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Weyburn Monitoring and Storage Project
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BRITISH GEOLOGICAL SURVEY

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The Weyburn project: Summary report for Task 3.1. Experimental geochemical studies of CO₂-porewater-rock interaction.

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Foreword

This report is the published product of a study by the British Geological Survey (BGS), and forms part of the international Weyburn Monitoring and Storage Project. This project aims to monitor and predict the behaviour of injected CO₂ in the Midale reservoir at the Weyburn field in southern Saskatchewan, Canada, using methods that include time-lapse geophysics, modelling its subsurface distribution and migration, and simulating likely chemical interactions with the host rock.

This report is a summary of Task 3.1 within the European part of the overall Weyburn project. It aims to provide a brief description of fluid chemical and mineralogical changes occurring in a series of experiments that have been conducted within the Hydrothermal Laboratory of the British Geological Survey. These experiments were undertaken to identify the geochemical changes that would result from the injection of CO₂ into the Midale Formations. The experiments utilised samples of actual Midale rocks recovered from boreholes within the Weyburn field, synthetic formation water based upon measured well fluid compositions, and either CO₂ or N₂ as a pressurising medium.

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The work reported here is only a summary of a much larger study that is described in a series of detailed reports (see references section). The authors wish to thank all those who contributed to the success of this larger study: B.D. Charlton, S. Reeder, R.A. Shaw, H. Taylor, G. Turner, S. Upton, H. Wallis and J. Wragg.

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Summary

This report describes work undertaken at the British Geological Survey (BGS) that forms part of the international Weyburn Monitoring and Storage Project. This project aims to monitor and predict the behaviour of injected CO₂ into the Midale reservoir at the Weyburn oil field in southern Saskatchewan, Canada, using methods that include time-lapse geophysics, modelling its subsurface distribution and migration, and simulating likely chemical interactions with the host rock. This report is a summary of Task 3.1 within the European part of the overall Weyburn project. It aims to provide a brief description of fluid chemical and mineralogical changes occurring in a series of experiments that have been conducted within the Hydrothermal Laboratory of the British Geological Survey. These experiments were undertaken to identify the geochemical changes that would result from the injection of CO₂ into the Midale Formations. The experiments utilised samples of actual Midale rocks recovered from boreholes within the Weyburn field, synthetic formation water based upon measured well fluid compositions, and either CO₂ or N₂ as a pressurising medium.

The experiments summarised in this report used actual samples of Midale core material and synthetic porewaters based upon actual measured well fluid compositions. The pressures and temperatures used within the experiments were representative of *in-situ* conditions (60°C, 150 bar [15 MPa]) and those anticipated near to injection wells (60°C, 250 bar [25 MPa]). As such, the study aims to replicate processes occurring in the deep subsurface at Weyburn as closely as possible, including those conditions that will exist even after oil production and CO₂ injection have ceased.

Upon reaction with CO₂, some dissolution of calcite within the Midale Marly material was identified, though it was relatively minor. By and large, the samples remained relatively unchanged, and significant disruption of the host formation appears not to take place. The Midale Evaporite showed slightly more reaction with CO₂ compared to the Midale Marly, though it was still relatively minor. Some dissolution of dolomite and anhydrite was identified, together with minor aluminosilicate mineral dissolution. There was also a small amount of gypsum precipitation. Significant dissolution of the caprock formation appears not to take place. The Midale Vuggy material showed the greatest potential for reaction with CO₂. Dissolution was mainly of calcite and anhydrite, but there was also a little aluminosilicate mineral dissolution. Precipitation of gypsum was widespread, with crystals at least 2.5 mm long being observed. Samples of borehole cement underwent carbonation of their outer portions upon exposure to CO₂, and this was associated with an apparent reduction in porosity. The monoliths remained intact and appear to have maintained much of their original strength.

1 Introduction

The Weyburn Monitoring and Storage Project is a collaborative investigation, involving geoscientists from North America and Europe (Moberg, 2001). It is studying the geological sequestration of CO₂ during an enhanced oil recovery (EOR) operation at the Weyburn oil field, Canada. By the end of the EOR phase, it is expected that approximately 20 million tonnes of anthropogenic CO₂ will have been stored deep underground. Climate-warming greenhouse gas emissions will have been reduced in an efficient and cost-effective manner.

The Weyburn oilfield is located in southern Saskatchewan, Canada. It was discovered in 1954 and is owned and operated by the EnCana Corporation (formerly operated by PanCanadian). Oil is recovered from the uppermost Midale Beds of the Charles Formation, a succession of upwards shoaling, shallow marine carbonate-evaporite sediments of Mississippian age. The Midale Vuggy unit contained most of the oil produced from the Weyburn field to date, and is now nearing exhaustion. This unit represents open marine conditions and is overlain by the shallow water dolomitic mudstones of the Midale Marly Beds. Post-diagenetic dolomitisation of this later unit created good reservoir properties, which are now the target for the miscible CO₂ flood. The Midale Marly Beds are overlain by the Midale Evaporite unit, which acts as a seal (caprock) preventing oil (and CO₂) migration.

During underground CO₂ storage operations in deep reservoirs, the CO₂ can be trapped in three main ways (with descriptors from Bachu *et al.*, 1994):

- as 'free' CO₂, most likely as a supercritical phase (physical trapping)
- dissolved in formation water (hydrodynamic trapping)
- precipitated in carbonate phases such as calcite (mineral trapping)

For CO₂-EOR operations, the CO₂ can also be trapped as a dissolved phase within residual oil remaining within the formation after the end of production.

During the early stages of storage, physical trapping is likely to be the most important trapping mechanism. However, over time, hydrodynamic trapping and eventually mineral trapping may make significant contributions to the long-term containment of CO₂. The experimental study summarised here, focussed on the reactions between CO₂, porewaters and rock within the Midale Formation. It therefore covers aspects related to both hydrodynamic trapping and mineral trapping.

