

Corrosion and Chemical Reactions in Simulated CO₂ Ship Transport Conditions

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ABSTRACT

Carbon capture and storage will require transportation of large quantities of CO₂ by pipelines or by ship. The captured CO₂ will usually contain traces of other components (impurities), typically at the ppm-level. Previous research at simulated pipeline conditions (100 bar, 25°C) showed that certain impurities could react and create reactants that are corrosive to carbon steel (typical construction material for pipelines and ship tanks). Despite extensive corrosion research on pipeline conditions for CO₂ transport, very little research has been carried out for ship transport conditions (-50 °C – -10 °C, 8 – 25 bara).

The present work tested chemical reactions and corrosion at simulated ship transport conditions -25°C and 20 bar. A number of impurities (H₂O, SO₂, NO₂, O₂ and H₂S) were continuously injected at a content of 10 ppm-mol mixed in the CO₂ bulk phase. The results indicate that essentially the same chemical reactions take place at pipeline and ship transport conditions. However, a separate aqueous phase did form at ship transport conditions but not on pipeline conditions. This is probably related to lower solubility at low temperatures. However, the corrosion rate that was measured was low.

INTRODUCTION

Carbon capture and storage (CCS) will require transportation of large quantities of CO₂ from the capturing site to the storage site. The transportation will mostly be carried out by ship or pipelines, although trailers or trains might be used in certain cases. The captured CO₂ will almost always contain additional components (impurities) from the flue gas and from the capturing process. Previous research has shown that some impurities, when present in certain combinations and concentrations, may react and create phases that are corrosive to carbon steel.¹⁻³

Almost all previous research on corrosion in the CO₂ transportation system has been concentrated at typical “pipeline conditions”, which is relatively high temperature (10 – 60 °C) and pressure (> 65 bar). Generally, phase change is not desired along a pipeline, and pipelines will therefore be operated at high enough pressures to keep the CO₂ in the supercritical state.

Even if CO₂ transport by ship is expected to be an important part of a full scale CCS network, the research on corrosion in “ship conditions” is fairly limited.⁴ The conditions in ship tanks and storage tanks may vary within a relatively large range, depending on the pressure rating and refrigeration capabilities, but it is clear that it will be low temperature and low pressure (see Table 1).

Previous work by the authors demonstrated that the impurities H₂O, H₂S, NO₂, SO₂ and O₂ will react and create a separate aqueous phase that contain sulfuric and nitric acids. These reactions have been relatively well investigated for pipeline conditions (25 °C and 100 bar). Initial testing⁴ showed that essentially the same reactions took place at low temperature (-25 °C, 70 bara), even though the corrosion rates were low (most likely due to the low temperature). However, the pressure in this initial test was high (70 bar instead of ~15 bar), and the test did therefore not fully simulate the conditions expected in ship transport.

The present work carried out new experimental testing in a modified test system that allows for both low temperature (-30 – 10 °C and low pressure (1 – 40 bara). Thus, the system could fully simulate the ship transport conditions. The impurity content that was applied in the present work was in previous work¹⁻³ shown to result in chemical reactions between impurities at pipeline conditions (25 °C, 100 bar), but corrosive phases did not form.

Table 1
Expected pressure and temperature for different types of CO₂ transport.

Temp. (°C)	Pressure (bara)	Comment	Source
<i>Pipeline</i>			
+4 – 50	>70	Pipeline to be operated outside the two-phase region(s).	5,6
<i>Bulk transport and storage (ship, train, trailer, ...)</i>			
-55 - -50	6 - 11	Known technology for LNG ships. Considered most likely for future large-scale transport. Can use semi-refrigerated ships.	6-8
-25	15	Well-known within CO ₂ transport for food/beverage industry.	7
-30	15 - 20	Currently used on CO ₂ transport ships.	6
+10	45	Least energy demanding.	7

EXPERIMENTAL PROCEDURE

Test system

The experiment was carried out in a system that was dedicated to mix CO₂ with impurities under simulated ship transport conditions, see Figure 1. The test chamber was an autoclave with transparent windows, which allowed for visual observation and photography during experiments. Only one carbon steel coupon was exposed (thus, reproducibility was not tested).

