Effects of impurities on subsurface CO2 storage in gas fields in the northeast Netherlands
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Chapter 2

Geology, experimental setup and effect of injection of pure CO$_2$ on the reservoir and caprock

Based on publications:


Chapter 2
Geology, experimental setup and effect of injection of pure CO$_2$ on the reservoir and caprock

Abstract
Depleted gas fields form in principle suitable candidates for geological sequestration of carbon dioxide (CO$_2$) in view of their proven reservoir and seal quality. Contrary to methane, injection of CO$_2$ can lead to dissolution and precipitation of minerals in reservoir and caprock, thus affecting porosity and permeability. In order to investigate this for a real case example, we have carried out medium term (30 days) along with some long-term (143 days) laboratory experiments on core samples from Rotliegend sandstone reservoir and Zechstein anhydrite and carbonate caprock from a selection of gas fields in northeast Netherlands. The rock samples were subjected to in situ conditions (300 bar, 100°C) with presence of brine, methane and CO$_2$.

In the reservoir samples quartz, feldspar and kaolinite dissolution was observed and permeability had increased by 10 to 30%. In addition, for the first time, the precipitation of dawsonite in reservoir samples was observed in a long term (143 days) experimental setting with CO$_2$ injection.

In the caprock samples calcite, dolomite and anhydrite were dissolved and permeability of caprock samples increased by a factor of 3 to 10.

2.1 Introduction
Over recent decades anthropogenic activities have caused a substantial rise in carbon dioxide (CO$_2$) emissions. One possible mitigation option is carbon capture, transport and (subsurface) storage (CCTS). Various geological settings such as depleted oil and gas reservoirs, saline aquifers and coal seams lend themselves as a storage medium. In the Netherlands numerous gas fields are currently in production and many will become depleted in the coming decades. In this context depleted means that the operational cost exceeds the production income (Herber and Jager, 2010).

Most gas fields in the Netherlands are situated at depths between 2500 and 4000 m. Under these conditions CO$_2$ will reach super critical state. Various modelling and experimental studies have been carried out to determine under these conditions the interaction of CO$_2$ with reservoir rock (mostly sandstones), caprock (anhydrites and carbonates) and well bore cement (Bachu, 2008; Gaus, 2010; Hangx et al., 2009; Scherer and Huet, 2009; Xu et al., 2007). In operational CO$_2$ storage sites it is difficult to sample the reservoir after CO$_2$ injection. Hence, experimental studies at in situ reservoir pressure and temperature conditions are an essential and elegant way to solve this problem (Fischer et al., 2010). For example, Kaszuba et al. (2003) studied the effects of CO$_2$ interaction with brine (pH=7.15) and arkosic sandstones via experiments at 20 MPa/200°C during 139 days. In this experiment dissolution of microcline, biotite and quartz was reported. In another
experimental study by Wigand et al. (2008) dissolution of dolomite, K-feldspar and albite was observed. In addition to mineral dissolution, potential carbonate storage during CO$_2$ sequestration is an important aspect. The CO$_2$ mineral storage can be larger if dawsonite (Na-Al carbonate) forms (Hellevang and Aagard, 2013). Dawsonite presence is observed in natural reservoirs which have high CO$_2$ pressure or have experienced CO$_2$ influx (Baker et al., 1995; Gao et al., 2009; Smith, J. W. and Milton, 1996). The currently available published experimental data is relatively limited and the present database is insufficient to draw conclusions solely based on the experimental study (Fischer et al., 2010). Therefore, to contribute in this field, we experimentally determined the effects of CO$_2$ on Rotliegend reservoir rocks and some components of Zechstein caprock. The core samples were subjected to CO$_2$ and brine at reservoir temperature and pressure for 30 days. In addition some longer period (143 days) tests were carried out to evaluate the possibility of dawsonite formation in the Rotliegend reservoir. The samples were analysed for mineralogical alterations using scanning electron microscope imaging (SEM) and x-ray diffraction (XRD). In addition, we measured and compared the permeability of the samples pre and post CO$_2$ injection.