The experiments summarised in this report used actual samples of Midale core material (cleaned and prepared), and synthetic porewaters based upon actual measured well fluid compositions. The pressures and temperatures used within the experiments were representative of *in-situ* conditions (60°C, 150 bar [15 MPa]) and those anticipated near to injection wells (60°C, 250 bar [25 MPa]). As such, the study aims to replicate processes occurring in the deep subsurface at Weyburn as closely as possible, including those conditions that will exist even after oil production and CO₂ injection have ceased.

This work built upon experience gained in earlier experimental studies (e.g. Czernichowski-Lauriol *et al.*, 1996; Gunter *et al.*, 1993; Rochelle *et al.*, 2002a). The procedures used are given in Rochelle *et al.* (2002b), and these were tested using some initial scoping experiments using a sample of Midale Marly material (Rochelle *et al.*, 2002c). Later, more detailed experiments provided a more thorough description of the reaction of CO₂ with samples of Midale Marly (Rochelle *et al.*, 2003a, Bateman *et al.*, 2004), Midale Evaporite (Rochelle *et al.*, 2003b), and Midale Vuggy (Rochelle *et al.*, 2003c). A few scoping experiments were also carried out using samples of borehole cements used at Weyburn (Rochelle *et al.*, 2004).

2 Experimental details

In order to obtain a better understanding of rock-water-CO₂ interactions, numerous long-term ‘batch’ experiments have been performed. This type of equipment is relatively simple and generally free from day-to-day maintenance. As a consequence, it is well-suited for running over prolonged time periods and has been used successfully in previous studies of CO₂-water-rock reaction (e.g. Czernichowski-Lauriol *et al.*, 1996; Rochelle *et al.*, 2002a).

The batch reactor vessels were of relatively small volume (<200 ml), and although it was possible to take several samples from each experiment, usually no more than six could be extracted. In order to allow more detailed information to be obtained (i.e. more samples), several similar experiments were run together, and their results combined. Combining results in this way also provided a check on the quality of the data (i.e. if the data sets did not agree, then something was wrong). In this way, confidence in the data was increased. Further details about the set up of the experiments can be found in Rochelle *et al.*, (2002b).

Two main types of experiments were conducted during this study in the batch reactor vessels:

- Experiments pressurised with N₂. These were done to provide baseline ‘non-reacting’ cases, which could then be compared to the ‘reactive’ CO₂ experiments. The N₂ experiments could also be compared with data from actual analyses of well fluids – being ‘non-reactive’ they should be comparable.
- Experiments pressurised with CO₂. These ‘reactive’ experiments were done to provide information on the chemical and mineralogical changes that might occur during the injection of CO₂ into the Midale Formations at the Weyburn oil field.

Three different types of solid material were utilised in both types of experiments outlined above:

- Experiments using ground solid material with ‘fines’ included (<250 µm size fraction). These experiments maximised reactive surface area, and as such were best able to investigate steady-state conditions within the limited timescale of this study. They had durations of up to 6 months, and a 10:1 fluid:rock ratio.
- Experiments using ground solid material, but with ‘fines’ removed (250-500 µm size fraction). These experiments had a lower solid surface area to those described above, and hence reacted slower. However, their surface area was measured, and this allowed for rates of element release (i.e. dissolution) to be calculated. They had durations of up to 3 months, and a 10:1 fluid:rock ratio.
- Experiments using ‘monoliths’ of solid material (approximately 1x1x4-5 cm). These experiments had the lowest solid surface area, and thus the slowest reaction. The monoliths were sometimes positioned so that they straddled the interface between the aqueous phase and the CO₂ phase. By doing this, it was possible to readily identify any difference in overall reactivity within either fluid phase. They had durations of up to 3 months, and a somewhat more variable fluid:rock ratio.

Also undertaken during this study were two column experiments. The aim of these experiments was to provide information on how Midale samples reacted to a flowing reactive fluid rather than a static one, and to provide a test case for coupled reaction-transport geochemical modelling codes. The column experiments used samples of Midale Marly material ground to 250-500 µm size fraction and cleaned of fines (the same material as used in the Marly batch experiments). They also used a similar synthetic formation water to that used in the Marly batch experiments.

3 Details of the Weyburn samples studied

Two Midale Marly samples were used in the experiments. The first (identifier = BGS2A) was from well 14-13-6-14W2 at a depth of 1403.54 m (4604.80 ft). This was used for the few preliminary test experiments (see Rochelle *et al.*, 2002b). The second sample (identifier = BGS14A) was from well B8-23-6-14W2 at a depth of 1398.30 m (4587.60 ft). This latter sample was used for the bulk of the batch experiments (see Rochelle *et al.*, 2003a). The Midale Marly material used in both of these experiments was a friable dolostone, comprising fine-grained euhedral dolomite rhombs with a well-developed intercrystalline porosity.

The Midale Evaporite sample used in these experiments was taken from well 14-1-6-14W2 at a depth of 1437.91 m (4717.55 ft). This sample was used for all the batch experiments detailed in Rochelle *et al.* (2003b). The sample consists of fine-grained, euhedral dolomite rhombs within a massive anhydrite matrix. Radiating clusters of elongate anhydrite needles are occasionally developed.

The Midale Vuggy sample used in these experiments was taken from well 12-11-6-14W2 at a depth of 1426.85 m (4681.25 ft). This sample was used for all the batch experiments detailed in Rochelle *et al.* (2003c). The Midale Vuggy is a crypto- to micro-crystalline, thin bedded, slightly argillaceous, recrystallised mudstone-wackestone with intergranular, intragranular, moldic and vuggy porosity.

