Geochemical impacts of CO₂ storage in saline aquifers with various mineralogy – results from laboratory experiments and reactive geochemical modelling

Claus Kjøller, Rikke Weibel, Keith Bateman, Troels Laier, Lars H. Nielsen, Peter Frykman, and Niels Springer

Abstract

Investigations of reservoirs, cap-rocks and traps in the Norwegian-Danish Basin have indicated a large potential for geological storage of CO₂ onshore Denmark. The possible reservoir rocks include a variety of sandstones with different mineralogical composition, ranging from the Bunter Sandstone Formation containing K-feldspar, clay minerals, calcite, and dolomite as primary reactive minerals to the Gassum Formation containing albite, clay minerals, siderite, and ferroan dolomite as the most reactive minerals.

A laboratory and modelling study was carried out to investigate the geochemical response of five potential reservoir rocks to CO₂ storage in order to constrain predictions of mineral-CO₂ reactions prior to geological storage. The study includes hydrogeochemical experiments, petrographical and mineralogical analyses, and reactive geochemical modelling. During up to 13 months of exposure to CO₂ at reservoir conditions (70°C; 20 MPa), the five different rock samples show little mineral reactivity as compared to similar rock samples exposed to N₂ for the same period of time. However, during the period covered by the experiments, dissolution of carbonates present in the host rock is observed both from petrographical analysis and geochemical analysis using speciation calculations. Thus, for the Bunter Sandstone Formation calcite dissolution is apparently taking place in the laboratory experiments while for the Gassum Formation samples ferroan dolomite and siderite dissolution are the dominant mineral dissolution reactions taking place.

As a result of the speciation calculations, a procedure for back calculation of chemical analyses to true experimental conditions is suggested in order to reflect the correct saturation state of the pore water with respect to carbonates, primary silicates and aluminosilicates. It is suggested that performing such back calculations is essential to the understanding of the future evolution of the hydrogeochemistry of aquifers aimed at as CO₂ storage reservoirs.

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Keywords: CO₂; CO₂ storage; laboratory experiments; mineral rock interaction; reactive geochemical modelling

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1. Introduction

Global warming caused by large CO\textsubscript{2} emission to the atmosphere owing to the use of fossil fuels is of increasing concern. Geological storage of CO\textsubscript{2} is one of the potential mitigation measures that receive growing recognition. Investigations of reservoirs, cap-rocks and traps in the Norwegian-Danish Basin have indicated a large storage potential onshore Denmark in the many gentle, four-way dip closures in the Mesozoic succession formed by movements of Zechstein salts. The possible reservoir rocks include a variety of sandstones with different mineralogical composition, ranging from the arkosic to sub-arkosic Bunter Sandstone Formation containing K-feldspar, clay minerals, calcite, and dolomite as primary reactive minerals to the sub-arkosic to sublitharenic Gassum Formation containing albite, clay minerals, siderite, and ferroan dolomite as the most reactive minerals.

A laboratory and modelling study was initiated to investigate the geochemical response of the potential reservoir rocks and cap-rocks to CO\textsubscript{2} storage in order to constrain predictions of mineral-CO\textsubscript{2} reactions prior to geological storage. The study includes reservoir condition (70°C; 20 MPa) hydrogeochemical experiments, petrographical and mineralogical analyses, and reactive geochemical modelling.

This paper reports on some of the first results from the investigations. The focus of the paper will be on the geochemical response of the reservoir sandstones to CO\textsubscript{2} injection, and on the present results from the reactive geochemical modelling. Reactive geochemical modelling as prediction tool is very important in the estimation of how much CO\textsubscript{2} is immobilized as mineral phase and thereby in the evaluation of storage security that must be performed on a site-specific basis as outlined by Frykman et al. [1].

2. Geological setting

The Danish part of the Norwegian-Danish Basin was formed by crustal stretching in Late Carboniferous-Early Permian times between the stable Precambrian Baltic Shield and the Ringkøbing-Fyn High consisting of shallow basement highs (cf. Figure 1).

Figure 1: A. Map of Denmark showing the potential regional CO\textsubscript{2} storage aquifer formations. The location of wells where rock samples were obtained is also shown. B. Stratigraphic scheme showing the Triassic-Jurassic stratigraphic sequence in Denmark. From [8].
The extension phase was followed by regional subsidence governed by thermal cooling during the Mesozoic. Alluvial conglomerates, and sandstones and lacustrine mudstones were deposited in half-grabens during the Rootliegendes followed by accumulation of a thick evaporitic succession dominated by halite in Zechstein (e.g. [2], [3]).