2.2 Methodology

2.2.1 CO$_2$ storage site and sampling

The reservoir in the majority of the gas fields in the northeast Netherlands is part of the Permian Rotliegend group, deposited at the southern margin of Southern Permian Basin in an alluvial-fan to desert-like environment. It includes conglomerates, sandstones, siltstones and mudstone forming sediments with a gross thickness increasing from 100 m in the south to over 300 m in the north of the basin (Grotsch et al., 2011). It is subdivided into 4 members, listed here from bottom to top: Lower Slochteren sandstone, Ameland claystone, Upper Slochteren sandstone and Ten Boer claystone. The upper parts of the Slochteren sandstones shale out towards the north into the Ten Boer member. Sand content in the Ten Boer member varies, making it act as a waste zone or as seal for the underlying Slochteren sandstone. Even if this member does not act as a top seal, it can still provide a lateral seal when it is juxtaposed against Slochteren reservoir. The main reduction of the Slochteren reservoir potential is by early carbonate cementation or fibrous illite formation associated with deep paleo-burial. Illite growth reduces permeability and occurs where the formation water contains the necessary ions for clay precipitation, for example where Slochteren is juxtaposed with shaly Carboniferous Westphalian. However, illite formation cannot take place at locations where the Slochteren was already gas bearing before deep burial. Hence for reservoir quality prediction, also for CO$_2$ storage purposes, a good understanding of depositional trend, time of trap formation, gas charge and temperature history is needed (Jager and Geluk, 2007).

The Rotliegend group is overlain by the thick evaporite-carbonate succession of the Permian Zechstein group (
The depositional thickness of the Zechstein group increases from less than 50 m in the southern Netherlands to over 1200 m in the northern offshore. The Zechstein group in the Netherlands is composed of 5 evaporite cycles (Z$_1$ to Z$_5$). The Z$_1$ deposition (Wera formation) starts with Coppershale or Kupferschiefer, finely laminated with average organic carbon content of up to 5%. The formation also consists of carbonate, anhydrite and salt. The Z$_2$ (Stassfurt formation) comprises a basal carbonate unit, basal anhydrite and salt. The Z$_3$ (Leine formation) composed of Gray Salt Clay, carbonate, main anhydrite and salt. The Z$_4$ (Aller) formation is made of a basal clay stone, the Red Salt Clay, followed by the thin pegmatite anhydrite and salt. The Z$_5$ (Ohre) formation is made up of a basal clay stone with several hundred thickness and is followed by 15 m of halite (Geluk, 2007).

In summary, the northeast Netherlands gas fields are the product of a suitable hydrocarbon system in combination of a prolific coal source, an extensive dry land reservoir, and an excellent evaporate seal. This is supported by the early formation of the structures which facilitates hydrocarbon trapping and long-term retention (Grotsch et al., 2011).
Figure 2.1 Stratigraphic column of a gas field in northeast of the Netherlands. The Zechstein group from bottom to top is Coppershale, Z1 carbonate member, Z1 anhydrite member, Z2 carbonate member and Z2 basal anhydrite member.

2.2.2 Sampling strategy
The studied core samples originate from reservoir and caprocks of 3 different gas fields in northeast Netherlands. Depth range is 2.8 – 3.2 km and porosity varies between 1 and 26% while permeability ranges between 0.008 mD and 6 D. (Figure 2.2).
In Figure 2.2, two sets of porosity-permeability relationships can be distinguished. This is the result of facies-controlled diagenesis of the Rotliegend sandstones in the northeast Netherlands. Semi-arid to arid depositional environments lead to reddening of the sediments with grain-coating metal (iron, aluminum, manganese and titanium) oxides and illitic, smectitic, and chloritic coating. In addition, quartz and sodium feldspar overgrowths are observed (Grotsch et al., 2011). In the very early diagenetic history, the precipitation of pore blocking minerals (calcite, dolomite, anhydrite and kaolinite) has been reported to initiate at shallow burial depths (Grotsch et al., 2011). Generally, the sediments which were deposited in drier environment have lower amounts of early cement. A south-to-north diagenetic trend can be observed in the gas fields in the north Netherlands. In the southern part cementation is less in fluvial and aeolian settings (Field
B in Figure 2.2). However, in the northern part more cementation took place in the playamargin setting (field A in Figure 2.2) (Grotsch et al., 2011).