Further details of the Midale samples used and how they were selected can be found in Pearce and Springer (2001). The selection of the samples was based on two factors:

- 1) That they came from wells which had been sampled for 'baseline' formation waters (Schevalier pers. comm.),
- 2) That they were from cored intervals which were co-incident with the location of slotted liners (i.e. for a specific depth, formation water chemistry and core material composition should be comparable).

Two cement samples were also studied, representing the types of borehole cement used at Weyburn. They were received as pre-prepared powders that only needed water adding. They were termed 'tail cement' and 'fill cement', and when set are both grey, uniform, fine-grained solids.

4 Summary of results

The following sections provide only a brief description of the findings from this study. More detailed information can be found as follows:

- Midale Marly (Rochelle *et al.*, 2003a, Bateman *et al.*, 2004)
- Midale Evaporite (Rochelle *et al.*, 2003b)
- Midale Vuggy (Rochelle *et al.*, 2003c)
- Borehole cements (Rochelle *et al.*, 2004).

4.1 MIDALE MARLY

The evolution over time of a selection of solutes is presented in Figures 1-6. Relative to the N₂ 'baseline' experiments, it was found that the impact of CO₂ was to:

- increase the concentrations of Ca, Si and HCO₃⁻
- decrease the concentrations of Sr and pH values
- have little impact on the concentrations of Mg, Mn, Al and total S

After 12 weeks of reaction, no differences in the degree of dissolution were observed between the N₂ and CO₂ experiments, either of the monolithic blocks or of the 250-500 µm crushed samples (Figure 7). However, after 9 weeks reaction, the <250 µm grains in both N₂ and CO₂ experiments were slightly more rounded relative to the starting material, which probably resulted from mechanical abrasion. After 26 weeks reaction, a slight increase in dissolution on the <250 µm grains reacted with CO₂-rich pore water was tentatively identified.

The changes described above were interpreted as being due to some calcite dissolution, and a little aluminosilicate mineral dissolution.

Column experiments flowing either N₂-pressurised or CO₂-pressurised synthetic porewater through a mass of granulated Marly material, showed some similar features to the batch experiments. The presence of CO₂ caused enhanced release of Ca and Si, but reduced release of Sr, relative to the N₂ experiment. Corrosion of the Marly sample was identified at the inlet end of the CO₂ column as a result of the constant input of fresh undersaturated solution. In particular, dolomite was corroded which revealed entrapped illitic clay.

Overall therefore, although some dissolution of the Midale Marly material was identified, it was relatively minor, and the samples remained relatively unchanged. Significant disruption of the host formation appears not to take place.

4.2 MIDALE EVAPORITE

The evolution over time of a selection of solutes is presented in Figures 1-6. Relative to the N₂ 'baseline' experiments, it was found that the impact of CO₂ was to:

- increase the concentrations of Mg, Mn, Si, HCO₃⁻ and possibly Al
- decrease the concentrations of Sr, total S and pH values
- have little impact on the concentrations of Ca, Sr and Ba

Following reaction in CO₂-rich synthetic pore waters, a clear 'tidemark' developed on the external surfaces of the monolithic blocks with the area above the water-CO₂ interface developing a lighter, creamy colour (Figure 8). Scanning electron microscopy revealed that this was due to a fine coating of halite that developed during the experiment.

Generally there was little petrographic evidence for dolomite corrosion, though anhydrite was slightly corroded in some experiments using CO₂-rich pore water (Figure 9). Euhedral, elongate prismatic gypsum crystals developed in both the CO₂-rich and N₂-baseline experiments, but were particularly well developed on the external surfaces of the monolithic blocks in the CO₂-rich experiments (Figure 9). These crystals grew up to 2 mm long after 4 weeks reaction in the CO₂ monolith experiments, but also grew up to 5 µm long in the experiments containing crushed grains. After 26 weeks of reaction there was little difference in the <250 µm crushed samples between the N₂ experiment and the CO₂ experiment, except for a possible slight decrease in the proportion of very fine dolomite rhombs, which may suggest dissolution had been restricted to the finer grains.

The changes described above were interpreted as probably being due to some dolomite and anhydrite dissolution, a little aluminosilicate mineral dissolution, and a small amount of gypsum precipitation.

Overall therefore, although some dissolution of the Midale Evaporite material was identified, it was relatively minor, and the samples remained relatively unchanged. Significant dissolution of the caprock formation appears not to take place.

4.3 MIDALE VUGGY

The evolution over time of a selection of solutes is presented in Figures 1-6. Relative to the N₂ 'baseline' experiments, it was found that the impact of CO₂ was to:

- increase the concentrations of Ca, Si and HCO₃⁻
- decrease the concentrations of total S and possibly Sr, and pH values
- have little impact on the concentrations of Mg, Mn and Al

It is noted that these fluid chemical changes are not dissimilar to those found in the Midale Marly experiments.

All monoliths reacted in CO₂-rich synthetic pore waters showed clear evidence of 'tidemarks' developed on their external surfaces (Figure 10). After 4 weeks of reaction of the monoliths, euhedral prismatic gypsum crystals up to 500 µm in length formed below the water line in the CO₂ experiment (Figure 11). By 8 weeks reaction the gypsum crystals were 2.5 mm long (Figure 11), and at 17 weeks reaction gypsum crystals up to 500 µm long also developed in the baseline N₂ experiment. In addition, most calcite and anhydrite surfaces were corroded to a depth of 10-30 µm in both the CO₂ and the baseline N₂ experiments. This porosity was easily distinguishable from the vuggy porosity developed during diagenesis.

