Effects of impurities on subsurface CO2 storage in gas fields in the northeast Netherlands
Bolourinejad, Panteha

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Chapter 4

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

Based on publication:
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Abstract

The most suitable candidates for subsurface storage of CO\textsubscript{2} are depleted gas fields. Their ability to retain CO\textsubscript{2} can however be influenced by the effect which impurities in the CO\textsubscript{2} stream (e.g. H\textsubscript{2}S and SO\textsubscript{2}) have on the mineralogy of reservoir and seal. In order to investigate the effects of SO\textsubscript{2} we carried out laboratory experiments on reservoir and caprock 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\textsubscript{2} and 100 ppm SO\textsubscript{2} under in situ conditions (300 bar, 100°C). The vessels also contained brine with the same composition as in the actual reservoir. Furthermore equilibrium modelling 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 to 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 modelling study. Hence, caprock with higher anhydrite content in comparison with carbonate minerals has a lower risk of leakage after co-injection of 100 ppmv SO\textsubscript{2} with CO\textsubscript{2}.

Keywords: CO\textsubscript{2} storage, impurities, permeability, sulphur dioxide, reservoir, caprock

4.1 Introduction

Based on current scenarios, carbon dioxide (CO\textsubscript{2}) 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\textsubscript{2} (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\textsubscript{2} stream. Dependent on the source and the capturing technology a CO\textsubscript{2} product stream will contain impurities such as H\textsubscript{2}S, SO\textsubscript{2}, NO\textsubscript{x}, H\textsubscript{2}, Ar, CO and NH\textsubscript{3} (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\(_2\) 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\(_2\) transport are directly related to the presence of impurities (Bolourinejad and Herber, 2014). With respect to subsurface storage, impurities in CO\(_2\) 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\(_2\) 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\(_2\) in order to reduce the cost of capture without affecting the integrity of storage system?

Different modelling studies have been performed to evaluate various aspects of impurities co-injection in geological formations (Koenen et al., 2011; Parkhurst and Appelo, 2013; Waldmann et al., 2013a; Xu et al., 2007). Waldmann et al., 2013a used PHREEQC (Parkhurst and Appelo, 2013) software and modelled CO\(_2\) and SO\(_2\) co-injection into Triassic Buntsandstein. The results revealed an enhanced level of K-feldspar dissolution next to anhydrite precipitation. Koenen et al. (2011a) also utilized PHREEQC software and modelled the impact of two CO\(_2\) streams: one from a pre-combustion and one from an oxy-fuel capturing process. Both processes resulted in multiple impurities such as SO\(_2\), H\(_2\)S and N\(_2\). They concluded that the short-term effects of impurities are insignificant compared to pure CO\(_2\). For the long-term the presence of impurities leads to minor mineralogical differences, when compared to the injection of pure CO\(_2\). They also concluded that the increase in porosity caused by pure CO\(_2\) could be counteracted by the presence of impurities due to the precipitation of secondary minerals like alunite and nontronite. Xu et al., (2007) modelled the co-injection of SO\(_2\) with CO\(_2\) using TOUGHREACT. They concluded that the co-injection of SO\(_2\) with CO\(_2\) leads to the formation of a wider and stronger acidified zone around the wellbore due to the formation of strong sulphuric acid in comparison with the formation of carbonic acid following pure CO\(_2\) injection. In addition, several researchers have developed new equations of state for modelling of subsurface storage of impure CO\(_2\) 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\(_2\) (Battistelli and Marcolini, 2009; Ziabakhsh-Ganji and Kooi, 2012).

In comparison with the number of modelling studies, experimental work on this subject is sparse. In general, results from experimental studies show that more accurate parameters need to be implemented in modelling. An example is the work of Bachu and Bennion (2009) who investigated the chromatographic partitioning of H\(_2\)S, SO\(_2\), CH\(_4\) and N\(_2\). 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 modelling results. The measured reactive surface areas were significantly higher than what is typically being used in
modelling studies (e.g. (Battistelli and Marcolini, 2009)), which leads to more dissolution / precipitation of minerals.

To the best of our knowledge no published experimental dataset exists for co-injection of CO\textsubscript{2} 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\textsubscript{2} in order to have both safe and economic CCTS projects. In operational CO\textsubscript{2} storage sites it is difficult to sample the reservoir after CO\textsubscript{2} 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\textsubscript{2} injection from specific depths (106 samples) was between 15-28% which was concluded to be comparable with the pre-injection porosity of 20-30% (Liebscher and The Ketzin team, 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\textsubscript{2}. In a previous study the impact of co-injection of H\textsubscript{2}S with CO\textsubscript{2} was assessed (Bolourinejad and Herber, 2014). The current article focuses on SO\textsubscript{2} 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\textsubscript{2} co-injection with CO\textsubscript{2} is experimentally analysed 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 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 modelling studies. In addition to permeability measurements, the mineralogical variation was monitored. Also, brine samples were collected and analysed. 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\textsubscript{2}+100 ppm SO\textsubscript{2}.

4.2 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\textsubscript{2}. 

