



# Chemical effects of sulfur dioxide co-injection with carbon dioxide on the reservoir and caprock mineralogy and permeability in depleted gas fields



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## ABSTRACT

The most suitable candidates for subsurface storage of CO<sub>2</sub> are depleted gas fields. Their ability to retain CO<sub>2</sub> can however be influenced by the effect which impurities in the CO<sub>2</sub> stream (e.g. H<sub>2</sub>S and SO<sub>2</sub>) have on the mineralogy of reservoir and seal. In order to investigate the effects of SO<sub>2</sub> we carried out laboratory experiments on reservoir and cap rock core samples from gas fields in the northeast of the Netherlands. The rock samples were contained in reactor vessels for 30 days in contact with CO<sub>2</sub> and 100 ppm SO<sub>2</sub> under in-situ conditions (300 bar, 100 °C). The vessels also contained brine with the same composition as in the actual reservoir. Furthermore equilibrium modeling was carried out using PHREEQC software in order to model the experiments on caprock samples.

After the experiments the permeability of the reservoir samples had increased by a factor of 1.2–2.2 as a result of dissolution of primary reservoir minerals. Analysis of the associated brine samples before and after the experiments showed that concentrations of K, Si and Al had increased, indicative of silicate mineral dissolution.

In the caprock samples, composed of carbonate and anhydrite minerals, permeability changed by a factor of 0.79–23. The increase in permeability is proportional to the amount of carbonate in the caprock. With higher carbonate content in comparison with anhydrite the permeability increase is higher due to the additional carbonate dissolution. This dependency of permeability variations was verified by the modeling study. Hence, caprock with a higher anhydrite content in comparison with carbonate minerals has a lower risk of leakage after co-injection of 100 ppmv SO<sub>2</sub> with CO<sub>2</sub>.

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## 1. Introduction

Based on current scenarios, carbon dioxide (CO<sub>2</sub>) emissions will increase by 63% in 2030 compared to today's level, which is 90% higher than the 1990 level (IEA, 2004). Carbon dioxide Capture, Transport and Storage (CCTS) is recognized as one of the primary technologies to mitigate the resulting increase in anthropogenic atmospheric concentration of CO<sub>2</sub> (IPCC, 2005).

According to Bachu et al. (2009) an important element in establishing the regulatory framework for CCTS and also in evaluating the economics of CCS operations, is to assess the impact of impurities and setting their acceptable limits (type and concentration) in the CO<sub>2</sub> stream. Dependent on the source and the capturing technology a CO<sub>2</sub> product stream will contain impurities such as H<sub>2</sub>S, SO<sub>2</sub>, NO<sub>x</sub>, H<sub>2</sub>, Ar, CO and NH<sub>3</sub> (Wilke et al., 2012), which may cause

unwanted effects during transport and storage. The degree of purification and hence the cost of capture is to some extent determined by the tolerance level of impurities in the transport and storage systems (Bolourinejad and Herber, 2014). In transport the degree of purity of CO<sub>2</sub> is decisive for the energy requirements and infrastructure integrity (Bolourinejad and Herber, 2014). Phase separation, hydrate formation and the presence of corrosive components during CO<sub>2</sub> transport are directly related to the presence of impurities (Bolourinejad and Herber, 2014). With respect to subsurface storage, impurities in CO<sub>2</sub> affect well integrity and injectivity as well as long-term cap-rock seal integrity and hence risk of leakage (Bolourinejad and Herber, 2014). This paper deals with the subsurface storage of impure CO<sub>2</sub> in depleted gas fields. The specific question can be formulated as follows: what type and quantity of impurities can be left in the injected CO<sub>2</sub> in order to reduce the cost of capture without affecting the integrity of storage system?

Different modeling studies have been performed to evaluate various aspects of impurities co-injection in geological formations

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(Waldmann et al., 2013; Parkhurst and Appelo, 2013; Koenen et al., 2011; Xu et al., 2007). Waldmann et al. (2013) used PHREEQC (Parkhurst and Appelo, 2013) software and modeled CO<sub>2</sub> and SO<sub>2</sub> co-injection into Triassic Buntsandstein. The results revealed an enhanced level of K-feldspar dissolution next to anhydrite precipitation. Koenen et al. (2011) also utilized PHREEQC software and modeled the impact of two CO<sub>2</sub> streams: one from a pre-combustion and one from an oxy-fuel capturing process. Both processes resulted in multiple impurities such as SO<sub>2</sub>, H<sub>2</sub>S and N<sub>2</sub>. They concluded that the short-term effects of impurities are insignificant compared to pure CO<sub>2</sub>. For the long-term the presence of impurities leads to minor mineralogical differences, when compared to the injection of pure CO<sub>2</sub>. They also concluded that the increase in porosity caused by pure CO<sub>2</sub> could be counteracted by the presence of impurities due to the precipitation of secondary minerals like alunite and nontronite. Xu et al. (2007) modeled the co-injection of SO<sub>2</sub> and H<sub>2</sub>S with CO<sub>2</sub> using TOUGHREACT. They concluded that the co-injection of SO<sub>2</sub> with CO<sub>2</sub> leads to the formation of a wider and stronger acidified zone around the wellbore due to the formation of strong sulfuric acid in comparison with the formation of carbonic acid following pure CO<sub>2</sub> injection. In addition, several researchers have developed new equations of state for modeling of subsurface storage of impure CO<sub>2</sub> in order to be able to accurately model the thermodynamic equilibrium of gas mixtures and brines in a range of pressures, temperatures and salinities applicable for subsurface storage of CO<sub>2</sub> (Battistelli and Marcolini, 2009; Ziabakhsh-Ganji and Kooi, 2012).