During Mesozoic times, 5-9 km of sandstones, mudstones, evaporites and carbonates were deposited in a wide range of environments [4]-[6]. Reservoirs potentially suitable for CO$_2$ storage in Denmark are found at several stratigraphic levels in this Mesozoic sequence - the most important being the Lower Triassic Bunter Sandstone Formation, the Triassic Skagerrak Formation, the Upper Triassic-lowermost Jurassic Gassum Formation, and the Middle Jurassic Haldager Sand Formation.

The Bunter Sandstone Formation, with up to 4 regional sandstone units of fluvial and aeolian origin, is present onshore Denmark in the North German Basin south of the Ringkøbing-Fyn High and in the southern to central parts of the Danish Basin (cf. Figure 1). Closer toward the northern and eastern margin of the Danish Basin, the Triassic sandstones changes from relatively well-sorted and mineralogical mature greywacke of the Bunter Sandstone Formation into the poorly-moderately sorted, alluvial subarkosic-arkosic sandstones and mudstones of the Skagerrak Formation (cf. Figure 1). The Skagerrak Formation encompasses a thick, heterogeneous basin margin succession formed during the Early-Late Triassic (e.g. [4], [7]).

The Gassum Formation is present in most of the Danish area as a 50-300 m thick succession of fluvial and marine sandstones interbedded with marine, lagoonal and lacustrine mudstones reflecting repeated fluctuations in sea-level during deposition [7]. The formation is overlain by thick, uniform marine mudstones (the Fjerritslev Formation) with large lateral continuity forming a highly competent cap-rock unit. The apparent regional continuity together with a large thickness probably makes the Gassum Formation one of the most promising reservoirs for CO$_2$ storage in the Danish subsurface. The source area of the Gassum sand probably comprised reworked sandstones of the Bunter Formation in the south-eastern part of the basin, whereas more heterogeneous bedrock to the north and east supplied the sand to the northern and central parts of the basin. This has caused a variable mineralogical composition and petrography of the Gassum Formation sandstones across the country.

The Haldager Sand Formation, dominated by marine and fluvial greywacke sandstones is mainly present in the fault-bounded Sorgenfrei-Tornquist Zone (cf. Figure 1) where it locally attain up to 200 m in thickness; outside this zone it wedges out rapidly [7].

3. Methodology

The methodology applied combines laboratory experiments with petrographical studies and reactive geochemical modelling. The petrographical study is presented elsewhere [8], while this paper describes the present results of the geochemical modelling.

3.1. Rock samples

Rock samples from the four potential reservoir formations were obtained from old cores of three different wells (Stenlille 18, Vedsted 1, and Tønder 4) located across Denmark (cf. Figure 1). The wells were originally drilled for hydrocarbon exploration purposes. In all, five sets of rock samples were selected in order to cover the variable mineralogy of the Gassum Formation sandstones across the country.

Prior to the laboratory experiments, information about rock sample mineralogy and petrography was obtained using transmitted light microscopy, X-ray diffraction (XRD), and scanning electron microscopy (SEM) (cf. [8]). A summary of the initial characterization of the rock samples is provided in table 1.
Table 1: Summary of mineral composition (% v/v) of five possible CO₂ storage reservoir sandstones in Denmark. The rock samples were used for reservoir condition experiments in the laboratory. “Other” includes plutonic and sedimentary rock fragments where quantification of the mineralogical composition has not been carried out.