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Wilke et al., (2012) carried out 42-day mono-mineral batch experiments with pure and impure (0.5% NO\textsubscript{2} or SO\textsubscript{2}) CO\textsubscript{2} injection on rock forming minerals (albite, microcline, calcite, dolomite, anhydrite, kaolinite and biotite). Nitric and sulphuric acid formed following NO\textsubscript{2} and SO\textsubscript{2} co-injection respectively and the pH reduced more than in the pure CO\textsubscript{2} scenario. They observed anhydrite corrosion by approximately 50 wt% and gypsum precipitation following the CO\textsubscript{2} plus NO\textsubscript{2} 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\textsubscript{2} and showed both calcite dissolution and anhydrite precipitation. Similar to Wilke et al., (2012) a single mineral system was used.

Palandri et al., (2005) investigated reactions of CO\textsubscript{2}-SO\textsubscript{2} with hematite (300 bar and 150 °C). They found precipitation of pyrite (after 17 hours), siderite (after 600 hours) and elemental S. Furthermore, Palandri and Kharaka, (2005) specified that in order to sequester all of the CO\textsubscript{2} as a mineral, when using a gas mixture representative of flue gas (e.g. <1% SO\textsubscript{2}), the targeted reservoir rock should contain other metals to make carbonate precipitation possible. The reason is that in this case there is no sufficient reducing agent (e.g. H\textsubscript{2}S and SO\textsubscript{2}) to reduce all of the iron and no siderite can be formed. Murphy et al., (2010, 2011) studied the formation of siderite and pyrite from hematite and ferrihydrite in the presence of CO\textsubscript{2} and aqueous sulfide. Lammers et al. (2011) mentioned that the relative yield of siderite compared to iron sulphide bearing minerals is a strong function of the initial sulphide concentration.

These researchers were able to provide valuable information on dissolution/precipitation of minerals. However, these experiments were all carried out on a single mineral phase. In such cases the interaction between the various minerals usually present in reservoir is not taken into account. Furthermore, bulk rock properties such as porosity and permeability cannot be measured in experiments with mono mineral samples. To determine these values actual reservoir and caprock core samples need to be used.

In order to obtain a realistic scenario for co-injection of impurities with CO\textsubscript{2} a representative flue gas needs to be selected (<1% SO\textsubscript{2}). These points were taken in to account in our research when selecting core samples and a representative flue gas.

### 4.2.1 Chemical background

Injection of a gas mixture containing CO\textsubscript{2}+ 100 ppm SO\textsubscript{2} into brine creates multiple forms of acids. Carbonic and sulphuric acid will form after injection of CO\textsubscript{2} and SO\textsubscript{2} respectively (Reaction 4.1 and 4.2). In addition, based on Reaction 4.2, H\textsubscript{2}S will form, which can dissociate into hydrogen and sulphur which further reduces the pH of the brine (Reaction 4.3).

\[
\begin{align*}
\text{CO}_2 + \text{H}_2\text{O} & \leftrightarrow \text{H}_2\text{CO}_3 \leftrightarrow \text{H}^+ + \text{HCO}_3^- & \text{Reaction 4.1} \\
4\text{SO}_2 + 4\text{H}_2\text{O} & \rightarrow 3\text{H}_2\text{SO}_4^- + \text{H}_2\text{S} & \text{Reaction 4.2} \\
\text{H}_2\text{S(aq)} & \leftrightarrow 2\text{H}^+ + \text{HS}^- & \text{Reaction 4.3}
\end{align*}
\]

The strength of the acids in question is determined by the acid dissociation constant (K\textsubscript{a}) which varies from 1×10\textsuperscript{3} in sulphuric acid to 4.3×10\textsuperscript{-7} in carbonic acid and 1×10\textsuperscript{-7} in...
hydrosulphuric acid. Hence, sulphuric acid has a higher impact on acidity of brine. When the pH of the brine reduces it is buffered by dissolution of minerals such as carbonates (Reaction 4.4 and 4.5)

\[
\text{CaCO}_3 + \text{H}^+ \leftrightarrow \text{Ca}^{2+} + \text{HCO}_3^-
\]

Calcite

\[
\text{CaMg(CO}_3)_2 + 2\text{H}^+ \leftrightarrow \text{Ca}^{2+} + \text{Mg}^{2+} + 2\text{HCO}_3^-
\]

Dolomite

Furthermore, due to the changes in pH different mineralizations can occur. The relevant reactions based on the mineralogy (Table 4.1) for our reservoir and caprock core samples are reactions (Reaction 4.6, 4.7 and 4.8)

\[
2\text{NaAlSi}_3\text{O}_8 + 4\text{H}^+ \leftrightarrow 2\text{Na}^+ + 2\text{H}_2\text{O} + 3\text{SiO}_2 + \text{Al}^{3+}
\]

Albite

\[
\text{KAlSi}_3\text{O}_8 + 4\text{H}^+ \leftrightarrow 2\text{H}_2\text{O} + 3\text{SiO}_2 + \text{K}^+ + \text{Al}^{3+}
\]

K-feldspar

\[
\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 6\text{H}^+ \leftrightarrow 5\text{H}_2\text{O} + 2\text{Al}^{3+} + 3\text{SiO}_2
\]

Kaolinite

Table 4.1 Mineralogy (wt%) and permeability of Rotliegend reservoir (R) and Zechstein caprock (C) core samples. K= permeability, Q= quartz, Anh= anhydrite, Kao= kaolinite, Dol= dolomite, Gyp=Gypsum, Alb=Albite, Kf=K/feldspar, Cal= calcite.

