



**British
Geological Survey**

NATURAL ENVIRONMENT RESEARCH COUNCIL

Geochemical interactions between supercritical CO₂ and the Utsira caprock.

I: Introduction to fluid-rock interaction experiments

Sustainable Energy and Geophysical Surveys Programme
Saline Aquifer CO₂ Storage (SACS) Project
Commissioned Report CR/02/238N

BRITISH GEOLOGICAL SURVEY

COMMISSIONED REPORT CR/02/238N (Released 07/05/08)

Geochemical interactions between supercritical CO₂ and the Utsira caprock. I: Introduction to fluid-rock interaction experiments

C.A. Rochelle

Key words

CO₂, carbon dioxide, storage, monitoring, SACS, Sleipner, Utsira Formation, caprock, experimental study, geochemistry, fluid-rock interaction.

Bibliographical reference

ROCHELLE, C.A. 2002. Geochemical interactions between supercritical CO₂ and the Utsira caprock. I: Introduction to fluid-rock interaction experiments. *British Geological Survey Commissioned Report*, CR/02/238N. 21 pp.

© NERC 2002

Keyworth, Nottingham British Geological Survey 2002

BRITISH GEOLOGICAL SURVEY

The full range of Survey publications is available from the BGS Sales Desks at Nottingham and Edinburgh; see contact details below or shop online at www.thebgs.co.uk

The London Information Office maintains a reference collection of BGS publications including maps for consultation.

The Survey publishes an annual catalogue of its maps and other publications; this catalogue is available from any of the BGS Sales Desks.

The British Geological Survey carries out the geological survey of Great Britain and Northern Ireland (the latter as an agency service for the government of Northern Ireland), and of the surrounding continental shelf, as well as its basic research projects. It also undertakes programmes of British technical aid in geology in developing countries as arranged by the Department for International Development and other agencies.

The British Geological Survey is a component body of the Natural Environment Research Council.

Keyworth, Nottingham NG12 5GG

☎ 0115-936 3241 Fax 0115-936 3488
e-mail: sales@bgs.ac.uk
www.bgs.ac.uk
Shop online at: www.thebgs.co.uk

Murchison House, West Mains Road, Edinburgh EH9 3LA

☎ 0131-667 1000 Fax 0131-668 2683
e-mail: scotsales@bgs.ac.uk

London Information Office at the Natural History Museum (Earth Galleries), Exhibition Road, South Kensington, London SW7 2DE

☎ 020-7589 4090 Fax 020-7584 8270
☎ 020-7942 5344/45 email:
bgs london@bgs.ac.uk

Forde House, Park Five Business Centre, Harrier Way, Sowton, Exeter, Devon EX2 7HU

☎ 01392-445271 Fax 01392-445371

Geological Survey of Northern Ireland, 20 College Gardens, Belfast BT9 6BS

☎ 028-9066 6595 Fax 028-9066 2835

Maclean Building, Crowmarsh Gifford, Wallingford, Oxfordshire OX10 8BB

☎ 01491-838800 Fax 01491-692345

Parent Body

Natural Environment Research Council, Polaris House, North Star Avenue, Swindon, Wiltshire SN2 1EU

☎ 01793-411500 Fax 01793-411501
www.nerc.ac.uk

Foreword

This report is the published product of a study by the British Geological Survey (BGS), and forms part of the international SACS (Saline Aquifer CO₂ Storage) project. The SACS project aims to monitor and predict the behaviour of injected CO₂ in the Utsira Sand reservoir at the Sleipner field in the northern North Sea, using methods that include; time-lapse geophysics, modelling its subsurface distribution and migration, and simulating likely chemical interactions with the host rock.

This report aims to provide a brief description of the laboratory experimental techniques that are being applied at the British Geological Survey to investigate the geochemical reactions between CO₂ and the Utsira caprock. Later reports will detail the results of these experiments.

Acknowledgements

The author would like to thank BGS colleagues whose contributions have helped make this report possible. In particular, Humphrey Wallis of the R&D workshops for providing technical assistance and design of the pressure vessels used for the experiments. Also Keith Bateman and Dave Birchall for various discussions and their previous efforts in helping to steadily improve the design and operation of the type of pressure vessels used for the experiments.

