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# Geochemical interactions between $CO_2$ and minerals within the Utsira caprock: A 5-year experimental study

K. Bateman*, C.A. Rochelle, G. Purser, S.J. Kemp and D. Wagner

*British Geological Survey, Keyworth, Nottingham NG12 5GG, UK*

## Abstract

Efficient storage of carbon dioxide ($CO_2$) in deep reservoirs will be dependent on the integrity of the natural seals above the $CO_2$. This experimental study focuses on geochemical reactions between $CO_2$, synthetic porewaters and Utsira caprock the sealing lithology of the Sleipner storage site. It provides data for experiments lasting 5 years, and extends the timescale of previously conducted experiments that ran for up to 14 months duration. In-situ conditions were replicated in the experimental 30°C, at 8 MPa [80 bar]. New experimental data, confirm the previous 14-month data, with experiments pressurised with $N_2$ showing little or no reaction. Reactions in experiments involving $CO_2$ were dominated by initial carbonate mineral dissolution. No definitive evidence of other changes in mineralogy (including clay mineralogy), could be identified in either the $CO_2$ or $N_2$ experiments. In terms of the overall impact of storing $CO_2$ at Sleipner, the results from these experiments show no indication of major deleterious, geochemical reaction processes occurring with the caprock.

*Keywords:* geochemistry; experimental; caprock; Sleipner; Utsira

## 1. Introduction

During the underground storage of carbon dioxide ($CO_2$) in deep reservoirs, its containment of $CO_2$ will be crucially dependent on the integrity of seals above the $CO_2$. These seals could be natural (e.g. a clay-rich caprock) or man-made (e.g. the engineered seals around a borehole). It is important therefore, to assess how the $CO_2$might impact these seals, as this could ultimately control the longevity of $CO_2$ storage. This experimental study focuses on geochemical reactions between $CO_2$, synthetic porewaters and disaggregated Utsira caprock. It provides data for experiments lasting 5 years, and extends the timescale of previously conducted experiments that ran for up to 14 months duration [1].

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* Corresponding author. Tel.: +44-115-9363262
*E-mail address:* kba@bgs.ac.uk.

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## 2. Description of the experiments

The main approach used during this study was of low maintenance 'batch' experiments of variable durations up to 5 years. This type of equipment is relatively simple and generally free from day-to-day maintenance. Consequently, it is well suited for running over prolonged periods. A schematic diagram of a typical 'batch' reaction vessel is shown in Figure 1. These had a useable internal volume in the order of 100 ml. Water saturated with $CO_2$ is relatively reactive, and this is especially so for saline fluids. For this reason PTFE liners were used in all vessels.

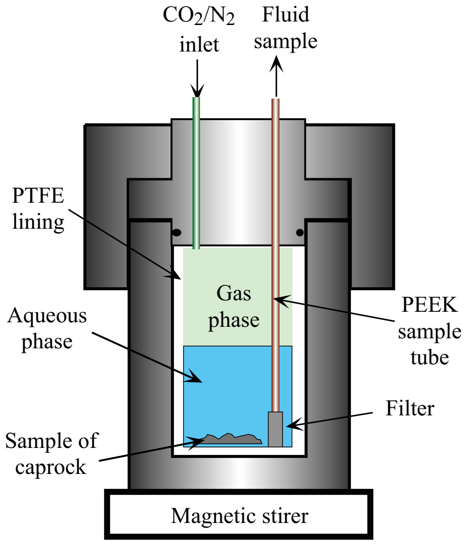

Fig. 1. Schematic diagram showing the typical layout for a series of $CO_2$ batch experiments

In the absence of actual caprock porewater chemistry data, a synthetic porewater having a similar composition to that used in experiments with Utsira Sand [2] was used. Details of the fluid composition used are given in [3] and in Table 1. Details of mineralogical analysis of the samples of Utsira cap rock (depth 910.20-910.40 m) used can be found in [4].

Approximately 8 g of disaggregated Utsira caprock was added to each experiment together with approximately 80 g of synthetic Utsira porewater (i.e. a 10:1 fluid:rock mass ratio). A small PTFE-covered stirrer bead was placed in the base of each experiment. The vessels were then placed into an LMS cooled incubator (accurate to better than ± 0.5°C) and connected to the appropriate pressure lines. The experimental conditions were representative of the in-situ conditions (i.e. 30°C and 80 bar [8 MPa]).