In the experiments containing crushed Midale Vuggy, euhedral tabular prismatic gypsum crystals up to 1.8 mm long developed after 2 weeks reaction. Only limited evidence for minor corrosion was tentatively observed. After 26 weeks of reaction, the only evidence for dissolution in the <250 µm crushed samples was slightly less 'dust' in the baseline N₂ experiment relative to the CO₂ experiment.

The changes described above were interpreted as probably being due to some calcite dissolution (probably more than observed in the Midale Marly experiments), some anhydrite dissolution, a little aluminosilicate mineral dissolution, and a fair amount of gypsum precipitation.

Overall therefore, the Midale Vuggy material showed the greatest potential for both dissolution and secondary mineral precipitation. It is unclear at the moment whether these would lead to an overall net increase or decrease in porosity or permeability. However, if significant gypsum precipitation reduced the permeability of the Midale Vuggy unit, then this may be a beneficial reaction in terms of the EOR operation, as it might reduce the potential for the injected CO₂ to 'under-ride' the target Marly unit.

4.4 BOREHOLE CEMENTS

The samples of borehole cement arrived relatively late in the experimental programme, and so only a preliminary description of the results has so far been done. The experiments were run for only 2 weeks and so steady-state solute concentrations were not achieved. However, initial observations showed that the CO₂ produced carbonation of the outer parts of the monolith samples (20% or so), and this was associated with an apparent reduction in porosity of the outer parts of the monoliths.

The monoliths remained intact, and appear to have maintained much of their original strength (Figures 12 and 13). Strength testing was done in a relatively simple way, by measuring the force required to snap a 5x1x1 cm monolith in half. That cement strength was not affected greatly is closer in comparison to most of the previous studies, but is in contrast to a few that have identified large reductions in cement strength on exposure to elevated CO₂ pressures (e.g. Robins and Milodowski, 1982).

5 Conclusions

A series of laboratory experiments were undertaken to identify geochemical changes resulting from the injection of CO₂ into the Midale Formations at the Weyburn oilfield. Most of the experiments utilised samples of actual Midale rocks recovered from boreholes, synthetic formation water based upon measured well fluid compositions, and either CO₂ or N₂ as a pressurising medium. A few experiments also studied the behaviour of borehole cements under similar conditions. Experiments were run for durations of up to 6 months, with conditions representing those found *in-situ* (60°C and 150 bar [15 MPa]) and those anticipated near to injection wells (60°C, 250 bar [25 MPa]). As such, the study replicated processes occurring in the deep subsurface at Weyburn, including those conditions that will exist after oil production and CO₂ injection have ceased.

Some dissolution of calcite within the Midale Marly material was identified on reaction with CO₂, though it was relatively minor. However, by and large, the samples remained relatively unchanged and significant disruption of the host formation appears not to take place.

The Midale Evaporite showed slightly more reaction with CO₂ compared to the Midale Marly, though it was still relatively minor. Some dissolution of dolomite and anhydrite was identified, together with minor aluminosilicate mineral dissolution. There was also a small amount of gypsum precipitation. Significant dissolution of the caprock formation appears not to take place.

The Midale Vuggy material showed the greatest potential for reaction with CO₂. Dissolution was mainly of calcite and anhydrite, but there was also a little aluminosilicate mineral dissolution. Precipitation of gypsum was widespread, with crystals up to 5mm long observed.

Samples of borehole cement underwent carbonation of their outer portions upon exposure to CO₂, and this was associated with an apparent reduction in porosity. The monoliths remained intact and appear to have maintained much of their original strength.

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Figure 1 Evolution of Ca concentrations within experiments using samples of Midale material (selected data).

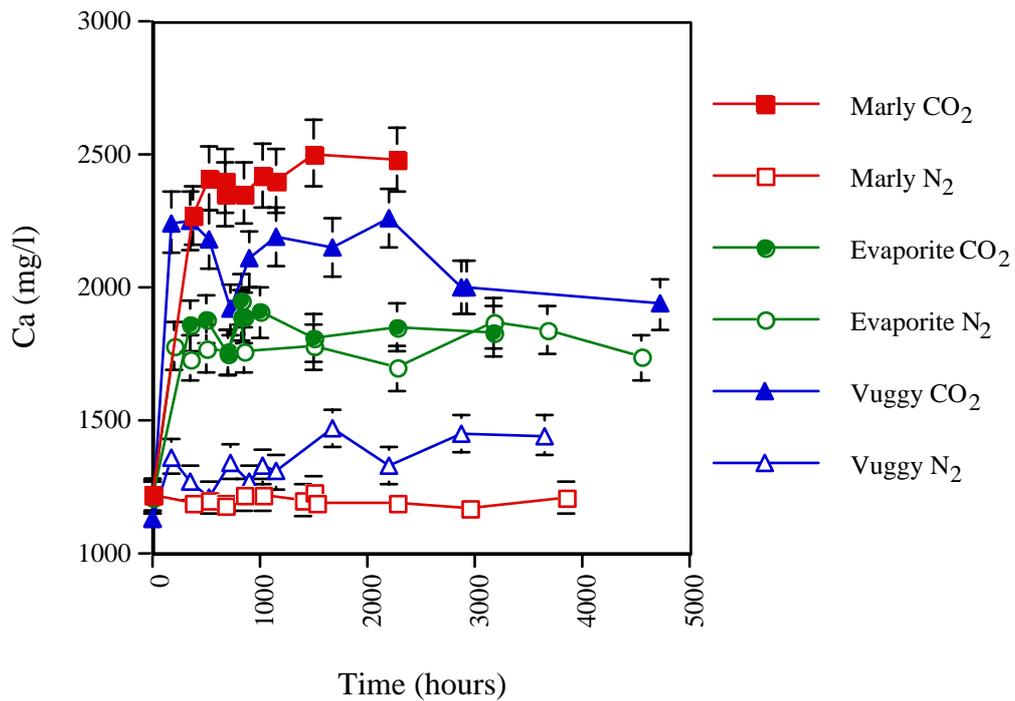


Figure 2 Evolution of Mg concentrations within experiments using samples of Midale material (selected data).