Contents

Foreword	i
Acknowledgements	i
Contents	ii
Summary	iv
1 Introduction	1
2 Baseline information and samples	1
2.1 Pressure and temperature	1
2.2 Aqueous fluid composition	3
2.3 Solid samples	3
2.4 Gases	4
3 Description of the experiments	4
3.1 Overall approach and aims	4
3.2 Experimental equipment	5
3.2.1 Initial considerations	5
3.2.2 'Batch' equipment	5
3.3 Experiments to be undertaken	6
4 Sampling and analysis	9
4.1 Sampling procedure	9
4.1.1 Experiments using samples of disaggregated Utsira caprock	9
4.1.2 Experiments using samples of intact Utsira caprock	9
4.2 Preparation of experimental products	10
4.2.1 Solid products	10
4.2.2 Fluid samples	10
4.3 Analytical techniques	11
5 Possible future experiments	12
6 Conclusions	13
References	13

FIGURES

Figure 1	Phase diagram for CO ₂ .	14
Figure 2	Schematic diagrams showing a typical batch reactor used for this study, compared to one used for previous studies.	15
Figure 3	Schematic diagram showing the typical layout for a series of batch experiments.	16
Figure 4	Schematic diagram showing a typical batch reactor used for studying the impact of CO ₂ on intact samples of caprock.	17
Figure 5	Schematic diagram showing the typical method of sampling aqueous fluids from a batch reactor.	18

TABLES

Table 1	‘Recipe’ for making synthetic Utsira porewater.	19
Table 2	Information on the 4 samples of Utsira caprock sent to the BGS.	20
Table 3	Range of possible analytes and likely detection limits.	21

Summary

This report describes work that will be undertaken at the British Geological Survey (BGS) that forms part of the international SACS (Saline Aquifer CO₂ Storage) project. The SACS project aims to monitor and predict the behaviour of injected CO₂ in the Utsira Sand reservoir at the Sleipner field in the northern North Sea, using methods that include; time-lapse geophysics, modelling its subsurface distribution and migration, and simulating likely chemical interactions with the host rock. Most of the work detailed in this report forms part of the TFE- (Total Fina Elf) extension of the SACS2 project (here described as SACS-TFE, but also known as SACS2-addendum). This extension will be of relatively short duration, and is planned to link the longer-term (and much larger) SACS2 and CO2STORE (effectively SACS3) projects.

This report aims to provide a brief description of the laboratory experimental techniques that will be applied at the British Geological Survey to investigate and quantify geochemical reactions between CO₂ and the Utsira caprock. The aim of the work under the SACS-TFE project will be to initiate a series of long-term experiments, and conduct some preliminary sampling. These experiments will be continued into the CO2STORE project, whose programme will also involve a series of shorter-term experiments. Although the experiments have not yet been started (at the time of writing this report [early September 2002]), it is hoped that this report will provide useful preliminary information to other researchers working on the SACS project. Later reports will detail the results of the experiments.

The experimental study is being undertaken in the Hydrothermal Laboratory of the BGS, where various measurements are being taken. The techniques that will be used are based upon those used in previous CO₂ projects (e.g. during the JouleII CO₂ storage project [Holloway, 1996; Czernichowski-Lauriol *et al.*, 1996], and during the SACS project [Rochelle *et al.*, 2002]). Use of similar techniques will hopefully allow for better inter-comparison between the various studies.

The experiments will utilise actual caprock core material from the Sleipner field, together with synthetic formation waters based upon measured compositions of porewaters squeezed from samples of the same core. The experimental conditions chosen for the investigation will concentrate upon those representative of *in-situ* conditions within the caprock (30°C, 8 MPa [80 bar]). However, it is possible that more elevated temperatures (e.g. 70°C) may be used in the future if it is necessary to increase reaction rates. Experiment durations are planned to range up to 2-3 years. Experiments will be pressurised with either nitrogen or carbon dioxide. The former will provide a 'non reacting' reference point from which to compare the possibly more reactive experiments containing CO₂. However, it is hoped that they will also help to provide increased confidence in the baseline conditions within the Utsira caprock prior to CO₂ injection into the Utsira Formation.

1 Introduction

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 in 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 will make significant contributions to long-term CO₂ containment. Physical trapping will necessitate a rock formation that will prevent the CO₂ rising (under its own buoyancy) back to the surface. As a consequence, the nature and reactivity of the caprock overlying stored CO₂ will be of great importance in controlling the longevity of CO₂ containment.