The cap-rock samples were selected from carbonate and anhydrite layers of the Zechstein seal (Z1-Z2 parts of Zechsein). The average mineralogy of reservoir and caprock samples is presented in Table 2.1.

![Figure 2.2](image.png)

**Figure 2.2** Porosity and permeability data for two gas fields in northeast Netherlands. Samples with higher porosity and permeability are selected for the experiments.

**Table 2.1** Average mineralogy (weight percentage) of Rotliegend reservoir sandstone (8 samples) and Zechstein caprock (5 samples).

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Reservoir samples</th>
<th>Caprock samples</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Anhydrite layer</td>
</tr>
<tr>
<td>Quartz</td>
<td>90%</td>
<td>0%</td>
</tr>
<tr>
<td>Albite</td>
<td>5%</td>
<td>0%</td>
</tr>
<tr>
<td>K-feldspar</td>
<td>2%</td>
<td>0%</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>1.5%</td>
<td>0%</td>
</tr>
<tr>
<td>Dolomite</td>
<td>&lt;1%</td>
<td>12.5%</td>
</tr>
<tr>
<td>Illite</td>
<td>&lt;1%</td>
<td>0%</td>
</tr>
<tr>
<td>Anhydrite</td>
<td>&lt;1%</td>
<td>87.5%</td>
</tr>
<tr>
<td>Halite</td>
<td>&lt;1%</td>
<td>0%</td>
</tr>
<tr>
<td>Calcite</td>
<td>0%</td>
<td>0%</td>
</tr>
</tbody>
</table>

**2.2.3 Experimental setup**

In order to simulate the pressure and temperature conditions present in the depleted gas fields, two types of pressure cells were specifically designed and manufactured for our experiments:
- **Closed cells**: made up of a metal alloy (38-46% Ni, 0-0.025% C, 1.5-3% Cu, balance Fe, 0-1% Mn, 19.5-23.5% Cr, 0-0.5% Si, 2.5-3.5% Mo, 0.6-1.2% Ti) capable of tolerating a maximum temperature of 150°C and a pressure of 350 bars. The capacity of this cell is 100 cc. The inside temperature of the vessels was measured with a “Type K” thermocouple consisting of 90% nickel and 10% chromium (Figure 2.3).

- **View cells**: made up of a metal alloy (less than 0.03 C, 16-18.5% Cr, 10-14% Ni, 2-35% Mo, less than 2% Mo, less than 1% Si, less than 0.045% P and less than 0.03% S) capable of tolerating a maximum pressure of 700 bar and temperature of 190°C. The volume is 63 cc. A view glass (36 mm in diameter) allows direct visual observation of the gas/fluid movements and reactions during the experiment. A camera connected to a computer enables on line recording of the images.

![Overall experimental setup](image)

**Figure 2.3** Overall experimental setup.

### 2.2.4 Analytical techniques and methods

The reservoir and caprock samples were analyzed for mineralogy using Scanning Electron Microscope (SEM) and X-ray diffraction (XRD) both before and after the experiments. SEM was carried out on a Philips XL-30 environmental SEM (ESEM) with Field Emission Gun (FEG). It is equipped with energy dispersive spectroscopy (EDS). Secondary Electron (SE) and Backscattered Electron (BSE) images were taken from the same location on the core samples before and after the experiments. The X-ray diffraction analysis on the rock samples was performed with Bruker D8 advance (40 Kv, 40 mA). Diffractometers were recorded between 5° and 110° 2-Theta with Cuα1=1.54060 Å, Cuα2=1.54439 Å. The detector step size was set to 0.02 with 5 s/step.

In addition, the permeabilities were compared before and after the experiments using the standard core laboratory permeameter (following section).

