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CO2EuroPipe study of the occurrence of free water in dense phase CO_2 transport

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Abstract

For carbon dioxide capture and storage (CCS), various specifications of the water content in CO_2 have been given. These specifications range from 40 to 500 ppm. Unfortunately, little has been published on the rationale behind these concentration limits. The present lack of clarity on the dryness requirements is undesirable, because eventually, we must come to a water content standard for CCS that ensures cost-efficient CO_2 transport. The work presented here aims at analyzing CO_2 transport to provide some basic input for this standard.

CO_2 captured from power plants always contains moisture. The water can be removed to a certain extent at the capture plant, but a small amount of water will remain. When the water is in solution in the CO_2, there is no problem, but free water combined with CO_2 is very acidic. The corrosive nature of wet CO_2 poses a threat to the transport system integrity. Economical considerations lead to the use of regular carbon steel, which is commonly used for most pipelines. Corrosion resistant steel would inhibit corrosion, but it would be prohibitively expensive to build CCS pipelines with this type of steel.

On one hand, using regular carbon steel requires corrosion tests to quantify the destructive effects of free water in case it is present in the CO_2. On the other hand, the occurrence of free water must be excluded as much as possible. No free water anywhere in the CO_2 transport system would be the most straightforward way of protecting it. Drying captured CO_2 costs both money and energy and reduces flexibility in the CCS chain, so a water concentration limit should not be more stringent than necessary.

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A quick overview of the solubility of water in CO_2 is given to enable a discussion of the operational limits of the CCS transport chain.

For normal operation, the pressure range of dense phase CO_2 in a pipeline transmission system is between 85 and 150 bars onshore and between 85 and 200 bars offshore. The lower limit is determined by the critical point of CO_2 (73,8 bars for pure CO_2, somewhat different for CO_2 with impurities). A pressure of 85 bars ensures the CO_2 remains in the dense phase in case of a temporary shutdown. The upper limits of 150 and 200 bars are chosen with regard to safety and economical optimization.

Expected CO_2 characteristics in the transport network include a minimum temperature of 0 °C (onshore) or 4 °C (offshore) and a maximum temperature of over 30 °C immediately after a compressor. This leads to a water solubility of at least 1500 ppm during normal operation.

Commissioning of a CO_2 pipeline and blowdown scenarios are discussed. The relation between the CO_2 conditions during planned blowdowns and the water content should be investigated. Unplanned blowdown could involve a rapid decompression and temperature drop, for which there are no validated models available. Therefore it is difficult to determine the right water concentration limit.

It was found that for a good technical and economical basis for determining the required water concentration limit some questions remain to be answered. Cost data of drying installations are needed. It should be found out what are acceptable blowdown conditions as a function of water concentration. Some thermodynamical issues are brought up as well. Finally the impurities present in the captured CO_2 will need to be taken into account.

Although in the USA, no serious problems seem to have surfaced with around 500 ppm water in CO_2, several research questions need to be addressed to arrive at a sound and cost efficient water concentration limit.

This work is carried out within CO2EuroPipe, an EU research project under the 7th Framework Programme. This project, which runs for 2,5 years, until November 2011, aims at paving the road towards large-scale, Europe-wide infrastructure for the transport and injection of CO_2 captured from industrial sources and low-emission power plants.

Keywords: CO2 transport; free water; operation; pressure; temperature

1. Introduction

The infrastructure necessary to capture, transport and store CO_2 requires a technical specification of several CO_2 characteristics, such as pressure, temperature, and composition. One of the most important constraints on the CO_2 composition will be the water content. CCS stakeholders have published a variety of water concentration limits. These specifications range from 40 ppm[1] to 500 ppm[2]. In the USA, where dense phase CO_2 has been transported for decades, the water content is usually limited to about 500 ppm.

Unfortunately, little has been published on the rationale behind these concentration limits. If the reason for a certain limit is given, it is just that the occurrence of free water could cause corrosion, which should be prevented. The prevention of hydrate formation is also mentioned sometimes as a reason to limit the water content. Usually it is not clear whether the given limit is lower than necessary or really sufficient to avoid free water in the pipeline. It is just an assertion that a certain limit is imposed. Known water concentration limits could have originated from an analysis of the physical processes involved in CO_2 transport, but the limit could also easily have been derived from the composition of the CO_2 source, which already supplied very dry CO_2. In the latter case, the technical limit could very well be much higher than the imposed limit.

In a business like CCS, where there is a strong emphasis on cost-efficiency, the approach in which a water concentration limit is given but not properly explained is not viable. It should be clear to all CCS stakeholders that only technical specifications are imposed and that they enable a CCS chain with minimized costs.

The present lack of clarity on the dryness requirements is undesirable, because eventually, we must come to a water content standard for CCS. The work presented here aims at analyzing CO_2 pipeline transport to provide some basic input for this standard.