The experimental programme outlined in this report will focus on the reactions between CO₂, porewater and caprock relevant to CO₂ storage at Sleipner. Most of the following details will form part of the TFE- (Total Fina Elf) extension of the SACS2 project (here described as SACS-TFE, but also known as SACS2-adendum). This extension will be of relatively short duration, and is planned to link the longer-term (and much larger) SACS2 and CO2STORE (effectively SACS3) projects.

2 Baseline information and samples

The experimental geochemical programme will be constrained by the baseline data available at the start of the study. This data will be based largely on information from samples of caprock core taken in the summer of 2002. BGS received four such samples (each 20 cm long), which were subjected to a variety of other studies, including; mineralogical analysis, porewater analysis, and investigation of gas transport properties.

A key output of the experimental programme will be the identification of any chemical reactions that occur between CO₂, porewater and caprock. If any reactions are identified, then the experiments can serve as well-constrained test cases that can be used as 'benchmarks' for geochemical modelling activities. The sort of experimental information that will be useful for modelling activities includes the types, rates and magnitudes of geochemical reactions. Predictions tested against actual observations will increase confidence in the predictive capabilities of modelling codes. Although experiments will be run under conditions that are broadly applicable to Sleipner, they will not simulate all possible conditions within the field. Instead, emphasis will be placed on simulating specific parts of the field.

2.1 PRESSURE AND TEMPERATURE

Previous geochemical experimental studies (Rochelle and Moore, 2002; Rochelle *et al.*, 2002) have reacted Utsira sand from Sleipner with CO₂ at 37°C and 70°C, and at 8-12 MPa (80-120

bar). However, most experiments were conducted at 37°C and 10 MPa (100 bar) – representing *in-situ* conditions within the Utsira Sand at the injection point.

The Utsira caprock lies above the Utsira Sand, and so *in-situ* pressure and temperature will be *less* than for the CO₂ host formation. Directly measured *in-situ* pressure and temperature data are unavailable for the Utsira caprock at the time of writing this report (early September 2002). Therefore, for the present study, it is necessary to estimate these. Use of a representative pressure and temperature is preferred because:

- CO₂ solubility (and hence reactivity) varies with pressure and temperature.
- fluid-rock reaction rates vary with temperature.
- higher temperatures may cause the formation of unrepresentative secondary phases.

However, it is also possible that a few higher temperature experiments *may* be conducted in the future if it is deemed important to ascertain the temperature dependence of reaction rates.

A value for *in-situ* pressure can be estimated by several methods. However, the aim of this study is to consider the longer-term reaction of CO₂ with Utsira caprock. It is assumed therefore that pressures are controlled mainly by hydrostatic factors, rather than lithostatic factors or shorter-term injection operations. This also concurs with pressure data for the Utsira Sand, which appears to be broadly hydrostatically controlled.

Data supplied by e-mail on 30/8/2002 for deviated well 0015/09-A11 were used to derive a true depth for the samples of Utsira caprock held at BGS (Chadwick pers. comm.). The 4 samples of caprock core held at BGS come from between 906.00m-910.40m (downhole depth, see Section 2.3 for further details), with 906m corresponding to a true depth below ordnance datum (i.e. sea level) of approximately 784m (Chadwick pers. comm.). With the well inclined at 42° at this point, this gives a true depth of the bottom part of the lower sample (910.4m uncorrected depth) below ordnance datum of approximately 787.3m.

The fluid within the Utsira Sand has a similar composition to that of seawater, and it has been assumed that the entire hydrostatic column of water above the samples of Utsira caprock has a seawater-like density. Seawater density varies with temperature, and for ease of calculation, an average temperature of 20°C has been chosen, which lies approximately midway between likely seabed temperatures in the North Sea (about 8°C) and those at about 785m depth (about 30°C). The density of seawater at 20°C is approximately 1.025 g ml⁻¹ (Pitzer, 1991). Consequently, the estimated *in-situ* fluid pressure within the Utsira caprock where the BGS samples were taken from is approximately $(785 \times 1.025 \times 9.81) / 1000 = 7.89$ MPa (78.9 bar). For the experiments within this study, the pressure will be rounded to 8 MPa (80 bar). Note that this simple calculation does not take into account overpressurisation, or phenomena occurring close to charged clay mineral surfaces.