<table>
<thead>
<tr>
<th>Samples</th>
<th>K(mD)</th>
<th>Q</th>
<th>Anh</th>
<th>Kao</th>
<th>Dol</th>
<th>Gyp</th>
<th>Alb</th>
<th>Kf</th>
<th>Cal</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>0.29±0.03</td>
<td>83</td>
<td>3.3</td>
<td>-</td>
<td>13.3</td>
<td>-</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>-</td>
</tr>
<tr>
<td>R2</td>
<td>71.8±3.6</td>
<td>87</td>
<td>1.6</td>
<td>4.1</td>
<td>2.8</td>
<td>-</td>
<td>3.6</td>
<td>&lt;1</td>
<td>-</td>
</tr>
<tr>
<td>R3</td>
<td>350±18</td>
<td>89</td>
<td>6.3</td>
<td>1.7</td>
<td>-</td>
<td>2.2</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>-</td>
</tr>
<tr>
<td>C1</td>
<td>0.029±0.006</td>
<td>1.11</td>
<td>98.65</td>
<td>-</td>
<td>0.24</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C2</td>
<td>0.085±0.017</td>
<td>-</td>
<td>89.35</td>
<td>-</td>
<td>10.65</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C3</td>
<td>0.003±0.001</td>
<td>-</td>
<td>55.95</td>
<td>-</td>
<td>44.05</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C4</td>
<td>0.028±0.006</td>
<td>-</td>
<td>43.17</td>
<td>-</td>
<td>56.83</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C5</td>
<td>0.016±0.003</td>
<td>6.67</td>
<td>3.32</td>
<td>-</td>
<td>46.13</td>
<td>-</td>
<td>-</td>
<td>43.88</td>
<td>-</td>
</tr>
<tr>
<td>C6</td>
<td>0.227±0.023</td>
<td>1.9</td>
<td>-</td>
<td>-</td>
<td>1.00</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>97.10</td>
</tr>
</tbody>
</table>

The presence of SO\textsubscript{2} in a gas mixture can lead to the formation of sulphate minerals due to the release of sulphate ions through the dissociation of sulphuric acid in brine. Moreover, H\textsubscript{2}S is a product of SO\textsubscript{2} when dissolved in brine (Reaction 4.2). Hence, sulphide and sulphur can also form (Reaction 4.9 and 4.10) (Palandri and Kharaka, 2005).

\[
\text{H}_2\text{S} \leftrightarrow 2\text{H}^+ + \text{S}^{2-}
\]

Reaction 4.9

\[
3\text{H}_2\text{S} + \text{H}_2\text{SO}_4 \leftrightarrow 4\text{S(native)} + 4\text{H}_2
\]

Reaction 4.10

From these reactions we can expect that several dissolution / precipitation mechanisms can occur when injecting CO\textsubscript{2}+ 100 ppm SO\textsubscript{2}. Therefore we will incorporate these reactions in our experiments and models. Consequently, based on the reactions we selected four analytical techniques for evaluating the core samples after the experiments:
pH measurement, microscopic study on mineralisation, brine composition analysis and permeability measurement.

### 4.3 Methods and materials

In this section we will elaborate on our methodology for the experiments and modelling. The workflow is summarized in Figure 4.1 and subsequently explained.

Figure 4.1 Work flow of the research presented in this paper. The methodology is divided into experimental and modelling sections. Abbreviations are: SEM (Scanning Electron Microscopy), XRD (X-ray Diffraction) and ICP-OES (Induced Coupled Plasma- Optical emission Spectroscopy).

#### 4.3.1 Experimental section

The experimental section is divided in sampling, experimental setup, procedure and analytical techniques.

##### 4.3.1.1 Sampling

The reservoir core samples were selected from Permian Rotliegend sandstone from Field A and Field B (Figure 4.2). The caprock core samples are from the Permian Zechstein anhydrite and carbonate components from Field C. Both are found in the northeast of the Netherlands (Figure 4.2).
The samples were taken from a depth ranging between 2.8 and 3.2 km. Porosity varies between 0.2% (caprock) and 26% (reservoir) while permeability ranges between 0.003 mD (caprock) and 350 mD (reservoir).

Figure 4.3 shows the porosity-permeability relationship for reservoir samples of Fields A and B.

The permeability of the selected samples and their mineralogy is presented in Table 4.1.