<table>
<thead>
<tr>
<th></th>
<th>Skagerrak (Vedsted 1)</th>
<th>Bunter (Tønder 4)</th>
<th>Gassum (Stenlille 18)</th>
<th>Gassum (Vedsted 1)</th>
<th>Haldager (Vedsted 1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>72.4</td>
<td>29.8</td>
<td>85.2</td>
<td>61.2</td>
<td>82.8</td>
</tr>
<tr>
<td>K-feldspar</td>
<td>8.4</td>
<td>16.8</td>
<td>0.6</td>
<td>6.8</td>
<td>8.0</td>
</tr>
<tr>
<td>Plagioclase</td>
<td>5.6</td>
<td>6.6</td>
<td>0.8</td>
<td>9.6</td>
<td>0.6</td>
</tr>
<tr>
<td>Mica</td>
<td>0.4</td>
<td>5.4</td>
<td>0.0</td>
<td>1.4</td>
<td>0.6</td>
</tr>
<tr>
<td>Calcite</td>
<td>0.0</td>
<td>1.2</td>
<td>0.6</td>
<td>1.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Dolomite</td>
<td>3.2</td>
<td>0.0</td>
<td>0.0</td>
<td>2.4</td>
<td>0.0</td>
</tr>
<tr>
<td>Siderite</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.4</td>
<td>0.0</td>
</tr>
<tr>
<td>Illite/chlorite</td>
<td>1.8</td>
<td>3.6</td>
<td>0.0</td>
<td>6.0</td>
<td>0.4</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>6.0</td>
<td>0.4</td>
<td>0.6</td>
<td>4.0</td>
<td>0.6</td>
</tr>
<tr>
<td>Fe-oxides</td>
<td>0.0</td>
<td>9.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Other</td>
<td>2.2</td>
<td>27.2</td>
<td>12.2</td>
<td>7.2</td>
<td>7.0</td>
</tr>
</tbody>
</table>

3.2. Pore water chemistry

In order to obtain experimental conditions that resemble the conditions of the reservoirs as much as possible, the chemical composition of the pore water was estimated for each of the five sets of reservoir rock samples that were used in the experiments [9]. In general, pore water chemical data were obtained from the nearest possible well with chemical information from well tests. The exception is the data on formation water chemistry concerning the Bunter Sandstone Formation of the Tønder 4 well. These data were obtained from waters collected in the Tønder 4 well close to the actual position of the core samples selected for the laboratory experiments.

Based on the pore water chemistry suggested by Laier [9], synthetic brines were produced for each set of reservoir rocks to be tested in the experimental set-up. The chemical composition of each synthetic brine (cf. Table 2) vary slightly from the composition suggested by Laier [9] due to the availability of commercial soluble salts.

Table 2: Chemical composition (mmol/L) of synthetic pore water used for batch experiments with rock samples representing Danish saline aquifers relevant to CO₂ storage (chemical composition modified slightly from [9]).

<table>
<thead>
<tr>
<th></th>
<th>Skagerrak (Vedsted 1)</th>
<th>Bunter (Tønder 4)</th>
<th>Gassum (Stenlille 18)</th>
<th>Gassum (Vedsted 1)</th>
<th>Haldager (Vedsted 1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.59</td>
<td>6.19</td>
<td>6.21</td>
<td>6.59</td>
<td>6.44</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>3872</td>
<td>4356</td>
<td>2842</td>
<td>3872</td>
<td>2547</td>
</tr>
<tr>
<td>Br⁻</td>
<td>11</td>
<td>16</td>
<td>4.5</td>
<td>11</td>
<td>3.4</td>
</tr>
<tr>
<td>Na</td>
<td>2262</td>
<td>4376</td>
<td>2227</td>
<td>2262</td>
<td>2090</td>
</tr>
<tr>
<td>Ca</td>
<td>424</td>
<td>706</td>
<td>249</td>
<td>424</td>
<td>159</td>
</tr>
<tr>
<td>Mg</td>
<td>101</td>
<td>63</td>
<td>55.8</td>
<td>101</td>
<td>52</td>
</tr>
<tr>
<td>K</td>
<td>37</td>
<td>38</td>
<td>25.0</td>
<td>37</td>
<td>5.8</td>
</tr>
<tr>
<td>Fe</td>
<td>0.39</td>
<td>0.04</td>
<td>0.85</td>
<td>0.39</td>
<td>0.6</td>
</tr>
<tr>
<td>Sr</td>
<td>6.5</td>
<td>0.01</td>
<td>6.4</td>
<td>6.5</td>
<td>3.7</td>
</tr>
</tbody>
</table>

3.3. Experimental procedure

The laboratory experiments comprised batch experiments in which the rock samples were reacted with the synthetic reservoir brines at reservoir conditions (70°C and 20 MPa) for a period of up to 13 months. The batch experiments were carried out in parallel, with either CO₂ or N₂ as the pressuring gas. The N₂-pressure experiments were performed in order to correct for fluid-rock interactions not related to the elevated concentrations...
of CO₂. Fluid samples were taken after 1, 2, 3, 7, 8, 10, and 13 months of reaction while rock samples are available after 7 months of reaction and at the end of the experiment.