A value for *in-situ* temperature has been derived from other parts of the SACS-TFE programme, and data supplied by e-mail on 16/9/2002 (Chadwick pers. comm.) gives a value of 30.4°C. For the experiments within this study, a rounded temperature of 30°C will be used.

It is noteworthy that the above temperature is just below the critical temperature for CO₂ (about 31.1°C, see Figure 1). Therefore, although the CO₂ that will be used within the experiments is above the critical pressure (and is a relatively ‘high density’ phase), in strict terms it can not be described as a supercritical fluid. It is possible therefore, that some of the properties of the CO₂ (including chemical reactivity) may differ from those occurring in previous studies (e.g. Rochelle *et al.*, 2002; Rochelle and Moore, 2002). However, even though temperatures are lower than used previously, the formation of CO₂ hydrate within the

experiments is unlikely. This is because the *upper* stability boundary for CO₂ hydrate at 8 MPa is about 10°C (based upon data in Sloan, 1998).

2.2 AQUEOUS FLUID COMPOSITION

At the time of writing preliminary drafts of this report (early September 2002) no porewater fluid compositions were available. However, subsamples from 3 samples of caprock core from well ‘Statoil 15/9A-11’ were subsequently squeezed to extract porewaters (Reeder pers. comm.). Of these subsamples, the one from the uppermost sample (i.e. subsample 906.00m-906.13m from sample S906.00m-906.20m [uncorrected depths]) appeared to be of poorer quality, and had an unexpectedly high apparent moisture content in the order of 40% (Reeder pers. comm.). Fortunately, the other sub-samples appeared to be of much better quality, and had a more appropriate moisture content, in the order of 15% (Reeder pers. comm.). It appears (initially) that drilling fluids might have invaded the samples (and in particular the former one), and may thus complicate any fluid chemical data related to them.

Subsequent to the production of preliminary drafts of this report, the results of the porewater analysis are now available. Drilling fluid contamination was indeed a problem, not just in the shallowest caprock core sample, but also in all the other samples. To compound this further, no tracer (such as Li) was used in the drilling fluid that would have helped calculate a drilling fluid:porewater ratio. It was also found that various analytes did not behave in a consistent manner, and it is possible that ion-exchange reactions had modified the concentrations of particular species. As a consequence, it was not possible to determine a caprock porewater composition with any degree of confidence.

As a result of the above problems, there was no other choice but to use a porewater composition based upon the only reliable data we have – namely that based upon analyses of porewaters from the Utsira sand. Thus the synthetic porewater used in this study will be very similar to that used previously (see Rochelle *et al.*, 2002). This synthetic porewater will be called ‘Synthetic Utsira Porewater 2’, or ‘SUP2’ for short.

Table 1 gives the ‘recipe’ for the preparation of the SUP2 fluid used in the experiments.

2.3 SOLID SAMPLES

In August 2002, 4 samples of Utsira caprock core were received at BGS. Each of these was 20 cm long and sealed in plastic liners with plastic end caps. The core was taken from a deviated well, and was thus not vertical (taken at approximately 42° [Chadwick pers. comm.]). Details of the core pieces can be found in Table 2.

Note that the samples used for porewater extraction are also suitable for use in geochemical experiments where the sample is to be disaggregated. This will allow for maximum use of the rather limited material available. However, the uncertain quality of the uppermost sample (906.0m-906.2m [uncorrected depth]) will probably mean that this sample will not be used.

The solids will be reacted in 2 forms within the experiments (see also Section 3):

- 1) Disaggregated solid – intact sample of previously ‘squeezed’ core carefully broken into a fine powder using a pestle and mortar. Significant grinding of the mudrock will be avoided. It is aimed to keep the size distribution of individual mineral grains exactly as they are in the original sample.
- 2) Small cores or ‘monoliths’ – an otherwise undisturbed sample of core will be carefully trimmed into small, solid blocks. In some experiments these *may* be allowed to react

on all surfaces. In other experiments the sample *may* be placed into a tightly fitting, non-reacting ‘cup’ so that the majority of any reaction occurs on just one surface.

It is hoped that by using two forms of solid in the experiments it will be possible to investigate:

- conditions where the degree of CO₂-porewater-caprock reaction is maximised.
- processes occurring at the interface of the caprock with a CO₂-filled porous/permeable medium.