Both $CO_2$ and $N_2$ pressurised experiments were conducted, the later to provide a 'non reacting' reference point. The $CO_2$ was supplied to the reactors from a syringe pump running in 'constant pressure' mode. $N_2$ gas was supplied via a gas bottle using a single-stage regulator. Good mixing between gas and porewater (and ground caprock) was achieved via periodic agitation using the stirrer bead in each vessel.

Table 1 Components used to make 8 litres of synthetic Utsira porewater.

| Component | Weight (g) |
|---|---|
| NaCl | 206.9 |
| KCl | 3.173 |
| $CaCl_2.2H_2O$ | 12.50 |
| $MgCl_2.6H_2O$ | 42.15 |
| $SrCl_2.6H_2O$ | 0.243 |
| $BaCl_2.2H_2O$ | 0.007 |
| $FeCl3.6H_2O$ | 0.077 |
| $NaHCO_3$ | 1.725 |

The Utsira caprock experiments ran for up to 5 years, with reactant fluids sampled relatively regularly in the first 13-14 months, and then once at 5 years.

Sampling of the aqueous phase was carried out via a PEEK dip tube fitted with a filter at the end, which ran to the base of the PTFE liner. Fluid samples were extracted whilst the experiment was still under run conditions. Sub samples of the sampled fluids were prepared for determination of pH, carbonate/bicarbonate and for major and trace cations/anions. Samples of the unreacted solid and the reacted materials, recovered from the vessels at the end of the experiments, were characterised using X-ray diffraction (XRD) techniques.

## 3. Changes in fluid chemistry

A summary of the fluid chemical data is given in Table 2. A more detailed description of the fluid chemistry can be found in [5].

### *3.1. Changes dominated by $CO_2$-porewater reactions*

$CO_2$ would have reacted with the synthetic porewater relatively rapidly and initiated changes to solution pH and the dissolved $HCO_3^-$ concentration. The majority of these changes are likely to have occurred prior to reaction with the solids in the experiments, though subsequent fluid-rock reaction may modify the changes as the experiments proceed.

The observed trends in pH values (as measured on depressurised and degassed samples, at room temperature) are as expected (Table 2). The $N_2$ experiments stay at a similar pH value to the starting value (about 7.8), but show some scatter. The $CO_2$ experiments show a consistent decrease in pH from the starting solution and the $N_2$ experiments - reflecting acidification of the porewater by addition of $CO_2$. Shorter-term experiments attained a stable pH value of $\approx$ 6.4, but the 5-year sample gave a pH value of 6.9. The reason for this apparent small increase is not clear; it may suggest a change in pH-buffering reactions over time.

The observed trends in dissolved bicarbonate concentrations (Figure 2) are also as expected. The $N_2$ experiments maintain relatively low concentrations ($<300$ mg $l^{-1}$) throughout the experiments. This indicates relatively little reaction of the solution with the sample of Utsira caprock, and apparent early attainment of equilibration of the solution with carbonate minerals in the caprock.

