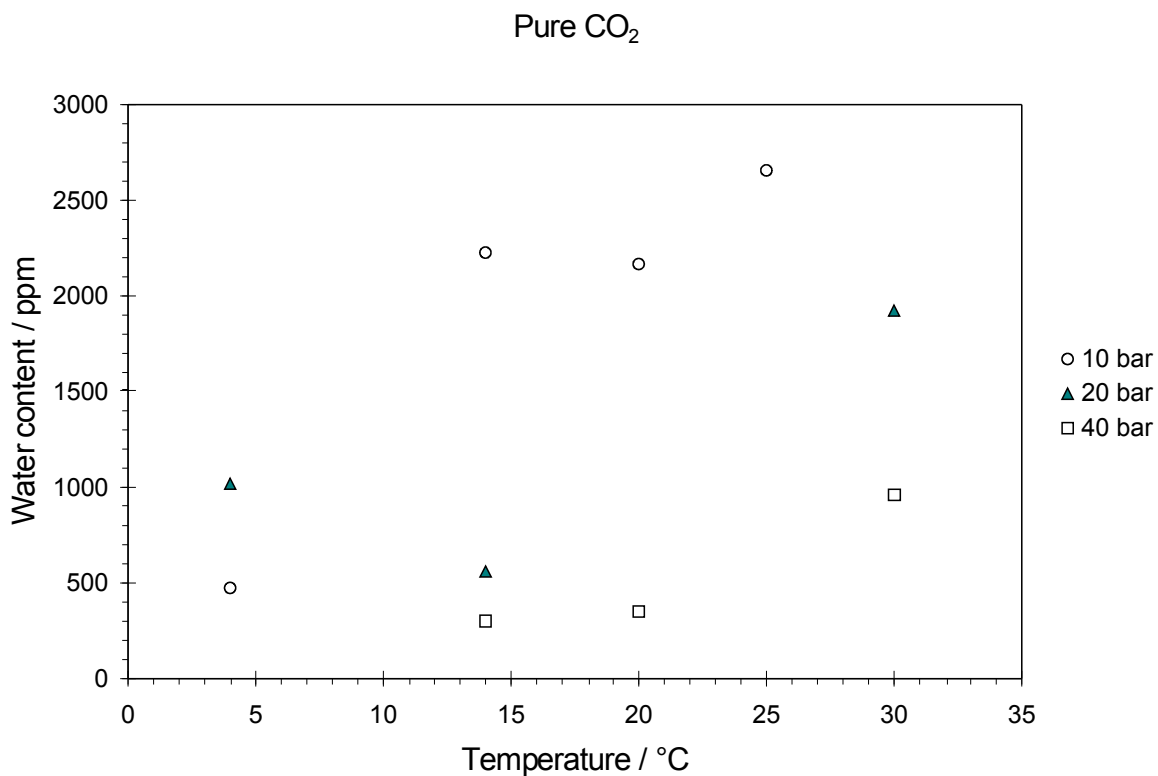
Pure CO_2

Figure 2   Water solubility in pure CO₂ versus temperature with pressure as parameter.

3. Corrosion studies

3.1.   Experimental

Figure 3 shows a schematic of the experimental set-up. It consists of an autoclave with a circulation pump. The total volume is 9 litre. The autoclave as well as the tubing is made in Hastelloy C. The autoclave can be evacuated with a pressure driven vacuum pump. The autoclave has a cooling and heating system and can be operated at 0 to 100 °C. It is certified for a pressure of maximum 75 bar.
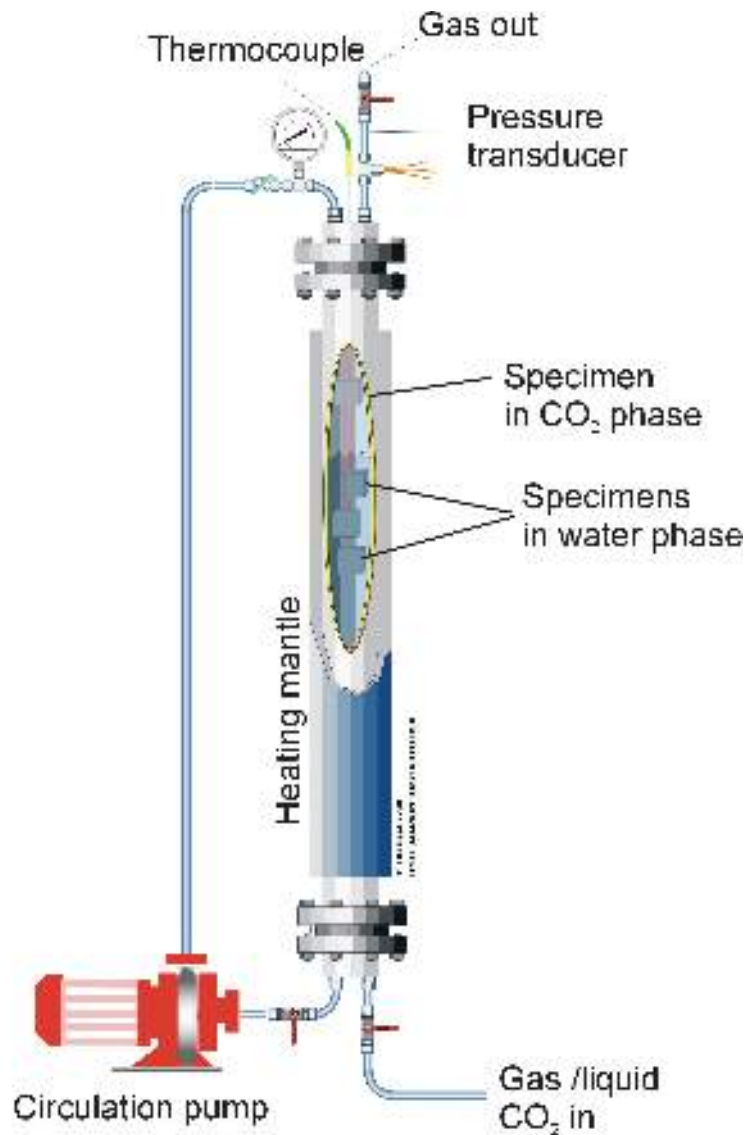
Figure 3   Autoclave for corrosion experiments at high CO_2 pressure