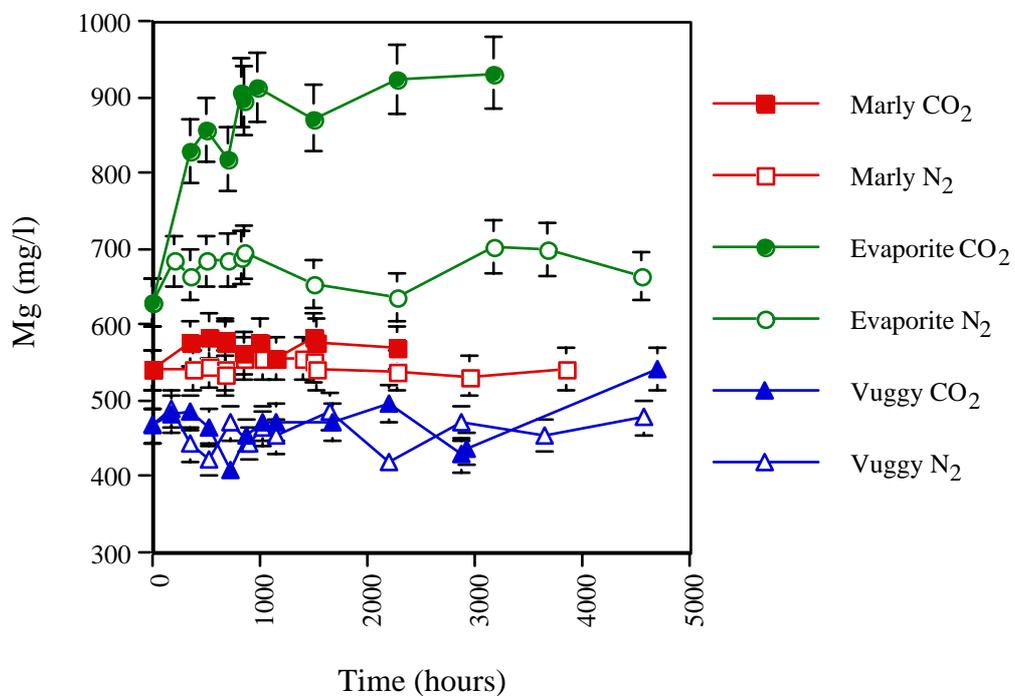


Figure 3 Evolution of Sr concentrations within experiments using samples of Midale material (selected data).

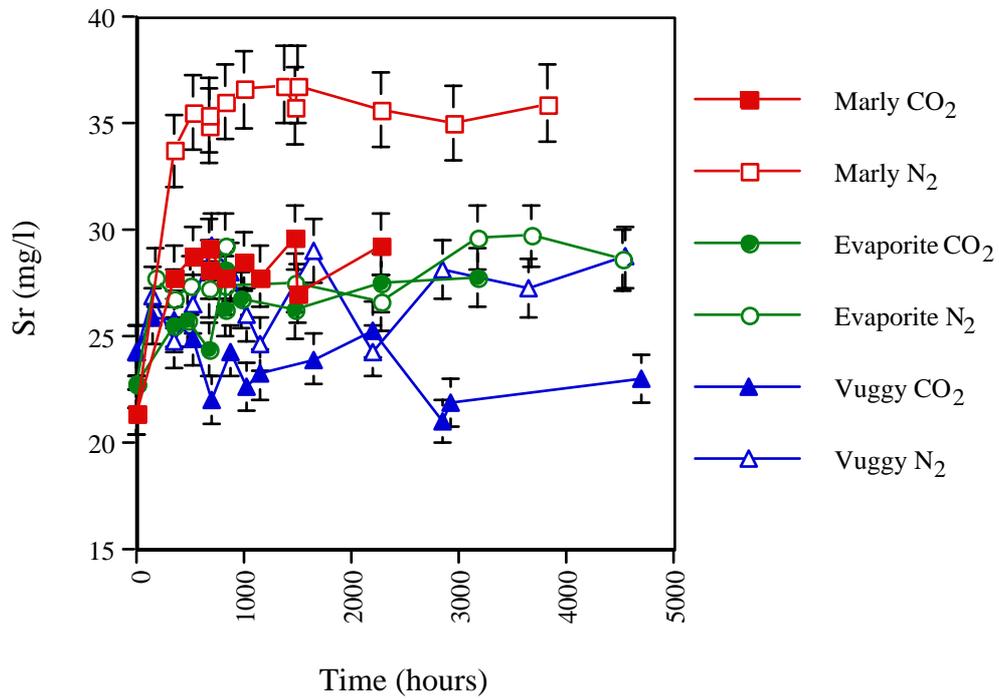


Figure 4 Evolution of Si concentrations within experiments using samples of Midale material (selected data).