2.4 GASES

Two gases will be used in the experiments: CO₂ and an inert gas such as N₂.

CO₂

It is anticipated that the CO₂ used in this study will be sourced from high purity (99.99%) liquid CO₂ (Air Products, 4.5 Grade). This liquid CO₂ is obtained in a cylinder fitted with a dip tube and pressurised with 2000 psi (approximately 14 MPa [140 bar]) of helium. However, the actual experimental pressure will be controlled by an ISCO syringe pump, which will have its pressure transducer periodically ‘zeroed’ to minimise drift, and also checked against an externally calibrated pressure transducer. Recorded pressures will be taken from the ISCO pump controller readout, which will display pressures in excess of atmospheric pressure (i.e. zero pressure = atmospheric pressure).

N₂

It is anticipated that the N₂ used in this study will be obtained from BOC Gases and classified as ‘oxygen free’ (99.998% pure). This gas is delivered in cylinders pressurised to 230 bar. However, the actual experimental pressure is likely to be controlled by a single-stage regulator. Recorded pressures will be taken from an independent pressure transducer reading line pressure (see descriptions in the following sections).

3 Description of the experiments

3.1 OVERALL APPROACH AND AIMS

The experimental study is being undertaken in the Hydrothermal Laboratory of the British Geological Survey, Keyworth. The techniques that will be used are based upon those used in previous CO₂ projects (e.g. during the JouleII CO₂ storage project [Holloway, 1996; Czernichowski-Lauriol *et al.*, 1996], and during the SACS project [Rochelle *et al.*, 2002]). Use of similar techniques will hopefully allow for better inter-comparison between the various studies. Work under the SACS-TFE project aims to *initiate* a series of longer-term experiments, and these will continue into the CO₂STORE project. Most of the sampling and analysis of these experiments will be conducted during the CO₂STORE project. Shorter-term experiments to study relatively fast processes/reactions (should they occur) will be conducted within the future CO₂STORE project.

3.2 EXPERIMENTAL EQUIPMENT

3.2.1 Initial considerations

Prior to performing the experiments, it is necessary to consider the use of equipment that is likely to perform well. Although dry supercritical CO₂ is relatively inert, in the presence of water or NaCl solution it is much more reactive. Previous investigations within the BGS Hydrothermal Laboratory and other studies (e.g. Schremp and Roberson, 1975) have shown that steel can corrode and standard O-ring seals can blister and fail.

To minimise both corrosion and experimental failure, exposed surfaces were chosen so as to be as inert as practicable. Therefore, the pressure vessels will be made of stainless steel (e.g. type 316) and will be lined with PTFE (polytetrafluoroethene) or titanium, high pressure tubing will be made of either 316 stainless steel or PEEKTM (polyetheretherketone), O-ring seals will be made of Viton[®], and pressurised sampling containers will be made of titanium.

3.2.2 'Batch' equipment

In order to obtain a better understanding of rock-water-CO₂ interactions, long-term 'batch' experiments will be 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. Indeed, it has also been used successfully in previous studies of CO₂-water-rock reaction (e.g. Czernichowski-Lauriol *et al.*, 1996; Gunter *et al.*, 1993; Rochelle *et al.*, 2002).

There are two main aims for the 'batch' experimental programme:

- To study the evolution of porewater chemistry and rock mineralogy over time during CO₂-porewater-caprock reaction. This will be achieved by using approaches that combine; repeated sampling of fluid from a single experiment, and initiating a series of identical experiments and terminating them at ever-increasing timescales. Evolving fluid chemistry will be followed as a series of 'snapshots', which can be used to indicate the direction of reaction, overall rates of reaction, and possibly the time required to approach steady-state conditions. Evolution of mineralogical changes will be followed through detailed analysis of reaction products extracted at the end of the experiments.
- To investigate whether the experiments themselves cause any fluid chemical or mineralogical changes (e.g. as a result of the conditions, equipment, or fluid:rock ratio used). This will be achieved by setting up identical experiments to those described above, but this time using an inert gas (in this case nitrogen) rather than CO₂ as the pressurising medium. These experiments thus serve as 'blanks' with which to compare the CO₂ experiments.