The autoclave has a shielded thermocouple mounted near the wall approximately midway between the top and the bottom. A pressure gauge with a transmitter is mounted at the top. There are valves for gas inlet and outlet and feed-through for electrical wires.

It is possible to perform experiments in water saturated CO_2 and CO_2 saturated water simultaneously. As the pressure is maximum 75 bar, water and water-MEG mixtures have a higher density than CO_2 and the water and the CO_2 phase will be well separated. This makes it possible to expose specimens both in the water- and the CO_2 phase. In the water phase, corrosion rate is determined by electrochemical measurements. Weight-loss coupons is used in the CO_2 phase.

Two set-ups are used for electrochemical measurements. In the simplest configuration, specimens are suspended at top of each other in isolated wires as illustrated in Figure 3. It is ensured that the specimens are isolated form each other and from the autoclave. This configuration can be used both in the water and the CO_2 phase. Electrochemical measurements in the water phase is only possible with two or more specimens. One of the specimens is used as reference and the autoclave as counter electrode. The configuration is only suited for measurement of corrosion rate by the linear polarisation resistance (LPR) technique not for slow potentiodynamic sweeps that can reveal more details on the corrosion mechanisms.

Figure 4 shows the three electrode set-up used to assess the corrosion mechanism. The specimen is mounted in the centre surrounded by a circular titanium counter electrode and with a reference electrode at a distance of approximately 1 cm distance. All wires and couplings are shield from the solution. The reference electrode is a 1 mm silver tread mounted in a PTFE bar in the counter electrode. The electrode was anodised in 0.1M HCl before each experiment. The resulting Ag/AgCl reference electrode as equilibrated with the solution, gave sufficient stability to follow the corrosion rate by low polarization resistance measurements and to make polarization scans. The potential at 40ºC in 1% NaCl is +270mV relative to SHE.

Corrosion rates are measured electrochemically with the linear polarisation (LPR) technique in three-electrode configuration. Impedance measurements are performed to assess the uncompensated electrolyte resistance (IR drop). These data are used for correction of the IR drop during subsequent corrosion rate calculations. The electrochemically measured corrosion rates are also calibrated by mass loss measurements. Slow potentiodynamic sweeps are performed to obtain additional information. All the electrochemical measurements are performed with Gamry PC3 potentiostats. A multiplexer is used when more than one specimen is exposed at the same time.
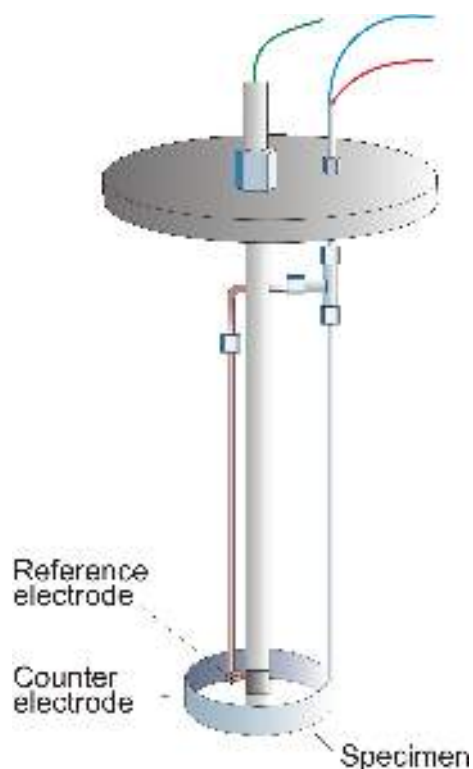
Figure 4   Three electrode set-up used for electrochemical measurements.