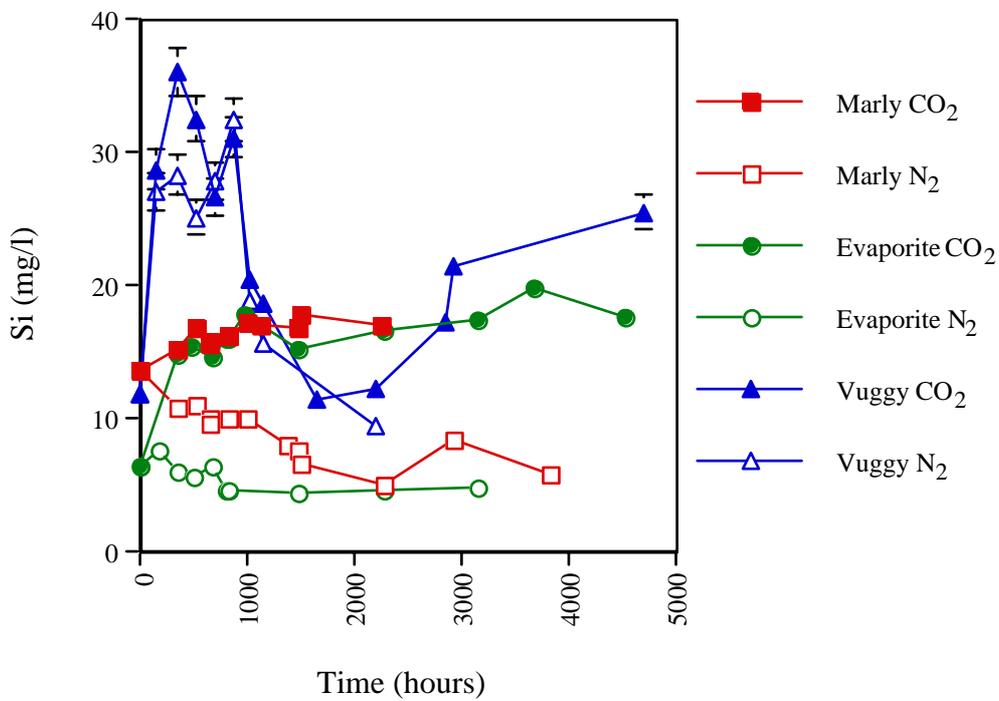


Figure 5 Evolution of Al concentrations within experiments using samples of Midale material (selected data).

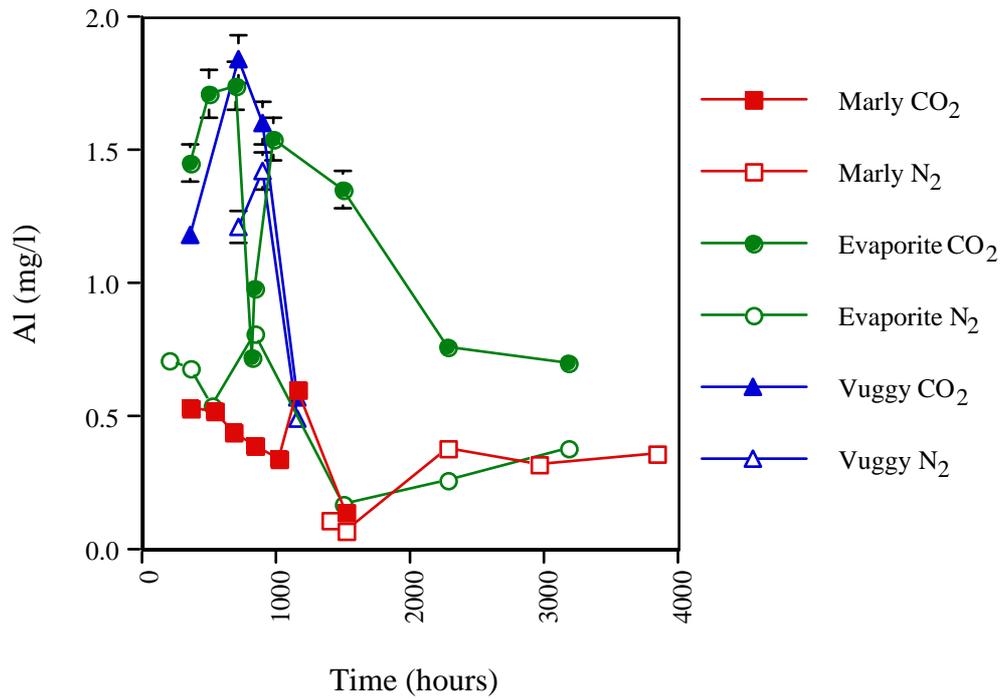


Figure 6 Evolution of total S concentrations within experiments using samples of Midale material (selected data).