Table 2 Fluid chemical data

| Time (h) | pH | Ca | Mg | Na | K | $HCO_3^-$ | Cl | $SO_4^-$ | $NO_3^-$ | $SiO_2$ | Ba | Sr | Mn | Fe | Al |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Starting Synthetic Utsira porewater | | | | | | | | | | | | | | | |
| 0 | 7.82 | 384 | 553 | 9923 | 230 | 150 | 19530 | <12.5 | <5.0 | <3.21 | 0.43 | 8.84 | <0.04 | 0.56 | <0.20 |
| $CO_2$ pressurised experiments | | | | | | | | | | | | | | | |
| 1795 | 6.27 | 1372 | 692 | 11534 | 313 | 3284 | 20616 | 7.89 | 25.2 | 25.8 | 1.08 | 12.6 | 8.09 | 11.4 | 0.38 |
| 3523 | 6.40 | 1377 | 680 | 11291 | 311 | 3241 | 20027 | 10.7 | 2.39 | 24.5 | 1.06 | 12.4 | 8.36 | 10.1 | 0.39 |
| 4702 | 6.33 | 1401 | 684 | 10772 | 281 | 3595 | 20667 | 13.3 | 7.25 | 26.6 | 1.21 | 12.5 | 8.90 | 10.9 | 0.51 |
| 6695 | 6.29 | 1443 | 702 | 10921 | 284 | 3214 | 20827 | 17.9 | 4.28 | 28.2 | 1.10 | 12.7 | 10.5 | 4.72 | 0.25 |
| 9383 | 6.46 | 1294 | 678 | 11045 | 273 | 3333 | 19080 | 72.8 | 4.27 | 20.8 | 0.87 | 12.1 | 9.10 | 0.67 | 0.35 |
| 43531 | 6.87 | 1438 | 758 | 10397 | 280 | 3676 | 16966 | <99.3 | 307 | <32.3 | 1.15 | 13.1 | 10.0 | 51.1 | <2.01 |
| $N_2$ pressurised experiments | | | | | | | | | | | | | | | |
| 1795 | 7.55 | 455 | 639 | 11368 | 297 | 238 | 20266 | 6.26 | 1.98 | 11.0 | 4.35 | 0.53 | 9.82 | 2.10 | 0.91 |
| 3523 | 7.69 | 445 | 626 | 11017 | 288 | 241 | 19980 | 11.0 | 2.40 | 13.2 | 3.31 | 0.48 | 9.53 | 2.07 | 0.68 |
| 4702 | 7.01 | 493 | 681 | 11507 | 293 | 259 | 20596 | 14.1 | 7.88 | 15.6 | 4.43 | 0.49 | 10.5 | 2.16 | 0.79 |
| 6695 | 7.55 | 443 | 628 | 10719 | 267 | 216 | 20370 | 15.5 | 2.80 | 15.5 | 4.65 | 0.49 | 9.60 | 1.91 | 0.70 |
| 9383 | 7.65 | 399 | 576 | 10154 | 247 | 217 | 17912 | 20.0 | 4.04 | 18.0 | 3.73 | 0.41 | 8.92 | 1.66 | 0.61 |
| 43531 | 8.25 | 450 | 682 | 10298 | 285 | 184 | 18404 | 112 | <39.7 | <50.3 | <32.3 | 0.46 | 8.80 | 1.52 | <2.00 |

All concentrations in mg $l^{-1}$

In the presence of $CO_2$ there is a marked, and rapid increase in bicarbonate concentrations. This will have come from two sources:

- $CO_2$ dissolving into the water directly.
- Dissolution of carbonates because of the slightly acid conditions caused by the presence of the $CO_2$.

Within a few weeks, the bicarbonate concentrations had reached ≈ 3200 mg $l^{-1}$. The rapid attainment of such a high concentration is consistent with the two processes outlined above. Thereafter the concentration slowly increased to ≈ 3500 mg $l^{-1}$ over the 5 years. The slow increase from 3200-3500 mg $l^{-1}$ may reflect:

- Continued (though slower) dissolution of carbonates minerals because of the slightly acid conditions caused by the presence of the $CO_2$.
- Slow reaction of aluminosilicate minerals, which effectively consumes acidity and dissolved $CO_2$, and in the process generates bicarbonate ions.

The near steady concentrations of bicarbonate are consistent with either equilibrium with the carbonate phases or the total consumption of these carbonate phases.

### *3.2. Changes dominated by dissolution of carbonates*

When $CO_2$ was introduced into the experiments, it will have rapidly reacted with, and acidified the synthetic porewater. This will have initiated dissolution of the carbonate minerals present – mainly shell fragments in these experiments. Such dissolution is indicated by changes in Ca concentrations (Figure 2), but more minor components within the carbonates also show similar behaviour (e.g. Mg, Sr, Ba and Mn), and bicarbonate concentrations also increase.

Ca concentrations, in the $CO_2$ experiments, show a rapid increase within the first few weeks to about 1400 mg $l^{-1}$. This reflects acidification of the synthetic porewater with the $CO_2$, and subsequent carbonate mineral dissolution. Thereafter, Ca concentrations stay effectively constant. That Ca concentrations stayed constant for up to 5 years suggests either that the fluid was at equilibrium with the small amounts of remaining $CaCO_3$, or that all the $CaCO_3$ had dissolved.

In the $N_2$ experiments, the Ca concentrations remain similar to the starting value (about 400 mg $l^{-1}$), even after 5 years. Given the non-reacting nature of these experiments, these Ca concentrations are thought to reflect saturation with respect to the $CaCO_3$ in the shell fragments.

The observed trends in Mg, Sr, Ba, Mn and Fe (Table 2) are consistent with carbonate mineral dissolution if it is assumed that these divalent metals are present in the carbonates (though at lower abundances than Ca). In general, they show attainment of approximately steady-state conditions in 1000-10000 hours, with higher concentrations in the $CO_2$ experiments. Concentrations in the $N_2$ experiments remain generally similar to those of the synthetic Utsira porewater starting fluid.

