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Corrosion in High Pressure CO2- Equipment for Water Solubility Measurements

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Abstract

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. In this paper, equipment for measurements of water solubility in CO2 fluids have been set up and successfully tested with liquid CO2 at 25 °C and 36 °C. The results have shown that it is difficult to obtain equilibrium between a water phase and gaseous CO2 at low temperature. The problems can probably be solved by equilibrating for longer time and by applying more vigorous shaking during the experiments.

Keywords: Carbon dioxide, water solubility, water solubility

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I. 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 CO2. Unless the captured CO2 can be used for enhanced oil recovery or other processes where CO2 can be utilized to increase product value, CO2 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 CO2 pressure. CO2 for deposition may contain trace elements from the separation process in addition to nitrogen and hydrocarbons. The corrosively of the trace components has to be evaluated. They may also have indirect effect on corrosion as they may enhance water precipitation from liquid CO2 in the same way as hydrocarbons and N2.

Carbon dioxide has been utilized 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 CO2 transportation. Despite this, there are few thorough investigations on the corrosion of steels and other materials in CO2 at pressures above 50 bar [4]. The reason is that there have been few problems with the recovery and transportation systems. The CO2 in this case, is pure and is dried to a dew point well below the ambient temperature before transportation. Table 1 summarizes experience with some candidate materials for CO2 injection equipment. It also shows the lack of experience with materials in environments that can be expected in process, transport, and injection systems for CO2 deposition. A cost factor for piping materials is also indicated.

Table1.Corrosion rates and experiences reported in the literature for candidate steels for CO2 pipelines and process equipment.

Environment	**Quantitative measurements or reported experience**		
	Carbon steel	**13% Cr steel**	**Duplex and other high alloy steels**
Dry pure CO2	Good	-	Good
Wet pure CO2	Some investigations indicate corrosion rate > 10 mm/y	Not investigated	Most are resistant; corrosion rate ~1μm/y
Dry CO2 withtraces 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 CO2 withtraces 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 forpiping material	1	2	≥4

It is evident from the table above that little is known about the performance of candidate steels for CO2 processing and transport. For injections areas located at some distance from the source, transportation costs are considerable. For a CO2 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 in the table 1 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 CO2 is less than anticipated, and that some wetting of the pipeline may be allowed for a limited period [4, 5]. Apart from cost considerations, the possibility of free water will determine the materials selection. Depending on its origin, CO2 for injection will contain other substances that may reduce the water solubility in the fluid. CO2 separated from natural gas may for instance contain up to 5% CH4. While the solubility of water in pure CO2 (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 CH4 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 CO2 injection pipelines and accurate determination of the solubility limit in the actual mixtures is required.

The objective of the paper is to establish a basis for materials selection for CO2 capture,compression, transportation, and injection. The paper will be closely coordinated with the CCP Transportation project run by SINTEF and Reinertsen Engineering (SINTEF/Reinertsen project).

II. EXPERIMENTAL PROCEDURE

One experimental procedurehas been set up in the project. It is for the measurement of water solubility in CO2 mixtures. It is described in detail in this paper with results of preliminary experiments.

1.1 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 CO2 phase at temperature. Samples of the gas phase are washed out with water to pick up the tritium labelled water in the gas phase and the resulting water is analyzed 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 °C. The autoclave and the sampling system can be evacuated to 0.1 bar. Tritium labelled water was obtained from the experimental reactor. It was thinned 10 times to obtain an activity of 6 Mbq (Mega Becquerel) in the test solution. A series of experiments is started by filling the autoclave with 100 ml tritium labelledwater.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 CH4 and CO2 mixtures are carried out by adding CH4 and let it equilibrate with the water phase at the correct partial pressure before CO2 is added and the pressure is stabilized 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 CO2 in the water phase. Liquid CO2 can be pumped in for high pressure studies.