#### 2.2.4.1 Permeameter

A standard core laboratory Permeameter was used to measure permeability of the samples. The Permeameter uses compressed dry air to flow through the samples at a flow rate regulated by a calibrated orifice. The pressure on the upstream end of a core sample is
registered by one of the following three instruments: a “C” gauge, a mercury monometer and a center water monometer (Figure 2.4). The pressure on the downstream end of a core sample is registered on the orifice water monometer.

Darcy’s equation for compressible fluid was applied to measure the permeability of the samples. (Equation 2.1 and Equation 2.2).

\[
\text{Permeability (mD)} = C \times \frac{\text{Orifice Q value} \times \text{Orifice water}}{200} \times \frac{\text{Sample length}}{\text{Sample area}} \quad \text{Equation 2.1}
\]

\[
C = \frac{\text{Pa} \mu (1000)}{(P_1 - P_2) \frac{(P_1 + P_2)}{2}} \quad \text{Equation 2.2}
\]

where, \( \mu \), \( P_1 - P_2 \) and \( \frac{(P_1 + P_2)}{2} \) are the gas viscosity (centipoises), differential pressure (Psia) and mean pressure (Psia), respectively. \( Q \) is the flow rate. In the permeameter a calibrated orifice forms a back pressure which causes the orifice water level to rise. The number 200 in denominator is a calibration constant.
2.2.5 Experimental procedure and design

The pressure and temperature conditions present in the depleted gas fields were simulated in reaction cells in order to perform batch reaction experiments. The round, disk shaped reservoir and caprock core samples with a diameter of 25 mm and thickness of 8 mm were reacting with brine, with pH of 6.8 and composition derived from formation fluid (Table 2.2), and injected gas (CO$_2$) in the cells at 300 bars and 100° C.
temperature. Furthermore, 2% initial methane was present in the reactors in order to represent depleted gas fields (duration: 30 and 143 days).

**Table 2.2** Brine composition

<table>
<thead>
<tr>
<th>Ions</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>80933</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>22097</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>2343</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>173648</td>
</tr>
<tr>
<td>K⁺</td>
<td>1461</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>203</td>
</tr>
</tbody>
</table>

**2.3 Results and Discussion**

**2.3.1 Reservoir samples**

After injection of CO₂, it partly dissolves in brine and forms carbonic acid which in turn dissociates in brine and releases H⁺ resulting in a pH reduction from 6.8 to 6.1 on average. This is the maximum pH due to the degassing of CO₂ by opening the reactor. The calculated in situ pH at the end of experiment is 4.3 as is obtained by TOUGHREACT modelling software (Bolourinejad et al., 2014).

Following injection of CO₂, several dissolution/precipitation mechanisms have been observed. In the reservoir samples albite, k-feldspar and kaolinite dissolution was observed after 30 days of experiment due to the formation of carbonic acid (Figure 2.5). Furthermore, fresh precipitation of kaolinite was observed in the core samples after CO₂ injection (Figure 2.5b). The kaolinite precipitation is associated with the dissolution of albite (Reaction 2.1) (Bolourinejad et al., 2014).

\[
\begin{align*}
2\text{NaAlSi}_3\text{O}_8 + 3\text{H}_2\text{O} + 2\text{CO}_2 & \leftrightarrow 2\text{Na}^+ + 2\text{HCO}_3^- + \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 4\text{SiO}_2^- \\
\text{Albite} & \quad \text{Kaolinite} \\
\end{align*}
\]

Reaction 2.1

In addition, dawsonite precipitation has been observed in a longer term (143 days) CO₂ experiment (Figure 2.6).
Figure 2.5 SEM images of Rotliegend sandstone before the experiment (a, c, e), after the CO$_2$ experiment (b, d, f). Alb= albite, Kf= K-feldspar and Kao= kaolinite. Dis=dissolution, Prec=precipitation. Circles show points of interests.

Figure 2.6 (a) SEM images of a Rotliegend reservoir sample after 143 days of contact with water and CO$_2$. Circles show dawsonite precipitation. (b) X-ray diffractometer of the same sample, dawsonite peak is annotated.