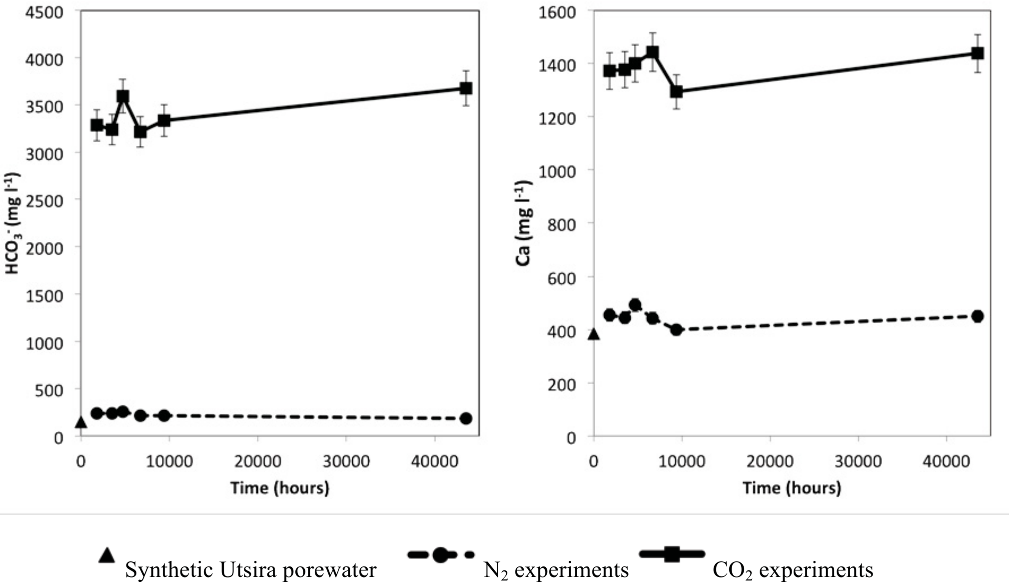

Fig. 2. $HCO_3^-$ and Ca concentrations with time

## 4. Changes in mineralogy

The results of quantitative whole-rock XRD analysis of the Utsira caprock samples are summarised in (Table 3). Powder XRD analysis of residues from the $CO_2$ experiments indicates a decrease in calcite content in the reaction residue (<0.5%), compared to the starting material (≈ 2.4%). No mineralogical change could be detected in the residue from the $N_2$ experiments. Most of the calcite is present as shell debris in the Utsira caprock, and the observed reduction in calcite content is consistent with the dissolution of carbonate minerals postulated from consideration of changes in fluid chemistry.

No definitive evidence of other changes in mineralogy, including clay mineralogy (Table 3) could be identified in either the $CO_2$ or the $N_2$ experiments. Although some previous modelling studies of $CO_2$-water-rock reactions at Sleipner have predicted dawsonite formation (Johnson *et al.*, 2004), none was detected as a reaction product in these experiments.

Table 3 Summary of quantative whole-rock X-ray diffraction analysis

| Sample | Silicates | | | | Carbonates | | Chloride / Sulphide | | Phyllosilicates / Clay minerals | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | quartz | albite | K-feldspar | amphibole | calcite | dolomite | halite | pyrite | 'mica' | kaolinite | chlorite |
| Utsira caprock | 34.6 | 10.2 | 9.1 | <0.5 | 2.4 | 0.8 | 1.0 | <0.5 | 32.3 | 7.4 | 2.0 |
| Reacted solids from $N_2$ experiments | 36.8 | 11.2 | 8.6 | <0.5 | 2.4 | 0.8 | nd | <0.5 | 31.5 | 7.1 | 1.4 |
| Reacted solids from $CO_2$ experiments | 37.1 | 11.3 | 8.1 | <0.5 | <0.5 | 0.9 | nd | <0.5 | 34.4 | 6.9 | 1.0 |

## 5. Summary of reactions and implications for $CO_2$ storage at Sleipner

Very similar fluid compositions were found in the 5-year long experiments as in the 1-14 month experiments. This suggests that reactions in the systems studied were relatively rapid, and largely completed in just a few weeks. Though the $HCO_3^-$ data possibly hint at some slower reactions there was no evidence for significant reactions beyond this timescale. However, it should be stressed that the contents of these experiments were very well mixed – to achieve maximum reaction on a short timescale. Conversely, slow transport processes in intact caprock may allow for the formation of reaction fronts - which may exist for some considerable time as $CO_2$ slowly migrates into the caprock.