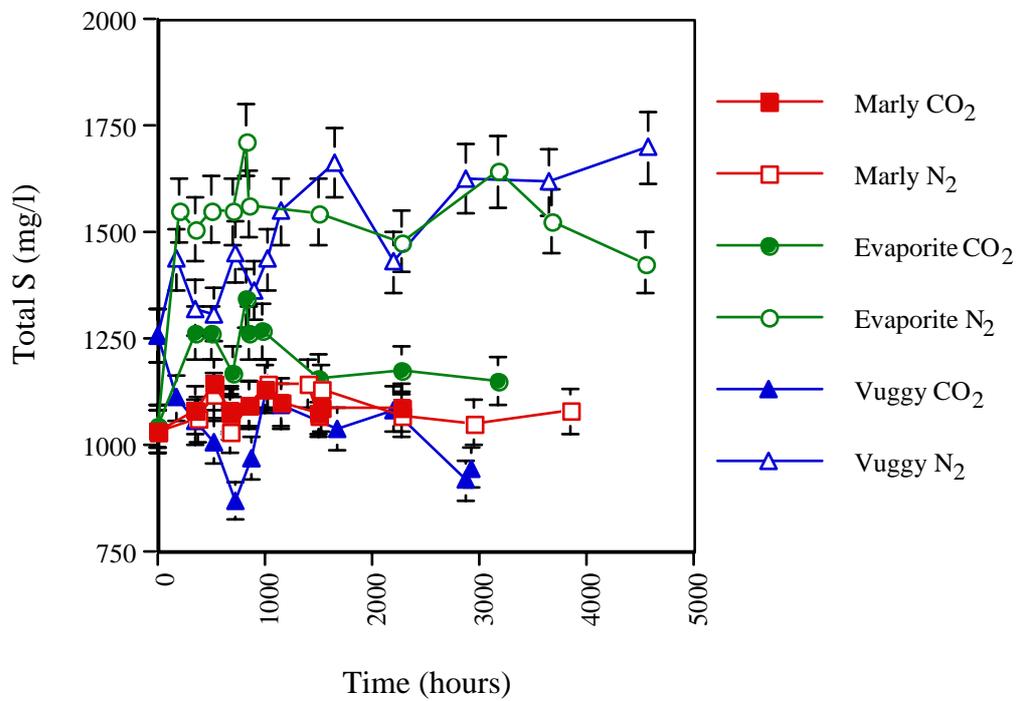


Figure 7 SEM photomicrographs of granular Midale Marly material showing no evidence of dissolution in either the N₂ control or CO₂ experiments, relative to the starting material.

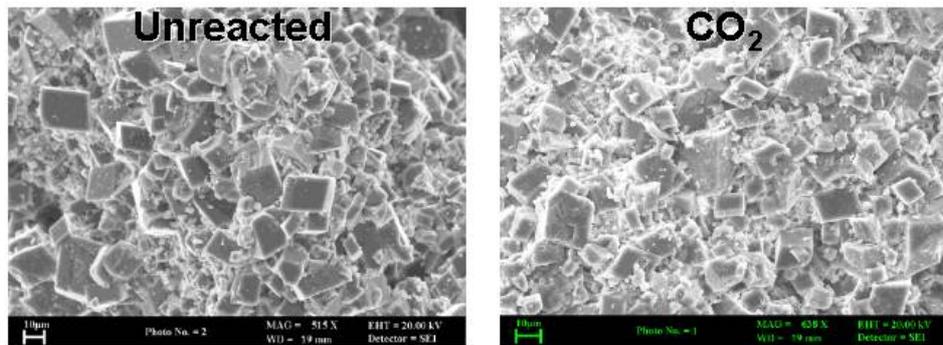


Figure 8 Photomicrographs of a monolith of Midale Evaporite showing a well developed 'tide mark' after exposure to CO₂.

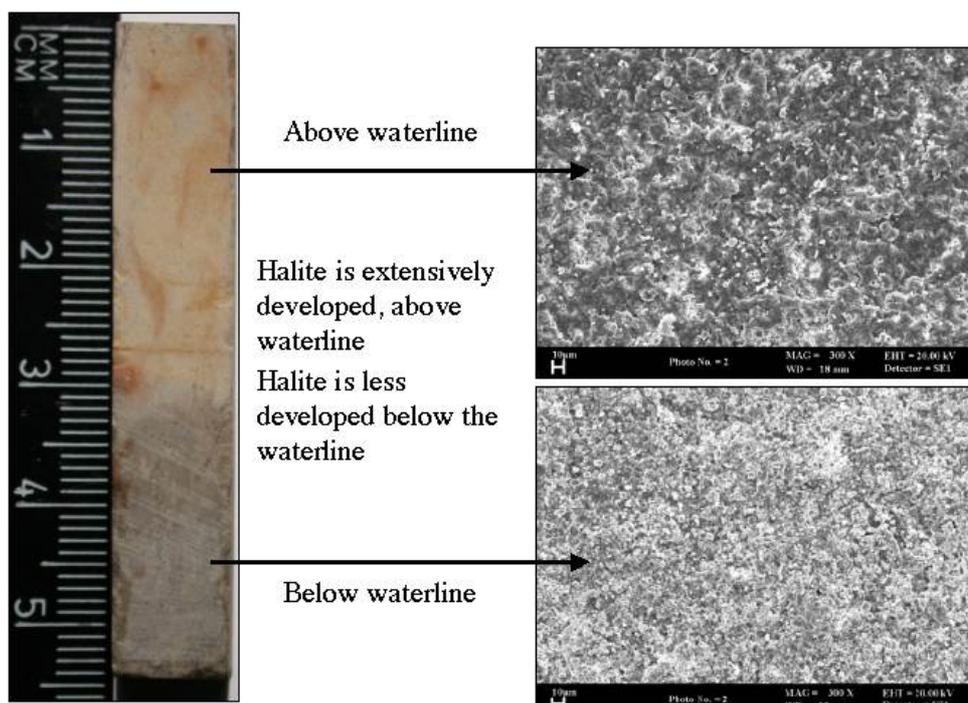


Figure 9 SEM photomicrographs of granular Midale Evaporite material showing some anhydrite corrosion, gypsum precipitation and relatively unaltered larger rhombs of dolomite.



Figure 10 SEM photomicrographs of a monolith of Midale Vuggy showing a well-developed 'tide mark' with increased dissolution within the water-rich phase (lower half of the image).

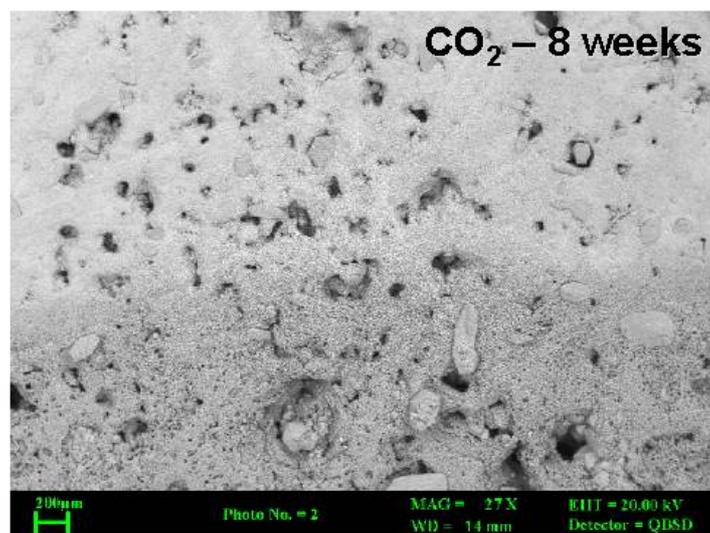


Figure 11 SEM photomicrographs of Midale Vuggy monoliths showing well-developed secondary growth of gypsum crystals within the aqueous phase. After 4 weeks with CO₂ the crystals were up to 500 μm long, and after 8 weeks they were at least 2.5 mm long.

