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# Experimental investigation of porosity and permeability variations in reservoirs and caprock following co-injection of sulfur dioxide and hydrogen sulfide with carbon dioxide

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## ARTICLE INFO

## ABSTRACT

Carbon dioxide ($CO_2$) capture, transport and storage (CCTS) in deep geological formations can mitigate the atmospheric concentration of greenhouse gases. Purity of this gas is an important aspect for CCTS since it drives up the cost of capture. When leaving some impurities from the flue gas in the $CO_2$ stream, a cost reduction may be achieved but the risks at transport and storage may increase. In order to investigate the effects of the possible impurities ($H_2S$ and $SO_2$) in the $CO_2$ stream during subsurface storage laboratory experiments were performed on Permian Rotliegend reservoir and Zechstein cap rock core samples from gas fields in northeast Netherlands. The rock samples were subjected for 30 days to static in situ conditions (300 bar, 100 °C) in the presence of brine and an injected gas mixture of $CO_2$ + 100 ppm $SO_2$ + 100 ppm $H_2S$. Following injection of the mixture permeability of the reservoir and caprocks increased by a factor of 1.02–1.9 and 1.2–3.1, respectively. Although an enhanced level of anhydrite precipitation was observed, the increase in permeability of the samples show that dissolution of carbonate, feldspar and kaolinite minerals is dominant. In addition it was shown that the initial porosity–permeability relation of the samples remains valid to predict the behavior of the reservoir after injection of the gas mixture. For the caprock, the precipitation of anhydrites results in a less enhanced permeability than in the case of injection of pure $CO_2$. This may lead to the conclusion that the addition of low quantities (100 ppm) of $SO_2$ and $H_2S$ in $CO_2$ during subsurface storage does not increase the risk of leakage through the Zechstein caprock more than when using pure $CO_2$.

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## 1. Introduction

The increasing concentration of greenhouse gas (GHG) in the atmosphere is a strong driver for development of new mitigating methods and technologies (Battistelli and Marcolini, 2009; IPCC, 2005). Anthropogenic carbon dioxide ($CO_2$) emission forms the largest contribution to rising GHG concentrations (IPCC, 2005). $CO_2$ capture from point sources (e.g. fossil fuelled power plants) and storage in geological formations such as saline aquifers, depleted oil and gas fields and coal seams is a potential means to reduce $CO_2$ emissions (Palandri and Kharaka, 2005; Audigane et al., 2007). Candidate geological formations for storage should have sufficient capacity, appropriate injectivity and be sealed by a layer of an impermeable caprock (Bos, 2007). In addition, the ability to predict both short and

long term effects of $CO_2$ on geological formations is a necessity for successful application (Balashov et al., 2013).

In general, $CO_2$ from power plants is not pure and contains various types of impurities (e.g. $H_2S$, $SO_2$, $NO_x$, $H_2$, Ar, CO and $NH_3$) (Wilke et al., 2012). It is estimated that 75% of the Carbon Capture and Storage (CCS) cost is related to the separation of $CO_2$ from the flue gas (Ji and Zhu, 2013; IPCC, 2005). The injection of $CO_2$ along with some of the impurities can help to save energy and cost in the capture process. However this might increase the risks related to the transport and storage (Ji and Zhu, 2013). Hence it is vital to study the additional impact of these impurities (type and concentration) on transportation system and storage site.

In the case of transport of $CO_2$ the presence of impurities can lead to phase separation, hydrate formation and corrosion (Bolourinejad and Herber, 2014; IPCC, 2005). At the storage site, impurity of $CO_2$ may affect well integrity and injectivity as well as long-term cap-rock seal integrity and hence risk of leakage. Many researchers studied impacts of different impurities on geological formations both experimentally and with the help of modeling software such as PHREEQC (Parkhurst

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and Appelo, 2013), TOUGHREACT (Xu et al., 2004) and CMG-GEM (CMG, 2011).

Wilke et al. (2012) performed experiments (77 bar, 49 °C, duration 42 days) with pure and impure (0.5% $NO_2$ or $SO_2$) $CO_2$ injection on single mineral phases (albite, microcline, calcite, dolomite, anhydrite, kaolinite and biotite). Co-injection of $NO_2$ and $SO_2$ resulted in the formation of nitric and sulfuric acid, respectively, and caused a stronger pH reduction than in the pure $CO_2$ scenario due to the formation of carbonic acid formation. In their $CO_2$–$NO_2$ experiment they reported a 50 wt% dissolution of anhydrite and associated precipitation of gypsum. Palandri et al. (2005) investigated $CO_2$–$SO_2$ reactions with hematite (300 bar, 150 °C) resulting in the formation of pyrite, siderite and elemental sulfur. Palandri and Kharaka (2005) mentioned that in a representative flue gas mixture (e.g. $< 1\% SO_2$) there is not sufficient reducing agent (e.g. $H_2S$ and $SO_2$) to reduce all of the iron and no siderite can be formed. Hence, the targeted reservoir rock should contain other metals than Fe in order to make carbonate precipitation possible and trap all of the $CO_2$ as a mineral. Parmentier et al. (2013) performed a 30 day experiment on calcite minerals by injection of pure $SO_2$ and showed both calcite dissolution and anhydrite precipitation. Bachu and Bennion (2009) investigated the impact of impurities ($H_2S$, $SO_2$, $CH_4$ and $N_2$) in the $CO_2$ stream. They showed that the impurities would, due to their differences in solubility, chromatographically partition at the front end of the gas plume advancing through the water-saturated porous medium. Koenen et al. (2011) modeled both short and long term effects of impure $CO_2$ injection in the presence of multiple impurities such as $SO_2$, $H_2S$, $N_2$ in a depleted gas field in the Netherlands. Using PHREEQC modeling software they concluded that the short-term effects of impurities are insignificant compared to that of pure $CO_2$. In the long-term, presence of impurities leads to a minor difference in mineralogy (precipitation of new mineral phases) when compared to pure $CO_2$ injection. Waldmann et al. (2013) used similar software and modeled $SO_2$ co-injection in Triassic Buntsandstein. The results showed an increase in K-feldspar dissolution next to anhydrite precipitation.