The specimens are ground to a 1000 mesh finish, cleaned with acetone in an ultrasonic bath and rinsed with isopropanol before they are mounted in the autoclave. The autoclave is flushed with gaseous CO_2 several times before it is evacuated and 8 litre of the pre-mixed and CO_2 saturated water-glycol solution is filled by vacuum. It is possible to inhibit the solution before the autoclave is filled.

For experiments with liquid or supercritical CO_2 above room temperature, the autoclave is cooled to 15 °C before liquid CO_2 is pressed into the autoclave from a gas cylinder. The gas cylinder is equipped with a surge pipe that assured that liquid CO_2 is pressed in. A high quality 99.9992% CO_2 is used in the experiments. The temperature is increased when the water phase was saturated with CO_2. The CO_2 pressure is reduced when the experimental temperature is reached. For the experiments below room temperature the water solution is cooled to the experimental temperature before CO_2 is added. The water is circulated to accelerate CO_2 uptake in the water phase. It takes approximately 0.5 – 1 hour after the water is let into the autoclave before stable conditions are obtained. Water is circulated at a rate of about 1 litre per minute during the experiment.

3.2.   Results

A series of experiments have been carried out for Statoil under another contract[10]. The corrosion rate of the pipeline steel X-65 was determined in glycol/water saturated with CO_2 and liquid CO_2. The CO_2 phase was not saturated with water as it was in equilibrium with a MEG/water phase not pure water. The specimens were 25x25x3 mm and they suspended on top of each other as shown in Figure 3.

The experimental matrix is summarized in Table 4. The experiments cover the temperature range below 30 ºC, which is of most interest for sub-sea transportation pipelines. The CO_2 pressure varied from experiment to experiment because it was chosen to be at the liquid/gas equilibrium line. The water phase contained 15 to 50 % technical quality (99%) monoethylene glycol. Salt (1% NaCl) was added to obtain sufficient conductivity in the water phase for electrochemical measurements. The effect of pH was studied in some experiments by adding NaOH to the solution. Sodium hydroxide reacts with CO_2 and forms $NaHCO_3$. The corrosion rate in the water phase was measured with LPR.

Table 4   *Overview of the experimental conditions*

Exp. No	Temp. °C	MEG conc. Wt%	CO_2 pressure bar	Total pressure bar	NaCl g/kg	NaOH g/kg	KI 350 ppm	Remarks
2	5	15	35	35	10	0	0	
3	5	50	44	60	10	14	0	
4	5	50	44	60	10	14	20	Leakage, exp. stopped
5	5	50	44	60	10	14	20	
6	15	50	52	60	10	14	20	
7	30	50	72	72	10	14	20	
8	30	50	72	72	10	0	20	
9	15	50	52	65	10	0	20	
10	30	50	72	72	10	0	0	

There was no corrosion on specimens exposed in the CO_2 phase. There were no sings of corrosion and a thorough scanning microscope investigation did not reveal any pits.

The corrosion rates measured in the water phase are summarized in Table 5. The final rates are lower than 1 mm/y without inhibitor and well below 0.1 mm/y with inhibitor. Increasing the pH has little effect, with inhibitor it may even seems that it increases the corrosion rate. It can thus be concluded from these experiments that if MEG is used as hydrate inhibitor, it is possible to inhibit corrosion in CO_2 pipelines even if there is water condensation.

Table 5   *Result summary for specimens exposed to water/MEG mixtures. The final corrosion rate is defined as the average corrosion rate during the last 24 hours of the experiment as measured by LPR. The average corrosion rate is determined by weight loss. All corrosion rates are averaged over at least two specimens.*

Experiment No	Tempe-rature °C	CO_2 Press bar	NaOH g/kg	Inhibi-tor ppm	Experiment duration hours	Iron conc. ppm	Corrosion rate Average mm/y	Final mm/y
2	5	35	0	0	308	35	0.21	0.22
3	5	44	14	0	358	40	0.20	0.21
5	5	44	14	20	526	3	0.01	0.002
6	15	52	14	20	282	3	0.02	0.01
7	30	72	14	20	186	8	0.09	0.01
8	30	72	0	20	236	<1	0.004	0.003
9	15	52	0	20	187	<1	0.003	0.001
10	30	72	0	0	311	33	0.13	0.10

The experiments in the CCP/Norcap project have started. These are aimed at revealing the corrosion mechanism at high CO_2 pressures. A tentative experimental matrix are given in Table 6. The matrix is a result of the discussion in the reference group meeting[11]. The temperatures are typical for offshore pipelines. CO_2 from a CO_2 capture process will typically have a temperature of 25 to 35 °C, and will be cooled to seabed temperature (~5 °C) during transportation.