The dawsonite 20 peak we recorded with our XRD set-up occurs at 15.88 Å. The characteristic value for Na-dawsonite is at 20 of 15.53 Å (Tambach and Hellevang,
2015). It should however be noted that we used intact reservoir samples in our analysis, contrary to powdered rock which is often used in literature. Due to the surface roughness of the sandstone sample we observe a small static shift in the peaks for the various minerals. For reference therefore we checked the peak for quartz (26.64 Å) on 2 samples, resulting in values of 26.82 and 26.94 Å. When applying the same static shift to the dawsonite peak, we concluded that the mineral is more likely to be Na-dawsonite. However, we agree with Tambach and Hellevang (2015) that the possibility of K-dawsonite (15.87 Å) precipitation cannot be excluded and more experimental data, acquired under the same conditions (300 bar, 100 °C, 143 days) are needed to provide more conclusive results (Bolourinejad et al., 2015).

In order to evaluate the magnitude of minerals dissolution/precipitation in the reservoir samples, we compared permeability of the samples before and after the experiments. After 30 days of CO₂, brine and rock interaction, the permeability of the samples increased in all cases (Table 2.3) due to the dominance of mineral dissolution over precipitation. Permeability increased by 10 to 30% except in one case where permeability increased by a factor of 5. This sample had the lowest initial permeability and more cement materials (feldspar, carbonate and anhydrite) compared to other selected reservoir samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Permeability before (mD)</th>
<th>Permeability after (mD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reservoir 1</td>
<td>149±7</td>
<td>791±40</td>
</tr>
<tr>
<td>Reservoir 2</td>
<td>216±11</td>
<td>278±14</td>
</tr>
<tr>
<td>Reservoir 3</td>
<td>1465±73</td>
<td>1638±82</td>
</tr>
<tr>
<td>Reservoir 4</td>
<td>3407±170</td>
<td>4177±209</td>
</tr>
<tr>
<td>Reservoir 5</td>
<td>832±41</td>
<td>910±45</td>
</tr>
</tbody>
</table>

Table 2.3 Comparison of permeability of Rotliegend reservoir samples before and after the CO₂ experiments. Error for permeability measurement is 5%.

2.3.2 Caprock samples

In the caprock samples anhydrite, dolomite and calcite dissolution could be observed (Figure 2.7) due to the formation of carbonic acid.
In the caprock samples, the permeability increased by a factor of 3 to 10 due to the mineral dissolution (Table 2.4). This may look severe, but it should be noted that the initial permeabilities were all in the micro Darcy range. Furthermore the effect of CO$_2$ injection will only occur at the interface between caprock and reservoir. Progression of CO$_2$ through fractures in the caprock may however result in a stronger effect on the properties of the bulk cap rock.

Table 2.4 Comparison of permeability of Zechstein caprock samples before and after the CO$_2$ experiments

<table>
<thead>
<tr>
<th>Sample</th>
<th>Permeability before (mD)</th>
<th>Permeability after (mD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Caprock 1</td>
<td>0.040±0.004</td>
<td>0.13±0.01</td>
</tr>
<tr>
<td>Caprock 2</td>
<td>0.017±0.001</td>
<td>0.084±0.008</td>
</tr>
<tr>
<td>Caprock 3</td>
<td>0.0060±0.0012</td>
<td>0.028±0.002</td>
</tr>
<tr>
<td>Caprock 4</td>
<td>0.0080±0.0016</td>
<td>0.080±0.008</td>
</tr>
</tbody>
</table>

2.4 Conclusion

In our study, we experimentally investigated the effects of injected CO$_2$ on reservoir and caprock. The experimental set up was designed to be able to simulate the reservoir conditions (pressure 300 bar and temperature 100°C) of a number of Rotliegend gas fields in northeast Netherlands.

The permeability of reservoir samples increased after CO$_2$ injection by 10-30%. In the caprock samples, permeability increased by a factor of 3 – 10.
Following CO₂ injection, dissolution of feldspar and kaolinite occurred due to the pH drop. In addition, secondary kaolinite precipitated in reservoir samples. Furthermore, dawsonite precipitation was observed after a medium term (143 days) experiment with CO₂ injection in reservoir samples. In the caprock samples dissolution of anhydrite and dolomite was observed.