The fluid composition was analysed for major and some minor cations (Si, Al, Fe, Sr, Ba, Co, Ni, Cu, Zn, Cr, Mo, Cd, P, Pb, V, Li, B, As, Se and total S) using inductively coupled plasma - optical emission spectroscopy (ICP-OES), and for major and some minor anions (F⁻, Br⁻, Cl⁻, SO₄²⁻, NO₃⁻, HPO₄²⁻) using ion chromatography (IC). Dilution of samples was carried out gravimetrically before analysis. Analysis of HCO₃⁻ was performed by titration against sulphuric acid, and pH was measured on cooled, depressurised samples.

3.4. Modelling

Reactive geochemical modelling was carried out to provide a supplementary interpretation tool to the petrographical analysis of the rock samples from the experiments. For this purpose speciation calculations were carried out using the geochemical code PHREEQC, which was also used to carry out reactive geochemical modelling to back calculate the measured fluid composition at laboratory conditions to “true” fluid composition at the experimental conditions (cf. section 4).

4. Results and discussion

4.1. Development of fluid chemistry in batch experiments

Comparing the results from the N₂ and CO₂ pressurised experiments, an almost identical evolution of fluid chemical composition is observed (cf. figure 2). Thus, independently on the specific reservoir, during the first month of experiments an increase in the aqueous concentration of nearly all solutes takes place. This initial period probably reflects the fact that even though the initial chemical composition of the synthetic brine was estimated from existing chemical analyses, it has not been possible to reconstruct the initial chemical compositions of the reservoir pore waters completely. Therefore, during the first month an “initialisation” of the experimental system takes place, illustrating that readily reactive minerals are present in the rock samples independently on the exposure to CO₂.

Figure 2: Evolution in chemical composition of selected parameters in the synthetic brine used for laboratory experiments with Danish reservoir rocks at 70°C and 20 MPa. Postfix “CO₂” refers to samples pressurised with CO₂ and postfix “N₂” refers to samples pressurised with N₂. Note that the Ca-concentration shown for the Bunter sandstone formation is 10x the measured Ca-concentration.

Judging from the petrographical analysis [8], the minerals being most reactive to CO₂ in the experiments are the carbonate minerals present in the reservoir rock. This corresponds well with the observed evolution in water
chemistry of the experiments. Thus, the increase in the aqueous Ca concentration of the CO₂ exposed Bunter Sandstone sample relative to the aqueous Ca concentration of the N₂ pressurised Bunter Sandstone sample is in agreement with the presence of calcite dissolution patterns in the CO₂ pressurised Bunter Sandstone sample as observed by Weibel et al. [8]. Likewise, dissolution of ferroan dolomite in the Gassum Formation sample pressurised by CO₂ has been observed [8] which corresponds well with the increased aqueous concentration of Fe and Mn for this sample (cf. Figure 2).

In the period from 3 months to 13 months of reaction time, the general pattern is a relatively constant chemical composition of the fluids showing minor variations that are typically within the uncertainty of the analysis. The exception is the drop in the Fe concentration between 7 and 9 months of reaction time of the Bunter Sandstone sample exposed to CO₂. At present, the reason for this sudden decrease in concentration is not fully understood.

The overall evolution of the chemical composition of the pore waters is in good agreement with findings from other similar laboratory studies. Often, fast dissolution of highly reactive carbonate minerals can be observed in the initial period covered by such experiments, while dissolution of other more slowly reacting minerals such as silicates and aluminosilicates is more difficult to detect (e.g. [10]). In the present study, this is further hampered by the low concentrations of Al and Si being below the detection limit.

4.2. Estimating the water-rock interactions using speciation calculations

The possible dissolution and precipitation of minerals may be further evaluated by calculation of mineral saturation indices. As mentioned, Si and Al concentrations were generally below the detection limit. Hence, in order to evaluate saturation states of the pore water with respect to silicates and aluminosilicates, the concentration of Si and Al was estimated. The Si concentration was estimated by assuming equilibrium with chalcedony in accordance with findings from other studies (e.g. [10]). The Al concentration was estimated assuming equilibrium with kaolinite, as kaolinite is the most abundant clay mineral in most of the rock samples investigated – the Bunter Sandstone sample being the exception though kaolinite is still present in this rock sample (cf. table 1).