2. Rationale for a water concentration limit

CO_2 capture processes result in captured CO_2 with some impurities. One of the impurities is water. It can be removed to a certain extent at the capture plant, but a small amount of water will remain. When the water is in solution in the CO_2, there is no problem, but free water combined with CO_2 is very acidic. The corrosive nature of wet CO_2 poses a threat to the transport system integrity, because a CO_2 pipeline will be built of carbon steel. Economical considerations dictate the use of regular carbon steel, which is commonly used for most pipelines. In theory, corrosion resistant steel could be used to prevent corrosion, but it would be prohibitively expensive to build CCS pipelines of this material.

Corrosion tests can be performed to determine what the corrosion rates would be if free water would happen to occur in a regular carbon steel CO_2 pipeline under typical transport conditions. In addition, efforts should be taken to exclude the occurrence of free water in a CO_2 pipeline as much as possible.

It is practically impossible to remove all water from the captured CO_2, although the water level can be brought down to very low levels, around dozens of parts per million. However, drying adds to the costs of CCS, both in money and energy, making it undesirable to adhere to an overly strict water content limit. Especially the drying method has an effect on the costs; with a mole sieve the lowest specs available can be attained, whereas a glycol dryer costs less but is unable to reach a water content level as low as that.

For the CO_2 producer, it is not only the capital investment in a drying installation that is important. Depending on the water concentration limit, the CO_2 producer has a certain degree of freedom in using the drying installation. When the water limit is higher than the level attainable by the installed drying installation, the producer can bypass part of the captured CO_2 and feed it into the transmission system directly, which would save drying costs. Furthermore, a short downtime of the drying installation can be acceptable or not, depending on the flexibility in water content allowed.

In short, although technically it is no problem to dry captured CO_2 to very low water concentrations, for economical considerations it should be investigated what is the highest water content limit that can be accepted.

3. Solubility of water in CO_2

The solubility of water in CO_2 depends on the CO_2 pressure, temperature and composition. In the Dynamis report, there is a convenient graph of the solubility as a function of pressure. The solubility in ppm at various temperatures is given.[2]

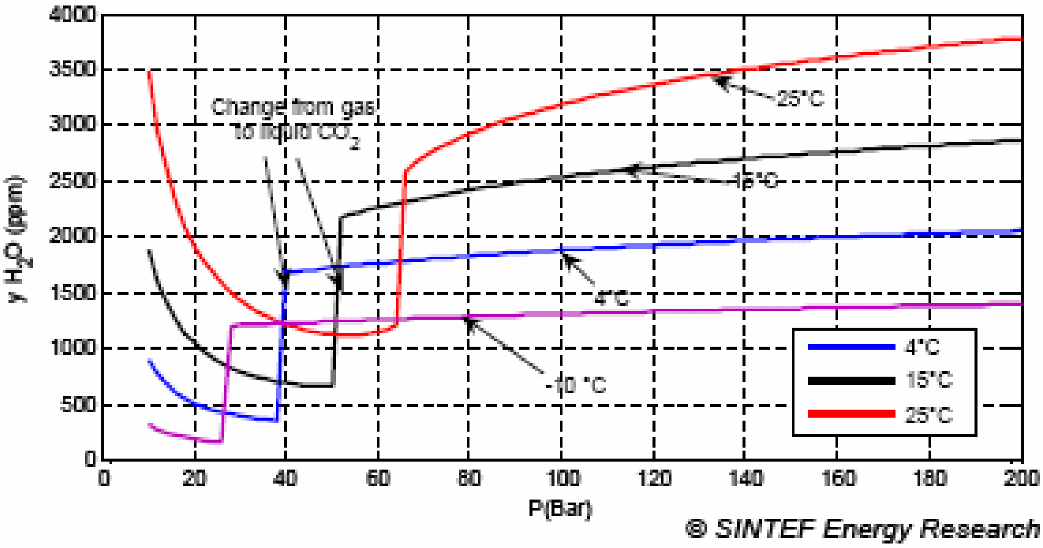

Figure 1 The solubility of water in CO_2 for varying temperatures as a function of pressure. Figure taken from the Dynamis report.[2]

We see in this graph that the solubility of water decreases on the path from atmospheric pressure to the point where the phase transition from gas to liquid occurs. At the phase transition, there is a sharp increase in solubility, and with increasing pressure, the solubility increases even more. It must be noted that this graph applies to pure CO_2. Impurities might increase or decrease the water solubility.

4. Operational regimes

To assess how the water solubility data translate to a water concentration limit, the various possible states of a CO_2 transmission system can be evaluated. The transmission system comprises everything between the CO_2 capture site(s) and the storage reservoir(s).

Normal operation

First of all, we consider the situation in which the system is operating the way it was designed to operate, without interruption, with all parameters within their specifications. A dense phase CO_2 transmission system is considered to be in normal operation when there are no flow interruptions and the pressure range in the pipeline is between 85 and 150 bars in case of onshore transport and between 85 and 200 bars offshore. The lower limit is determined by the critical point of CO_2 (73,8 bars for pure CO_2, somewhat different for CO_2 with impurities[3]). A pressure of 85 bars ensures the CO_2 remains in the dense phase in case of a temporary shutdown. Two phase flow in the pipeline should be avoided. The upper limits of 150 and 200 bars are chosen with regard to safety and economical optimisation.