Reservoir sample selection is based on permeability in order to cover both low and medium permeabilities. These samples are more sensitive to the chemical effects caused by increasing brine acidity due to the presence of more cementing materials such as feldspars and carbonates. Caprock samples were selected based on mineral composition (high, medium and low anhydrite or carbonate content).
The details of the permeability measurements and mineralogical analysis techniques are explained in section 2.2.4.1 and Figure 2.4

4.3.1.2 Experimental setup and procedure
A batch experimental setup with reaction cells was used to create the high pressure/high temperature (300 bars and 100° C) reservoir conditions (Figure 2.3, section 0). The disk-shaped reservoir and caprock samples with a diameter of 25 mm were obtained from core plugs. The samples were cut to an average thickness of 15 mm. The cylindrical reservoir and caprock core samples were brought in contact with brine (30 ml), in line with the in-situ reservoir fluid composition obtained from well test data from the gas fields (Table 2.2). The gas mixture of CO$_2$ and 100 ppm (volume) SO$_2$ was injected up to a pressure of 300 bar at a temperature of 100° C. The duration of the experiments was 30 days. After the experiments the samples were dried at room temperature.

4.3.1.3 Analytical techniques
Prior to the experiments, the mineralogical composition of the samples is determined with X-Ray Diffraction (XRD) and Scanning Electron microscopy (SEM) (Table 4.1). 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 degree with 5 s/step. Rather than making use of a powder, we used full core samples for the XRD analysis. This enabled us to use the same samples for mineralogical analysis prior and during the experiments. Following the XRD analysis, we used GSAS (General Structure Analysis System) software (Larson, and Von Dreele, 2004) in order to quantify different phases in the samples. It should be noted that XRD was solely used prior to the experiments for mineralogical analysis.

The SEM measurements were carried out on a Philips XL-30 environmental SEM (ESEM) with a Field Emission Gun (FEG), which is equipped with energy dispersive spectroscopy (EDS). Secondary Electron (SE) and Backscattered Electron (BSE) images were taken before and after the experiments on the same core sample and at the same spot on the samples.

Following the mineralogical analysis, the permeability of the samples was measured before and after the experiments on the same sample. The measurement error for permeability is between 5 and 20% (lower error for higher permeability samples). Since we also calculated the post to pre ratio of permeability, the error propagation was calculated by (Equation 4.1).

\[
Z = \frac{Y}{X}, \quad \frac{DZ}{Z} = \frac{DX}{X} + \frac{DY}{Y}
\]

Equation 4.1

X and Y are permeability values before and after the experiments respectively. DX and DY are errors in the permeability measurement before and after the experiment. Z is the post to pre permeability ratio and DZ is the error in Z.
The next measurement technique is related to the brine used in the experiments. The pH of the brine was compared before and after the experiments and the measurements where done under atmospheric conditions. The brine composition was analyzed by an ICP-OES (Induced Coupled Plasma- Optical Emission Spectroscopy). The standard deviation of the measured value was less than 3%. Finally, after the experiments, the solid residuals in the brine were separated using a centrifuge machine. These residuals were dissolved in hydrofluoric acid and measured using the ICP-OES.

4.3.2 Model description

The purpose of the modelling is to compute the change in the permeability of the caprock samples in relation to their initial mineralogy and compare that with the experimental results. PHREEQ (version 3.1.0) (Parkhurst and Appelo, 2013) is utilized to calculate the chemical equilibrium between brine, gas and minerals. Hence, several input parameters are required. These are a thermodynamic database, an initial mineral assemblage, porosity values, permeability values, the initial brine composition and the gas phase.

For our modelling study the LLNL (Lawrence Livermore National Laboratory) database was selected. LLNL is based on ion-associations and Debye-Hückel expressions. The ionic strength term of Debye-Hückel expressions was expanded by Truesdell and Jones (1974) in order to be applicable for higher ionic strengths. Generally, the brine found in the gas fields of NE Netherlands has a high ionic strength and needs a precise interaction approach to thermodynamic properties for modelling (Pitzer, 1973; Plummer et al., 1988). However, this approach is not implemented in the LLNL database. It is worth mentioning that the Pitzer database, which is included in the PHREEQC database, does account for higher ionic strengths but has the drawback that some of the important and necessary elements namely Al, Si, Fe are not accounted for. Moreover, the Pitzer database is limited to relatively low temperatures and pressures (Waldmann et al., 2014a; Zhu and Anderson, 2002). Taking all this into consideration, we selected the LLNL database. A comparison between different thermodynamic databases has been made by Dethlefsen et al., (2011), who concluded that the choice of thermodynamic databases could affect the amount of sequestered CO$_2$. Finally, Waldmann et al., (2014b) cautioned that for a complex system like fluid/gas bearing reservoir no general statement could be made on how the different ion activity models may influence detailed water–mineral reactions.

4.3.2.1 Model input

We have modelled six cases representative of the caprock samples listed in Table 4.1 (C1 to C6). In order to input the initial weight percentage of the minerals, obtained by XRD, into PHREEQC we need to convert them to mole concentrations (Table 4.2).
Table 4.2 Initial amounts of minerals in moles utilized in the PHREEQC. This is based on their initial wt% obtained by XRD.