In general, the $N_2$ experiments showed little reaction, and the final fluid chemistry was very similar to that of the starting fluid, even after 5 years reaction under simulated in-situ pressures and temperatures. This indicates that the composition of the starting synthetic porewater was broadly in equilibrium with minerals in the Utsira caprock. As this porewater composition was based upon analyses of fluids extracted from the Utsira Sand, it also shows that that the porewater in the Utsira caprock is broadly similar to that in the Utsira Sand.

The main solid phase reaction observed upon addition of $CO_2$ was carbonate mineral dissolution:

$$CaCO_3 + CO_{2(aq)} + H_2O \Leftrightarrow Ca^{2+} + 2\ HCO_3^-$$

This gave rise to pronounced increases in concentrations of dissolved Ca, Mg, Sr, Ba, Fe and Mn (and also bicarbonate). The amount of carbonate mineral dissolution can be quantified by considering both fluid chemical and mineralogical data (the mudstone sample originally contained ≈ 2.4 wt% calcite). Changes in Ca concentration in solution (from ≈ 400 mg $l^{-1}$ to ≈ 1400 mg $l^{-1}$) suggest that all of the calcite in the sample dissolved when equilibrated with $CO_2$ under *in-situ* pressures and temperatures. For the caprock, XRD data show that calcite contents in the unreacted and reacted mudstone went from ≈ 2.4% to <0.5%. This appears to indicate that addition of $CO_2$ caused at least 80% of the calcite in the mudstone sample to dissolve. The amount of dissolution observed in the experiments reported here is greater to that seen in shorter duration, but otherwise comparable experiments reacting samples of Utsira sand [2]. In those experiments using a fluid of similar composition (but at 37°C and 10 MPa [100 bar]), fluid chemical changes indicated that approximately 70% of the original calcite dissolved, and XRD data indicated that at least 85% had dissolved.

It is noted that a previous modelling study [6] of $CO_2$-water-caprock reactions at Sleipner predicted the precipitation of Ca/Mg/Fe carbonates, and not their dissolution as we have found. The reason for not predicting calcite dissolution appears to be that it was omitted from the modelled starting mineral assemblage representing the Utsira mudstone (see Table 2 in [6]). Although that modelling study predicted dawsonite formation, none was detected as a reaction product in these experiments.

Fluid chemical data do indicate that a small amount of silicate mineral dissolution occurred when $CO_2$ was added. It is possible that this could be due to reactions involving clay minerals, feldspars or a silica phase, but it was not possible to determine the nature of the reacting phase.

The behaviour of trace metal concentrations may reflect carbonate dissolution as described above, but pyrite dissolution is another possibility. They also appear consistent with desorption reactions caused by the reduction in pH due to addition of $CO_2$. Further work would be necessary to identify which of these possible processes was operating in these experiments.

## 6. Conclusions

An experimental study was undertaken to identify the geochemical impact of $CO_2$ on minerals within the caprock of the $CO_2$ store at Sleipner. This paper presents new data from a pair of 5-year long experiments in the context of data from similar experiments that have been reported previously [1]. The batch experiments utilised Sleipner caprock core material, synthetic formation waters based upon measured compositions of nearby samples, and experimental conditions representative of actual in-situ conditions within the caprock (30°C, 8 MPa [80 bar]). Experiments were pressurised with either $N_2$ or $CO_2$. The former provided a 'non reacting' reference point from which to compare the more reactive $CO_2$ experiments.

Fluid analytical data for the 5-year long experiments closely match data from the previous 14 month-long experiments. That no significant changes in fluid chemistry were found indicates that $CO_2$-water-mineral reactions were essentially complete early on in the experiments. However, it should be noted that the contents of these experiments were very well mixed to maximise the rate of $CO_2$-water-mineral reaction. Conversely, slow transport processes in intact caprock may allow for the formation of reaction fronts - which may exist for some considerable time as $CO_2$ slowly migrates into the caprock.

The new experimental data confirm previous results, with experiments pressurised with N2 showing little or no reaction, indicating that the synthetic Utsira porewater used in the experiments was a reasonable approximation for the actual in-situ porewater composition. Reactions in experiments involving high-pressure $CO_2$ were dominated by carbonate mineral dissolution. Fluid chemical data from the 5-year long tests confirm previous findings that at least 80% of the calcite in the mudstone caprock dissolved, and again provided no evidence for the formation of secondary precipitates such as Ca/Mg/Fe carbonates or dawsonite.

In terms of the overall impact of storing $CO_2$ at Sleipner other than some dissolution of carbonate phases, data from these experiments show no indications of major or deleterious reaction processes occurring.

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