In our research project the impact of various impurities on subsurface storage of $CO_2$ was studied both experimentally. The experiments were carried out on Permian Rotliegend reservoir and Zechstein caprock core samples from depleted gas fields. The use of actual core samples rather than using a single mineral phase enabled us to measure porosity and permeability of the samples pre and post experiments. In a previous paper (Bolourinejad and Herber, 2014) the impact of injection of pure $CO_2$ and also co-injection of $CO_2 + 100$ ppm $H_2S$ were already discussed. In the current article the focus is on the subsurface storage of $CO_2$ in combination with a mixture of 100 ppm $SO_2$ and 100 ppm $H_2S$. The objective is to assess to which degree the impact of a combination of sulfur gasses on the reservoir is different from that of the individual components. The geochemical impact of the gas mixtures is experimentally evaluated on reservoir as well as caprock core samples at in-situ subsurface pressure and temperature conditions as encountered in gas fields in northeast Netherlands. In order to simulate the local subsurface conditions as much as possible, a small (2%) methane component is included in the mixture although the chemical interaction between the impurities and methane is very limited. Prior to the experiments, the mineralogical composition of the samples is determined with X-ray Diffraction (XRD) and Scanning Electron microscopy (SEM). After the experiments, the change in the mineral composition was monitored by SEM. Brine samples were also collected and analyzed by Induced Coupled Plasma–Optical Emission Spectroscopy (ICP–OES) techniques. Furthermore, after the experiments the porosity of the samples was measured to establish whether the initial porosity–permeability relationship in the reservoirs still holds after injection and thus can be utilized for post-injection scenarios.

## 2. Methods and materials

### 2.1. Sampling

The core samples for Permian Rotliegend sandstone reservoir and Permian Zechstein anhydrite/carbonate caprock were obtained from wells in northeast Netherlands. Depth range of the selected samples is between 2.8 and 3.2 km and their porosity varies between 0.3 and 22% while permeability ranges between 0.005 mD and 459 mD. The samples are selected from three different fields (Fig. 1). Reservoir samples are selected from field A and B (Fig. 1a). Caprock samples are selected from field C (Fig. 1b). Depth, permeability and mineralogy of selected samples are presented in Table 1. The permeability measurement and mineralogical analysis techniques are explained in the next section.

### 2.2. Analytical techniques

Prior to the experiments the mineralogy of the samples was obtained using X-ray Diffraction (XRD) and Scanning Electron microscopy (SEM) (Table 1).

The XRD analysis on the bulk rock samples was performed with Bruker D8 advance (40 kV, 40 mA). Diffractometers recorded between 5° and 100° 2-Theta with $Cu\alpha_1 = 1.54060$ Å, $Cu\alpha_2 = 1.54439$ Å. The detector step size was set to 0.02° with 5 s/step. Use of intact core samples for XRD analysis, rather than in the form of a powder, enabled us to use the same sample for XRD analysis and the experiments, thus linking mineralogy with porosity and permeability. Following the XRD analysis GSAS (General Structure Analysis System) software was used (Larson and Von Dreele, 2004) to quantify different phases in the samples. It should be mentioned that XRD was solely used prior to the experiments for mineralogical analysis.

SEM was performed with a Philips XL-30 environmental SEM (ESEM) with Field Emission Gun (FEG). It is equipped with energy dispersive spectroscopy (EDS). Secondary Electron (SE) and Back-scattered Electron (BSE) images were taken on the same location on the core samples before and after the experiments.
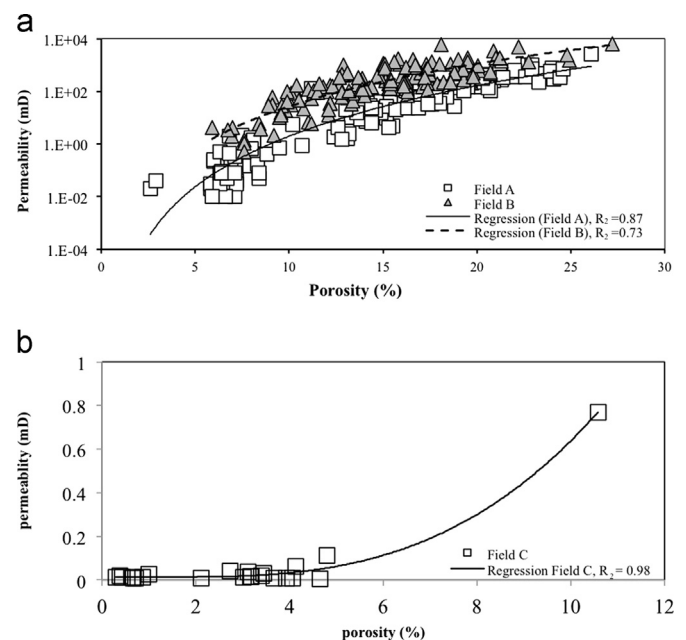


**Fig. 1.** Porosity–permeability relation in three different gas fields. (a) Porosity–permeability relation of the reservoir samples from Field A and Field B. (b) Porosity–permeability relation of the caprock samples from Field C.