<table>
<thead>
<tr>
<th>Cases</th>
<th>Sample</th>
<th>Anhydrite (Initial mole)</th>
<th>Dolomite (Initial mole)</th>
<th>Calcite (Initial mole)</th>
<th>Quartz (Initial mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case 1</td>
<td>Caprock 1</td>
<td>0.0943</td>
<td>0.00016</td>
<td>-</td>
<td>0.0021</td>
</tr>
<tr>
<td>Case 2</td>
<td>Caprock 2</td>
<td>0.1322</td>
<td>0.011</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Case 3</td>
<td>Caprock 3</td>
<td>0.097</td>
<td>0.0544</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Case 4</td>
<td>Caprock 4</td>
<td>0.0404</td>
<td>0.0375</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Case 5</td>
<td>Caprock 5</td>
<td>0.005</td>
<td>0.049</td>
<td>0.083</td>
<td>0.0203</td>
</tr>
<tr>
<td>Case 6</td>
<td>Caprock 6</td>
<td>-</td>
<td>0.001</td>
<td>0.183</td>
<td>0.0057</td>
</tr>
</tbody>
</table>

These are calculated based on the multiplication of sample volume, porosity, density of the mineral, weight fraction of the mineral and inverse of the molecular weight.

For the equilibrium calculations the reactive mineral surface area is not required as an input parameter. Equilibrium constants of the minerals utilized in the simulation are presented in Table 4.3.

Table 4.3 Composition, reactions and equilibrium constants of the minerals utilized in the simulation. Equilibrium constants are presented both at atmospheric and high pressure/temperature conditions. Anh=anhydrite, Dol= dolomite, Cal=calcite, Q= quartz

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Chemical composition</th>
<th>Reaction</th>
<th>Log k (Equilibrium constant) (25 °C and 1.013 bar)</th>
<th>Log k (Equilibrium constant) (100 °C and 300 bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anh</td>
<td>CaSO₄</td>
<td>CaSO₄⇌Ca²⁺ + SO₄²⁻</td>
<td>-4.3</td>
<td>-5.35</td>
</tr>
<tr>
<td>Dol</td>
<td>CaMg(CO₃)₂</td>
<td>CaMg(CO₃)₂+2H⁺⇌Ca²⁺+Mg²⁺+2 HCO₃⁻</td>
<td>2.51</td>
<td>0.13</td>
</tr>
<tr>
<td>Cal</td>
<td>CaCO₃</td>
<td>CaCO₃+ H⁺⇌Ca²⁺+HCO₃⁻</td>
<td>1.81</td>
<td>0.79</td>
</tr>
<tr>
<td>Q</td>
<td>SiO₂</td>
<td>SiO₂⇌SiO₂⁻</td>
<td>-3.75</td>
<td>-3.06</td>
</tr>
</tbody>
</table>

Since the initial porosity of the samples was not measured, an assumption had to be made. According to Hangx et al., (2009) the porosity and permeability of Zechstein anhydrite is in the range of 0.1%-0.3% and around 10⁻⁷ mD. Since our samples have a higher permeability we assumed a slightly higher porosity of 0.4%. A sensitivity analysis of this assumption is presented in the discussion Section (section 4.5). The final porosity was calculated from the change in the mineral amounts in moles.

The initial permeabilities of the caprock samples used in the modelling are those measured and listed in Table 4.1. The final permeability in the model is calculated using the Carman-Kozeny relation (Bear, 1972). According to Luquot and Gouze (2009), rock permeability depends on pore and pore-throat geometry and more importantly the connectivity of the voids at full sample scale. Despite these complexities, the gross permeability behavior can be predicted using the Carman-Kozeny equation based on porosity.
Initial brine composition and volume are similar to those used for the experiments (Table 2.2). The pH was set to 6.8 and the pe, which is an indication of the redox conditions, to -2.

The partial pressure of each gas in the model was based on the gas mixture composition (CO$_2$ + 100 ppmv SO$_2$) and the fugacity coefficients of CO$_2$ and SO$_2$ at 100°C and 300 bar are 0.503 and 0.148 respectively (Lee and Kesler, 1975).

As most of the input parameters in the models are the same as those in the experiments we are able to compare the modelling and experimental results for the caprock samples.

4.4 Results

4.4.1 pH evolution

After the experiments the pH of the brine of 6.8 was reduced to 5.2 (reservoir) and 5.4 (caprock) (Table 4.4).

<table>
<thead>
<tr>
<th>Samples</th>
<th>Measured pH (Atmospheric conditions)</th>
<th>Simulations</th>
<th>Modeled pH (300 bar, 100°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>5.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>R2</td>
<td>5.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>R3</td>
<td>5.08</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C1</td>
<td>5.05</td>
<td>Case 1</td>
<td>3.5</td>
</tr>
<tr>
<td>C2</td>
<td>5.7</td>
<td>Case 2</td>
<td>3.9</td>
</tr>
<tr>
<td>C3</td>
<td>5.17</td>
<td>Case 3</td>
<td>3.9</td>
</tr>
<tr>
<td>C4</td>
<td>5.6</td>
<td>Case 4</td>
<td>3.9</td>
</tr>
<tr>
<td>C5</td>
<td>5.8</td>
<td>Case 5</td>
<td>4</td>
</tr>
<tr>
<td>C6</td>
<td>5.13</td>
<td>Case 6</td>
<td>4</td>
</tr>
</tbody>
</table>

The equilibrium modelling of the caprock samples resulted in a pH of 3.9 on average, at 300 bar and 100°C (Table 4.4).