![Figure 3: Evolution in saturation index of the porewater in the batch experiments with rock samples from Danish reservoirs relevant to CCS. Calculated on the basis of measured pore water chemistry, assuming chalcedony and kaolinite equilibrium (see text for further details).](image)

As shown in figure 3, there are large differences in the saturation indices calculated for the N₂ and CO₂ pressurised samples, respectively. Calcite and dolomite of the Gassum and Bunter samples show distinct super-
saturation in the CO₂ pressurised samples, suggesting that only precipitation can take place in these samples, while in the corresponding N₂ pressurised samples, the calculated saturation indices suggest equilibrium with calcite and dolomite after 3 months of reaction.

The super-saturation calculated for the CO₂ pressurised samples does not correspond well with the observations from the petrographical analyses that dissolution of carbonate minerals take place in these samples. This is because the saturation indices shown in figure 3 are calculated on the basis of the measured fluid chemical composition at laboratory conditions, i.e. on the basis of pH and HCO₃⁻ measurements of depressurised and cooled samples. Thus, in order to reflect the true saturation state of the samples, the measured chemical composition of the pore water has to be corrected by back calculation to experimental conditions.

During depressurisation and cooling of the samples, degassing of CO₂ from the samples is inevitable, thereby causing an increase in the pH and possibly precipitation and super-saturation with respect to carbonate minerals as exemplified for calcite in the following reaction which will be driven towards the left at degassing of CO₂:

\[ \text{CO}_2(aq) + \text{CaCO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{Ca}^{2+} + 2\text{HCO}_3^- \]

That degassing of CO₂ has taken place during analysis of the samples can also be seen from the calculated CO₂ partial pressure (log(pCO₂); figure 3) which is far below the fugacity of CO₂ in the experiments of approximately 9.8 MPa (corresponding to log(pCO₂) = 1.99).

Back calculation of the fluid composition to experimental conditions was carried out by equilibrating the measured chemical composition of the fluids with a CO₂ partial pressure of 9.8 MPa in addition to the equilibration with chalcedony and kaolinite. The corrected saturation indices and pH values are shown in figure 4 together with the calculated saturation indices and measured pH of the N₂ pressurised samples.

![Figure 4: Evolution in saturation index of the porewater in the batch experiments with rock samples from Danish reservoirs relevant to CCS. CO₂ related data are calculated on the basis of measured main porewater chemistry, assuming a CO₂ partial pressure of 9.8 MPa, and chalcedony and kaolinite equilibrium. N₂ related data are calculated on the basis of measured main porewater chemistry (See text for further details).](image-url)

The back calculated dataset corresponds much better with the remaining observations of the study. Thus, the slight sub-saturation with respect to calcite and dolomite shown in figure 4 for the CO₂ pressurised samples of the
Bunter Sandstone Formation corresponds well with the increased Ca concentrations and the visible dissolution of calcite in these samples. In addition, the identical saturation indices in N₂ and CO₂ pressurised samples of the Haldager Sand experiment corresponds well with the almost identical evolution in the pore water chemical composition of N₂ and CO₂ pressurised samples for this reservoir rock (cf. figure 2).

The results presented above are in agreement with the findings of Newell et al. [11] who state that an accurate determination of the variables related to the carbonate aqueous system is of great importance for the evaluation of possible dissolution/precipitation reactions in reservoirs exposed to CO₂. In carbonate containing rocks, the pH of the pore water is most often controlled by the CO₂ partial pressure (or rather fugacity) and equilibrium with carbonate minerals. Hence, an accurate determination of the variables in the carbonate system is essential to the understanding and evaluation of possible future chemical reactions in such reservoirs – also when evaluating mineral/water reactions of minerals other than carbonate minerals.

Thus, back calculation to experimental conditions has in the present study resulted in a distinct sub-saturation with respect silicates and aluminosilicates in the CO₂ pressurised samples, suggesting the possible dissolution of these minerals over longer time scales. For comparison, the N₂ pressurised samples generally show super saturation with respect to primary silicates such as albite and K-feldspar and equilibrium with respect to illite.

5. Conclusions

During up to 13 months of exposure to CO₂ at reservoir conditions (70°C; 20 MPa), five different rock samples representing possible reservoir rocks for CO₂ storage in Denmark show little mineral reactivity as compared to similar rock samples exposed to N₂. However, during the period covered by the experiments, dissolution of carbonates present in the host rock is observed. As a result of geochemical speciation calculations, a procedure for back calculation of chemical analyses to true experimental conditions is suggested in order to reflect the correct saturation state of the pore water with respect to carbonates, primary silicates and aluminosilicates.

6. Acknowledgement

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7. References