The first experiment has been carried out. Figure 5 shows the corrosion rate measured in the water phase in experiment CCP_K1. It is surprising low; less than 0.1 mm/y, an indication that corrosion is inhibited. This was also revealed in reference experiments. There are probably trace contaminants in the technical MEG that inhibits corrosion. This is another confirmation that corrosion in a MEG containing water phase is easy to inhibit. The experiment will be repeated with purified MEG.

Table 6   *Overview of experimental conditions in the first series of corrosion experiments in the CCP/Norcap project*

Exp. No	Temp. °C	MEG conc. Wt%	CO_2 pressure bar	NaCl g/kg	NaOH g/kg	Remarks
CCP_K1	5	50	44	10	0	
CCP_K2	5	50	5	10	0	
CCP_K3	25	50	1-64	10	0	Pressure increase during experiment
CCP_K4	25	0	64	10	0	
CCP_K5	25	50	64	10	0	
CCP_K6	25	90	64	10	0	
CCP_K7	25	50	64	10	0	
CCP_K8	5	50	10	10	0	
CCP_K9	5	50	20	10	0	
CCP_K10	5	50	44	10	0	

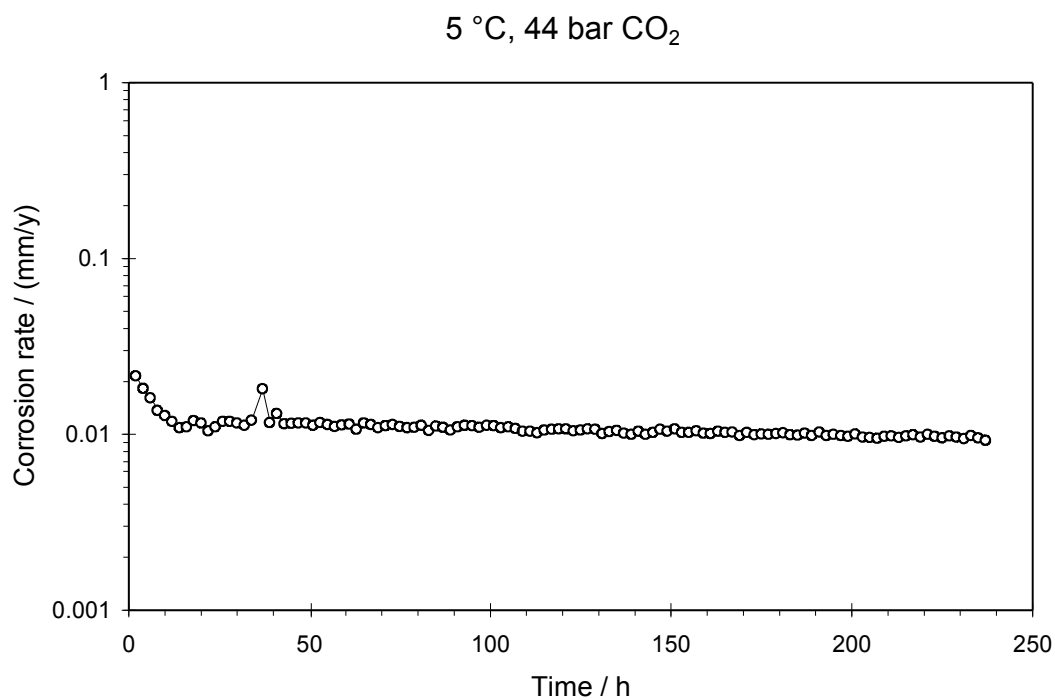5 °C, 44 bar CO_2

Figure 5   *Corrosion rate of steel X-65 as function of time in 50% technical MEG at 5 °C and 44 bar CO_2.*

4. Conclusions

Equipment for measurements of water solubility in CO_2 fluids have been set up and successfully tested with liquid CO_2 at 25 and 36 °C. The results have shown that it is difficult to obtain equilibrium between a water phase and gaseous CO_2 at low temperature. The problems can probably be solved by equilibrating for longer time and by applying more vigorous shaking during the experiments.

An experimental set-up for corrosion studies in liquid water/glycol solutions as well as in CO_2 with high water content has been constructed and utilised in corrosion studies. The results show that the corrosion rates are manageable at temperatures lower than 30 °C and that it is possible to obtain corrosion rates that are lower than 0.1 mm/y with corrosion inhibitors.

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