The reason for this discrepancy is that the pH after the experiments could not be measured at in-situ pressure and temperature conditions. After opening of the reaction cells the pressure and temperature drop and the degassing of the samples resulted in an increase of the pH compared to the modelling conditions.

When comparing the modelling results for each case in relation to the initial mineral composition of the caprock samples a proportional decrease in the pH was observed. The highest pH value of 4 is found in samples C5 and C6 with higher carbonate content, due to their higher potential to buffer the pH of the brine (Reaction 4.4 and 4.5). The lowest pH of 3.5 is found in the C1 sample, which has the lowest carbonate content and therefore
less buffering potential. This relation was not found in the experiments due to the non-in-situ conditions during the measurements.

4.4.2 Mineral dissolution and precipitation

Each of the minerals in the sandstone reservoir and carbonate/anhydrite caprock shows some evidence of participating in rock and fluids reactions. SEM analysis at the same spot on the core samples before and after the experiments revealed dissolution of quartz, K-feldspar, albite, calcite, dolomite and kaolinite. (Figure 4.4).
Figure 4.4 SEM images of Rotliegend reservoir and Zechstein caprock samples before and after the experiment with injection of CO$_2$ and 100 ppm of SO$_2$. Images were taken at the same spot on the sample. Mineral abbreviations are: dolomite (Dol), quartz (Qrz), K-feldspar (Kf), Albite (Alb), kaolinite (Kao), Halite (Hal), anhydrite (Anh) and calcite (Cal).(a) Rotliegend reservoir sample (Field A) before experiment and (b) after the experiment. (c) Higher magnification of (b) showing kaolinite precipitation. (d) Higher magnification of (b) showing dolomite dissolution. (e) Zechstein caprock sample (Field C) before experiment and (f) after experiment showing anhydrite precipitation. (g) Zechstein caprock sample (Field C) before experiment and (h) after experiment showing replacement of calcite by dolomite.

Mineral precipitation occurred in the form of kaolinite and anhydrite overgrowth. In the samples containing dolomite and calcite minerals, dissolution of calcite was stronger than that of dolomite. Also, dolomite had precipitated where calcite was dissolved (Figure 4.4). Overall, the observed dissolution of silicate and carbonate minerals is in line with Reactions (Reaction 4-4 to 4-8). When it comes to precipitation, three minerals are of interest: kaolinite, anhydrite and dolomite. In our experiments, dissolution of calcite and dolomite buffered the pH of the brine, thereby moving reaction 4.8 towards kaolinite precipitation. In the case of the reservoir samples, this was further enabled through the provision of Al$^{3+}$ ions by dissolution of K-feldspar (KAlSi$_3$O$_8$) and albite (NaAlSi$_3$O$_8$). Anhydrite precipitation in the experiments was induced by the presence and subsequent
dissociation of sulphuric acid in the brine (Reaction 4.2) producing sulphates which in turn react with calcium forming anhydrite. Dolomite is formed by replacement of calcite, which has a higher dissolution rate (0.5 molm$^{-2}$s$^{-1}$) compared to dolomite ($6.4 \times 10^{-4}$ molm$^{-2}$s$^{-1}$) (Palandri and Kharaka, 2004). Hence, calcite dissolves faster, buffers the pH of the brine and provides the ions for dolomite precipitation ($\text{Ca}^{2+}$ and $\text{CO}_3^{2-}$). Furthermore, dolomite precipitation can also occur in samples with no initial calcite content. In that case the buffering of brine, combined with provision necessary ions from the initial brine composition ($\text{Mg}^{2+}$, $\text{Ca}^{2+}$) and dissolution of $\text{CO}_2$ in brine ($\text{CO}_3^{2-}$) lead to dolomitisation. The PHREEQC modelling of the injection of $\text{CO}_2$ plus 100 ppm $\text{SO}_2$ in the caprock samples corroborated the above experimental observations quantitatively (Table 4.5).

**Table 4.5** Change in the amount of minerals (moles) obtained from PHREEQC modeling. A plus-sign signifies precipitation and a minus-sign signifies dissolution. $\Delta$mole is the difference between final and initial mineralogy.

<table>
<thead>
<tr>
<th>Cases</th>
<th>Anhydrite ($\Delta$mole) $\times 10^{-5}$</th>
<th>Dolomite ($\Delta$mole) $\times 10^{-5}$</th>
<th>Calcite ($\Delta$mole) $\times 10^{-5}$</th>
<th>Quartz ($\Delta$mole) $\times 10^{-5}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case 1</td>
<td>+0.834</td>
<td>-16.2</td>
<td>-</td>
<td>-3.027</td>
</tr>
<tr>
<td>Case 2</td>
<td>+0.628</td>
<td>-27.7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Case 3</td>
<td>+0.375</td>
<td>-27.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Case 4</td>
<td>+0.527</td>
<td>-28.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Case 5</td>
<td>+0.696</td>
<td>+301</td>
<td>-674</td>
<td>-2.97</td>
</tr>
<tr>
<td>Case 6</td>
<td>-</td>
<td>+300</td>
<td>-674</td>
<td>-3</td>
</tr>
</tbody>
</table>

In addition to the above results we also analysed the modelling result for the brine composition using the saturation index of the minerals (SI). For almost every case and for all the minerals the final SI of the minerals was zero, which means that the brine is fully saturated with those minerals. An exception to this was Case 1, which had an SI of -1.36. This means that the brine is under saturated with dolomite due to the low wt% of dolomite in this case (0.2%).