The system had a continuous injection and bleed-off of CO₂ with impurities. The impurity mixing was carried out by low rate injection of several impurity stock solutions through individual lines into the test chamber, see Figure 2. The injection lines were small diameter (1/16 inch) tubing to reduce lag time. Pure dry CO₂ and moist CO₂ was also injected. Thus, the desired impurity content in the test chamber could be reached by adjusting the injection rate of each individual stream relative to the total injection rate. The impurity stock solutions were held in piston cylinders with nitrogen back pressure. All piston cylinders were connected to the same nitrogen source, which gave an equal back pressure for all injected streams. The pressure in the piston cylinders was high enough to keep the CO₂ in the dense phase state (70 – 100 bar), which increased the capacity of the cylinders. The pressure of the impurity stock solution was reduced to about 25 bar and injected as gas controlled by mass flow controllers. In addition, pure

CO₂ was injected directly from a standard CO₂ bottle, through an electrical pressure regulator (that set the system pressure).

The test chamber was located inside a cooled cabinet (modified freezer) with temperature control. There was about 1 metre length of each injection line inside the cooled cabinet, which gave each injected stream enough residence time to reach the desired temperature before it entered the test chamber and the stream was now changed from gas to liquid.

The exhaust CO₂ was continuously taken through a separate line from the test chamber to a heated gas regulator outside the freezer. The regulator reduced the pressure to near ambient (1-2 bara) before the gas was sent to the analysing system, which consisted of a series of laser-based instruments. The analysing equipment was set up to detect H₂O, H₂S, SO₂, NO₂, NO, CO, NH₃ and O₂ at concentrations down to about 1 ppm-mol.

The exposed corrosion coupon was examined with scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). Mass loss corrosion rate was calculated by comparing initial weight and weight after chemical stripping using inhibited hydrochloric acid (Clarke's solution).



Figure 1: Picture of the test system (left) and picture inside cooling chamber with transparent autoclave, tubing, camera and LED light (right).

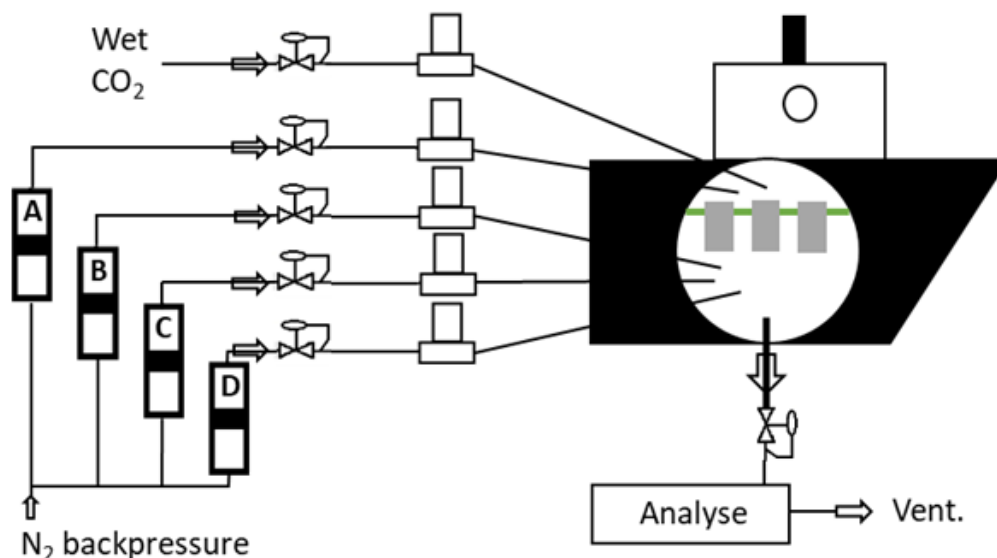


Figure 2: Principal sketch of the injection system, autoclave and exhaust system with analysis.