In comparison with the number of modeling studies, experimental work on this subject is sparse. In general, results from experimental studies show that more accurate parameters need to be implemented in modeling. An example is the work of Bachu and Bennion (2009) who investigated the chromatographic partitioning of H<sub>2</sub>S, SO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>. Their results revealed that the impurities, due to their different solubility, would chromatographically partition on the front end of the gas plume advancing through a water-saturated porous medium. Furthermore, Bolourinejad et al. (2014) investigated the effects of reactive surface area of minerals on the modeling results. The measured reactive surface areas were significantly higher than what is typically being used in modeling studies (e.g. Xu et al., 2007), which leads to more dissolution/precipitation of minerals.

To the best of our knowledge no published experimental dataset exists for co-injection of CO<sub>2</sub> and impurities in a real case example (on reservoir and/or caprock core samples) to investigate the effects of these gas mixtures on the permeability of the samples due to the mineral dissolution/precipitation. Such experiments enable us to determine type and maximum acceptable concentration of impurities for co-injection with CO<sub>2</sub> in order to have both safe and economic CCTS projects. In operational CO<sub>2</sub> storage sites it is difficult to sample the reservoir after CO<sub>2</sub> injection and it is also not possible to compare post- with pre-injection mineralogy, porosity and permeability from the same location. For example, at the Ketzin site in Germany (start of injection was June 2008) the measured porosity of the reservoir after CO<sub>2</sub> injection

from specific depths (106 samples) was between 15% and 28% which was concluded to be comparable with the pre-injection porosity of 20–30% (Liebscher et al., 2013). However, the uncertainty is high in these types of measurements because they were not carried out on the same samples and locations. Hence, experimental laboratory studies at in-situ reservoir pressure and temperature conditions are essential to help understanding the reactions that take place within the rock in a controlled setting and establish causal relationships for the changes which are taking place (Fischer et al., 2010). In addition, experimental studies can help us to overcome problems such as the measurements on the same sample and on the same spot of the samples before and after the experiments (e.g. mineralogical and permeability comparison).

In our research project we investigated the impacts of various impurities on storage of CO<sub>2</sub>. In a previous study the impact of co-injection of H<sub>2</sub>S with CO<sub>2</sub> was assessed (Bolourinejad and Herber, 2014). The current article focuses on SO<sub>2</sub> as one of the possible impurities, selected based on the results of capturing technology development (Walspurger and Dijk, 2013). The impact of 100 ppm SO<sub>2</sub> co-injection with CO<sub>2</sub> is experimentally analyzed on reservoir and caprock samples from depleted gas fields in northeast Netherlands under subsurface conditions. In this context, depleted means that the operational cost exceeds the production income from the natural gas (Herber and De Jager, 2010). The selection of actual reservoir and caprock core samples rather than using single minerals enabled us to measure permeability of the samples pre- and post-injection. This allowed us to evaluate the effect of mineral dissolution/precipitation on bulk rock properties which can be used for calibration purposes in future modeling studies. In addition to permeability measurements, the mineralogical variation was monitored. Also, brine samples were collected and analyzed. Following the experimental study, we utilized PHREEQC software in order to model the effect of caprock composition on permeability due to the injection of CO<sub>2</sub> + 100 ppm SO<sub>2</sub>.

## 2. Background

In this section we provide an overview of the published experimental work carried out on the effects of impurities on subsurface storage of CO<sub>2</sub>.

Wilke et al. (2012) carried out 42-day mono-mineral batch experiments with pure and impure (0.5% NO<sub>2</sub> or SO<sub>2</sub>) CO<sub>2</sub> injection on rock forming minerals (albite, microcline, calcite, dolomite, anhydrite, kaolinite and biotite). Nitric and sulfuric acid formed following NO<sub>2</sub> and SO<sub>2</sub> co-injection respectively and the pH reduced more than in the pure CO<sub>2</sub> scenario. They observed anhydrite corrosion by approximately 50 wt% and gypsum precipitation following the CO<sub>2</sub> plus NO<sub>2</sub> experiment (pressure and temperature of 77 bar and 49 °C respectively).

Parmentier et al. (2013) performed a 30-day experiment on calcite minerals by injection of pure SO<sub>2</sub> and showed both calcite dissolution and anhydrite precipitation. Similar to Wilke et al. (2012) a single mineral system was used.

**Table 1**  
Mineralogy (wt%) and permeability of Rotliegend reservoir (R) and Zechstein caprock (C) core samples.

Samples	Permeability (mD)	Quartz	Anhydrite	Kaolinite	Dolomite	Gypsum	Albite	K-feldspar	Calcite
R1	0.29 ± 0.03	83	3.3	–	13.3	–	<1	<1	–
R2	71.8 ± 3.6	87	1.6	4.1	2.8	–	3.6	<1	–
R3	350 ± 18	89	6.3	1.7	–	2.2	<1	<1	–
C1	0.029 ± 0.006	1.11	98.65	–	0.24	–	–	–	–
C2	0.085 ± 0.017	–	89.35	–	10.65	–	–	–	–
C3	0.003 ± 0.001	–	55.95	–	44.05	–	–	–	–
C4	0.028 ± 0.006	–	43.17	–	56.83	–	–	–	–
C5	0.016 ± 0.003	6.67	3.32	–	46.13	–	–	–	43.88
C6	0.227 ± 0.023	1.9	–	–	1.00	–	–	–	97.10

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