### 4.4.3 Change in brine composition in the experiments

In order to verify whether the mineral dissolution/precipitation in the samples was in line with changes in concentration in the brine, we measured the concentration of the main elements (Mg, Ca, K, Si, Al and S) before and after the experiments in the brine as well as in the solid residue after the experiments (Figure 4.5).
Figure 4.5 Concentration of different elements in the brine before and after the experiment as well as in the solid residue after the experiments. Mg (a) and Ca (b) are measured for caprock samples. K (c), Si (d) and Al (e) are measured for reservoir samples and S (f) is plotted for both reservoir and caprock samples. Al and Si were not initially present in the brine. R and C stand for reservoir and caprock respectively.

Analyses of the brine samples in the caprock experiments reveal an increase in the concentration of Mg and Ca after the experiments (Figure 4.5a and b). This is due to the dissolution of calcite and dolomite minerals. The enrichment of K, Si and Al in the brine of the reservoir experiments confirms the microscopic observation of K-feldspar, albite, quartz and kaolinite dissolution (Figure 4.5c, d and e). The increase of the sulphur concentration in the brine samples is related to the dissolution of SO$_2$ in the brine as it is shown in Reaction 4.2 (Figure 4.5f). The concentration of sulfur in the brine for the R1 and R2 reservoir samples is slightly reduced, which can be attributed to either anhydrite precipitation or potential degassing of the brine after opening of the reactors.
The elemental analyses of the solid residues precipitated from the brine revealed the presence of Ca, Mg, K, Si, Al caused by dissolution of carbonate and silicate minerals. The presence of sulfur in the solid residue is caused by precipitation of sulfur containing components such as anhydrite. In some cases the temperature reduction after completion of the experiments caused extra precipitation of some elements (e.g. Al, Figure 4.5e).

4.4.4 Permeability measurements

Following injection of the gas mixture into the reservoir samples, the permeability of the samples increased on average by a factor of 1.18 to 2.20 due to the dominance of mineral dissolution over precipitation. In the caprock samples permeability changed by a factor of 0.79 to 23.34 (Table 4.6).

Table 4.6 Post injection sample permeability. R is reservoir and C is caprock.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Final permeability (mD)</th>
<th>Factor of variation (Post/ pre permeability ratio)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>0.43±0.04</td>
<td>1.48</td>
</tr>
<tr>
<td>R2</td>
<td>158.3±7.9</td>
<td>2.20</td>
</tr>
<tr>
<td>R3</td>
<td>414±21</td>
<td>1.18</td>
</tr>
<tr>
<td>C1</td>
<td>0.023±0.005</td>
<td>0.79</td>
</tr>
<tr>
<td>C2</td>
<td>0.071±0.014</td>
<td>0.83</td>
</tr>
<tr>
<td>C3</td>
<td>0.010±0.002</td>
<td>3.33</td>
</tr>
<tr>
<td>C4</td>
<td>0.282±0.028</td>
<td>10.07</td>
</tr>
<tr>
<td>C5</td>
<td>0.345±0.035</td>
<td>21.56</td>
</tr>
<tr>
<td>C6</td>
<td>5.30±0.53</td>
<td>23.34</td>
</tr>
</tbody>
</table>

The wide range of variation in the caprock samples can be explained by their mineralogical composition. In line with our microscopic observations, the higher the carbonate content in the samples (Table 4.1) the more the permeability increases due to carbonate dissolution (for example C5 and C6). On the other hand, in the samples with higher anhydrite content, the permeability decreases (for example C1 and C2) due to further anhydrite precipitation and the absence of carbonate dissolution (Figure 4.6).

Figure 4.6 Comparison of permeability variation, obtained from modelling and experiments, in relation to initial anhydrite (a) and carbonate (b) content of the caprock samples.
As stated in the methodology section, the main purpose of the modelling study was to model the change in the permeability of the caprock samples in relation to the carbonate to anhydrite ratio. To that aim we compared the permeability variations obtained from the modelling with the actual measurements from the samples used in the experiments (Figure 4.6).

Modelling and experimental results for pre- to post- injection permeability variations in caprock samples show large similarity as a function of carbonate and anhydrite concentration. Dissolution of carbonate minerals in the presence of the CO₂/SO₂ mixture leads to an increase in permeability. On the other hand, when the anhydrite concentration increases the permeability is reduced as anhydrite precipitation becomes dominant.

4.5 Discussion

When subjecting the samples and brine to the CO₂/SO₂ mixture in our experimental system at subsurface pressure/temperature conditions we observed a variety of mineralogical changes as the result of changes in pH.