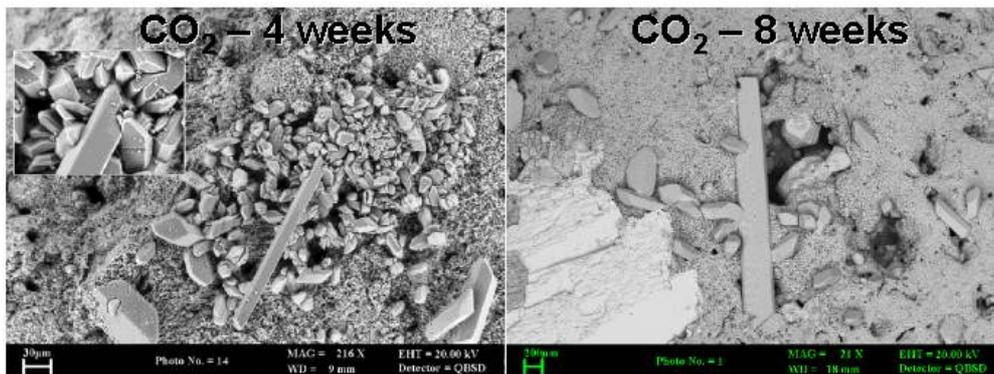


Figure 12 Relative strength of different monoliths of 'fill cement' under constantly increasing strain as recorded by a force transducer (sudden drop = sample failure). Most samples give similar maximum readings to the starting materials ('blank' monoliths). The failure of sample 'CO2 only – monolith A' at lower loads may reflect a pre-existing weakness, as its comparable sample (monolith B) failed under much higher loads.

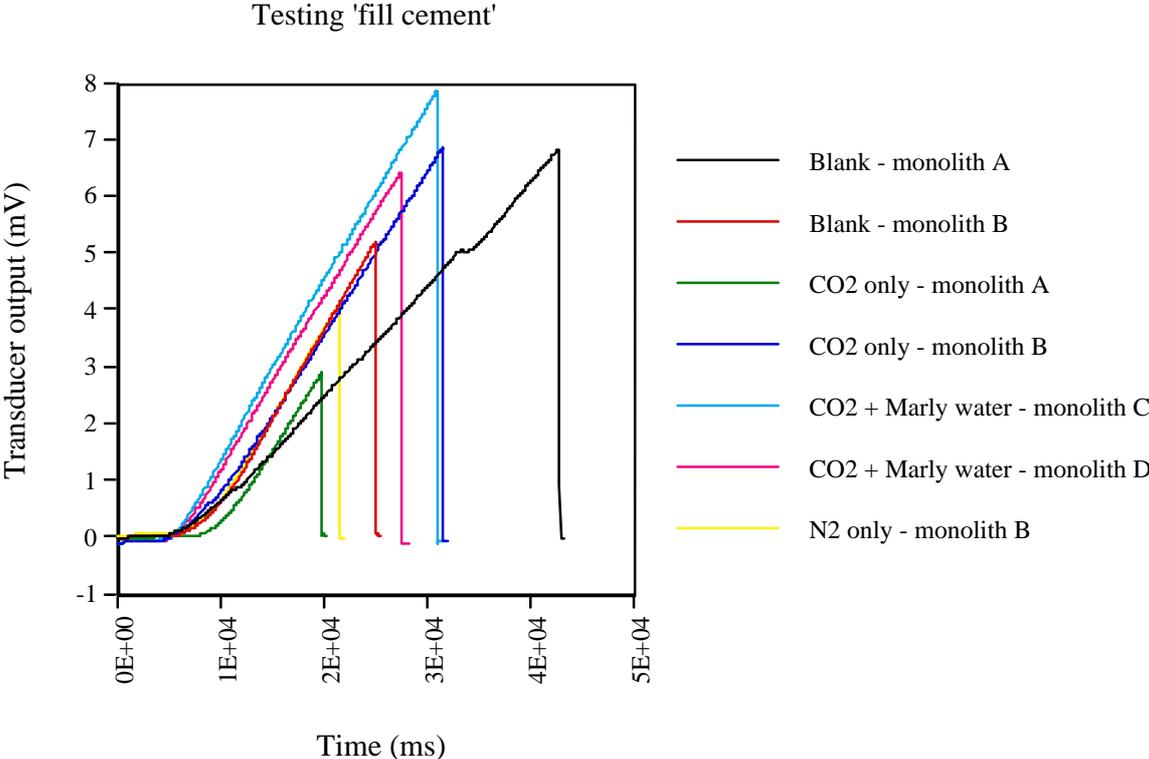


Figure 13 Relative strength of different monoliths of 'tail cement' under constantly increasing strain as recorded by a force transducer (sudden drop = sample failure). Most samples give similar maximum readings to the starting materials ('blank' monoliths). Note that both of the 'CO2 + Marly water' monoliths failed at about half of the load that the starting materials failed at. The reasons for this are unclear at this stage. Note also, that the 'tail cement' was generally not as strong as the 'fill cement' shown in Figure 13.