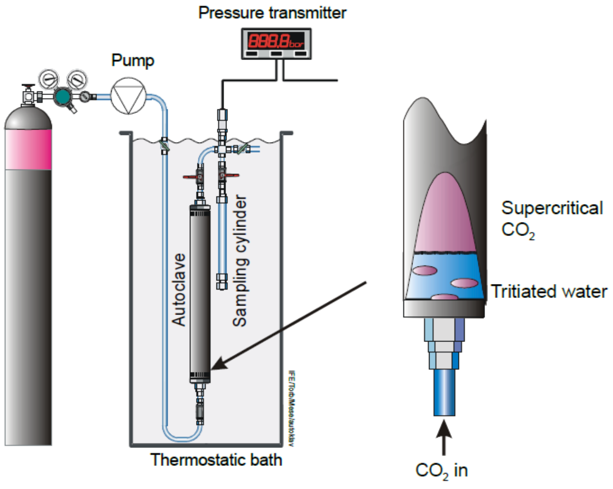

Figure1. Apparatus for measurements of water solubility in liquid/gaseous CO2.

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 quantum low background level liquid scintillation counter. The samples are diluted one to ten by low level tritium Ultra Gold scintillation liquid.

III. RESULTS

3.1 Verification Test

A series of experiments was carried out to verify the experimental set-up. The test conditions of 25 °C and 100 bar were chosen as this is one of the parameter sets with most literature values. 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 2. The results show that 8 hours are needed to reach equilibrium at 25 °C, while equilibrium is obtained after 2 hours at 36 °C.

Table2. Water solubility in pure CO2 at 100-103 bars.

Temperature / °C	**Mole fraction water in CO2/ ppm (X * 10^6)**	**Comments**
25	2743	Equilibrium time 2 hours
25	2909	Equilibrium time 2 hours
25	3381	Equilibrium time 2 hours
36.5	4145	Equilibrium time 2 hours
36.5	4312	Equilibrium time 2 hours
36.5	4199	Equilibrium time 2 hours
25	3539	101 bar, Data from Wiebe [7]
25	3374	103 bar, Data from Song [6]
25	3270	101 bar, Data from King [8]
25	3360	101 bar, Data from Dewan [9]
35	4070	101 bar, Data from King [8]

3.2 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 2. 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.

Table3. Measured water solubility in CO2 and CO2-CH4 mixtures

NO	**Temperature (°C)**	**Total Pressure (bar)**	**CO2 Pressure (bar)**	**CH4 Pressure (bar)**	**Moll Fraction H2O *$10^6(ppm)$**
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

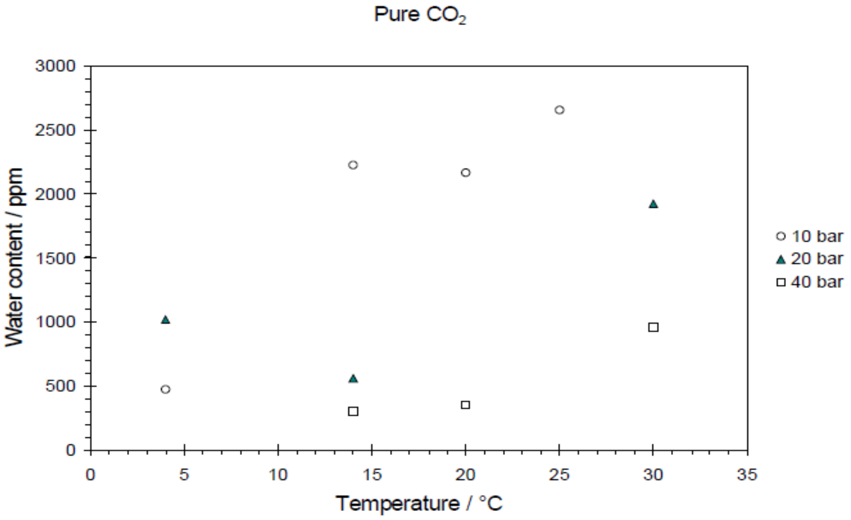

Figure2. Water solubility in pure CO2 versus temperature with pressure as parameter.

IV. CONCLUSIONS

Equipment for measurements of water solubility in CO2 fluids have been set up and successfully tested with liquid CO2 at 25 and 36 °C. The results have shown that it is difficult to obtain equilibrium between a water phase and gaseous CO2 at low temperature. The problems can probably be solved by equilibrating for longer time and by applying more vigorous shaking during the experiments.

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