Our main finding is related to the Zechstein caprock samples: an increase in the weight percentage of the carbonate minerals leads to an increase in the ratio of post over pre-experiment permeability. On the other hand, an increase in the weight percentage of anhydrite reduces this ratio due to the dominance of anhydrite precipitation over dissolution of carbonate minerals. Our results are in agreement with a previous study by Waldmann et al., (2013b) who also observed anhydrite precipitation.

The experimental results presented in this paper provide new information in the form of geochemical consequences of subsurface co-injection of CO₂ and SO₂. Our results are however constrained by the limitations of some of the measurement techniques. Firstly, in our experimental setup we were only able to measure pH under atmospheric conditions whereas the most accurate way would have been to do this under in-situ (high pressure / high temperature) conditions. However, we did account for this effect by calculating the pH at high pressure and high temperature in a modelling study. This resulted in modelled pH values which are lower in comparison with the experimental measurements.

Secondly, the SEM images of the samples after injection showed considerable halite precipitation (Figure 4.4b). In the reservoir samples this is caused by the drying-out effect as a consequence of the injection of a gas mixture, as well known in literature (e.g. (Pruess and Müller, 2009)). In our experimental setting salt precipitation can however also be due to the evaporation of water during the drying of the samples after the experiments which was necessary for the mineralogical analyses. Consequently, we cannot discriminate which of the two processes was responsible for the halite precipitation.

Thirdly, in the analysis of the brine in our experiments we observed an increase in the concentration of several elements. These results are similar to those in the synthetic mono-mineral experiments of Wilke et al., (2012) who mentioned an increase in the concentration of cations dissolved in the brine due to mineral dissolution caused by the formation of sulphuric acid following injection of CO₂ and 0.5% SO₂. In our experiments
we used multi-mineral core samples. Hence, the determination of the effect of dissolution of each individual mineral on brine composition was not possible due to the multiple presence of elements in the minerals (e.g. Ca is present in anhydrite, calcite as well as dolomite). Our choice to use Permian core samples was driven by the main objective of our research: to determine the permeability of the samples as a function of mineralization caused by the injection of the CO$_2$/SO$_2$ mixture.

Fourthly, we measured the solid residues after the experiments. Cooling of the brine and depressurization could have led to extra precipitation of some of the dissolved elements in the brine, hence increasing their concentration in both fluid and solid residue. In addition, in the case of less cemented reservoir sandstone samples, part of the solid residue can be the result of separation of grain particles from the core sample itself.

Finally, the experiments were carried out in batch reactors in a static state. In subsurface reservoirs both brine and gas are subject to flow dynamics. Therefore, this research will have to be expanded in the form of flow-through experiments and reactive transport modelling in order to capture more aspects of the actual subsurface processes.

For the modelling study different sources of uncertainty remain. We have attempted to reduce these uncertainties by using experimental data such as mineralogy and brine composition. However, this data was not complete since we did not have porosity measurements of the caprock samples prior to injection. In order to overcome this we carried out a sensitivity analysis on the effect of porosity. Modeling was repeated in 12 simulations within a range of 25% variation around the base case initial porosity (0.4%) whilst all other parameters were kept unchanged. The results are shown in Figure 4.7.

![Figure 4.7](image)

**Figure 4.7** Post to pre permeability ratio of caprock samples as a function of carbonate weight percentage for three initial porosities: 0.3, 0.4 and 0.5%.

It is concluded from the analysis that for the caprock samples, with more than 50% carbonate weight percentage, an increase in the initial porosity results in a decreasing post/pre injection permeability ratio. This is due to the lower amount of minerals available for dissolution. Contrary to that, when porosity is lower than the base case more mineral volume is available to dissolve. This leads to a higher post to pre permeability ratio. Higher carbonate content samples are more sensitive to a change in porosity (**Figure 4.7**). This is due to the fast dissolution of these minerals when exposed to strong sulphuric acid.
4.6 Conclusion
In this study we have carried out a combined experimental and modeling study of co-injection of 100 ppm SO$_2$ with CO$_2$ in Permian reservoir and caprock from gas fields in Northeast Netherlands. Following the injection of the gas mixture the permeability of the reservoir samples increased by a factor of 1.2 to 2.2 due to dissolution of quartz, dolomite, K-feldspar, albite and kaolinite minerals. Analysis of the associated brine samples before and after the experiments showed that concentrations of K, Si and Al had increased after the experiments, indicative of silicate mineral dissolution. In the caprock samples permeability changed by a factor of 0.79-23. The concentrations of anhydrite and carbonates have the largest effect on this permeability variation. Samples with higher carbonate content showed increased permeability due to the strong dissolution caused by the formation of sulphuric acid. However, with lower concentrations of carbonate and higher concentrations of anhydrite the post to pre permeability ratio decreases due to the lack of carbonate and anhydrite dissolution and incremental anhydrite precipitation. Carbonate dissolution was confirmed by increased Ca and Mg concentrations in the brine. The dissolution of SO$_2$ in brine gave rise to increasing sulphur concentrations in the brine as well as in the solid residue, both in the case of reservoir and caprock samples. The experimental results for the permeability variation of caprock samples were corroborated by modelling using PHREEQC and the Carman-Kozeny equation. This increased confidence in the modelling parameters used and hence extrapolation to longer periods.