The lowest temperature that can be expected during normal operation is about 0 °C, as can be deducted from the data in the Pipe Line Rules of Thumb Handbook.[4] The seawater temperature is typically around 4 °C. The maximum temperature in the transport system is found downstream of the main compressor, where CO_2 exits the final stage at above 30 °C, depending on the compressor and the required pressure. Along the pipeline the CO_2 temperature will decrease towards the ambient temperature. The operating conditions described above correspond with a water solubility of at least 1500 ppm.

Commissioning

When a CO_2 pipeline has been built, it must undergo hydrostatic testing before being put into use. DNV's Recommended Practice [3] mentions that, alternatively, air, N_2 and CO_2 could be used instead of water, but that does not concern this work. To prevent a corrosive mixture of CO_2 and water, the pipeline should be dried. This is not a technical but and economical challenge. A stringent water concentration limit implies higher commissioning costs, so again, for the sake of cost-efficiency the required maximum water concentration should be as high as possible.

Blowdown

A blowdown of CO_2 can be intentional or the result of some incident. When the CO_2 is evacuated from the pipeline during an intentional blowdown operation, e.g. for maintenance, the decrease in pressure and temperature can be controlled, enabling the pipeline operator to steer clear of free water formation. Again, the more relaxed the water concentration limit is, the more leeway the operator has in blowing down a pipeline, and the faster the blowdown procedure will be carried out. A fast blowdown is preferred because it could reduce downtime of the pipeline.

A different case is unintended blowdown, e.g. due to a valve malfunction, operational error or external damage. In such a case, by definition, the pressure decrease is not controlled. Mitigation measures, such as a SCADA system (Supervisory Control And Data Acquisition) will have been installed in CO_2 pipeline transmission systems, but nevertheless, if there is a leakage or valve malfunction in the CO_2 pipeline, pressure and temperature could decrease rapidly. However, regarding the physics of the CO_2 outflow there is limited knowledge. Presently, there is a lack of validated models that are able to adequately describe the CO_2 conditions during outflow.

5. Discussion

In the process of identifying scenarios for free water formation in CO_2, we encounter several issues to be solved in order to determine the water concentration limit necessary for safe, reliable and economical CO_2 transport by pipeline.

For the correct evaluation of the economical impact of water concentration limits, cost data of suitable drying installations should be gathered.

Another research question is: What is the relation between the water concentration and acceptable blowdown conditions? For the most cost-efficient solution, some balancing will need to be done by comparing the economics of the blowdown speeds and the corresponding downtime of the transmission system to CO_2 drying costs?

In CO_2, free water will form when at the given CO_2 conditions, the water concentration becomes higher than the solubility. Obviously this situation will have to be avoided. But this does not mean that absolutely no free water can be present when the water content is lower than the solubility. The solubility data represent equilibrium conditions. Therefore, an upset in the CO_2 flow might give rise to free water even if the water concentration is below the solubility.

Another question that deserves an answer is: If free water forms, under what circumstances do the droplets stay in suspension in the CO_2 and when is a water puddle formed? If free water manifests itself as a collection of suspended droplets, all being carried along with the CO_2 and dissolving into it as soon as pressure and temperature conditions allow it, there is no danger of corrosion.

For the evaluation of the aforementioned research questions the expected impurities in the captured CO_2 should be taken into account. The same applies to research into hydrate formation, which is outside the scope of this paper.

As this paper shows, several issues have to be addressed before the best water specification can be determined. It should be noted, however, that CO_2 transport operators in the USA, to our knowledge, have not expressed any concerns about their water concentration limits, which indicates that a limit of several hundred ppm should suffice. A thorough investigation should indicate what is the best water concentration limit.

6. Conclusion

In CCS, there have been several statements of the desired water concentration limit in CO_2, varying from 40 to over 500 ppm. While the reasoning behind these limits has been expressed in many cases, the terse explanations mostly just consisted of the assertion that the given limit is necessary to prevent the unwanted occurrence of free water at all costs. Because of the energetic and economic costs associated with drying the captured CO_2, it is worthwhile to evaluate the precise water concentration limit that is needed for a safe and reliable CO_2 transport operation.

Under normal operating conditions dense phase CO_2 can be transported containing 500 ppm water without any risk of free water formation, because the water solubility is at least 1500 ppm under these circumstances.

When a CO_2 pipeline is commissioned, it needs to be dried after hydrostatic testing. The more relaxed the water concentration limit is, the less time and money will be involved in commissioning the pipeline. Therefore, having a water concentration limit that is too stringent affects both the drying costs at the capture site and the drying during commissioning of the pipeline.

In the range of water concentration limits encountered, the lower extremes of 40 and 50 ppm are probably rather conservative. In any case, a limit of 500 ppm water will prohibit free water formation during normal operation. Due to the current lack of validated models for the thermodynamics of CO_2 outflow it is not possible to assess what water content is acceptable when uncontrolled CO_2 release is taken into account. The existing US experience notwithstanding, additional analysis, both physical and economical, is needed to arrive at a water concentration limit that enables reliable and cost-efficient CO_2 transport.

7. Acknowledgements

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