The batch reactors used in this SACS-TFE study will be a slightly modified version of those used during the proceeding SACS2 studies (Rochelle *et al.*, 2002). The modifications are meant to reduce gas loss through slow leakage, and reduce corrosion within the pressure vessels. At the time of writing this report (early September 2002), the new batch reactors are being manufactured, and so their final configuration is not yet fixed. However, the main differences between the two designs are:

- 1) Reducing the number of O-ring seals from 2 to 1 (halves the potential for leakage).
- 2) Moving from 'face seal' O-rings to an 'edge seal' O-ring (a more efficient method of sealing, and so reduces the potential for leakage).

- 3) Using a 2-part rather than a 1-part head assembly (allows for better alignment of O-rings, and so reduces the potential for leakage).
- 4) Producing the metal parts of the pressure vessel to better tolerances than previous versions (allows for better alignment of O-rings, and so reduces the potential for leakage).
- 5) Using 316 stainless steel for the main body of the pressure vessel rather than EN54 stainless steel (will probably have better corrosion resistance).
- 6) Using 2 different steels for the threaded part of the pressure vessel assembly (will reduce 'snatching'/sticking of the threads which is a problem with certain stainless steels).
- 7) Possibly gold coating of the inside of the pressure vessel (will reduce the potential for corrosion - though note that the efficacy of the coating process and its long-term chemical resistance is as yet untested).
- 8) Machining integral filter holders within the top of the vessel (should these be needed).
- 9) Making the vessels marginally larger than previously (in the order of 250 ml rather than 100/150 ml) (will allow for larger specimens to be tested, and more fluid samples to be taken).

A schematic diagram of a typical 'batch' experiment using disaggregated rock is shown in Figure 2, together with a comparable diagram of previous equipment. The likely total volume of each new vessel will be approximately 250 ml, although this will only be partly filled with solid and aqueous fluid, the rest being filled by CO₂ or N₂.

Water saturated with CO₂ is relatively reactive, and this is especially so for saline fluids. For this reason PTFE (polytetrafluoroethylene) liners were used in the modified vessels, as per the earlier equipment. Experience gained from the SACS2 project has shown that some corrosion can occur on the inside of the stainless steel vessels, even though the steel does not usually come into direct contact with aqueous fluids. Should preliminary tests be encouraging, the inside of the pressure vessels *may* be coated with a thin layer of gold to minimise any corrosion due to 'damp' CO₂. This should provide a non-reacting layer to protect the steel. At the time of writing this report (early September 2002) the inside of the vessels are still to be coated with gold, and the exact coating process used (i.e. electroplating versus sputter coating) and its efficacy (i.e. how it stands up to mechanical abrasion and contact with high pressure CO₂) are still to be ascertained.

3.3 EXPERIMENTS TO BE UNDERTAKEN

It is anticipated that 8 experiments in total will be started as part of the SACS-TFE programme. These are planned to run for timescales measurable in months or even years. As a consequence, they have been designed to be as simple as possible so that technical problems (and thus the chance of possible failure) can be reduced. It is currently planned to terminate these experiments within the future CO₂STORE project. During the CO₂STORE project it is also planned to conduct other, shorter-term, experiments.

The experiments in the SACS-TFE programme will be run in pairs, as per previous SACS2 experiments (see Rochelle *et al.*, 2002). One experiment of each pair will be the 'reacting' case and be pressurised with CO₂. The other experiment will be pressurised with an inert gas such as nitrogen. Thus there will be 4 possible variations of experiment that can be started in the SACS-TFE project. The following list briefly describes the four types of experiments that *may* be undertaken:

- 1) *Disaggregated Utsira caprock + synthetic porewater (medium-timescales)*. The aim of these experiments will be to study possible changes in fluid chemistry and caprock mineralogy in the presence of *dissolved* CO₂. The experiments will maximise the rate of fluid-rock reaction to give an indication of likely long-term steady-state conditions. Changes in fluid chemistry will be monitored on a monthly/bimonthly interval. The overall lifetime of the experiments is likely to be in the order of a year, at which point the samples of reacted caprock will be extracted.
- 2) *Disaggregated Utsira caprock + synthetic porewater (long-timescales)*. The aim of these experiments is as above, but they will focus on longer timescales. Changes in fluid chemistry will not be monitored during the SACS-TFE project, but will be monitored as part of the CO2STORE project, and this is likely to be at 6 monthly intervals. The overall lifetime of the experiments is likely to be in the order of 2-3 years, at which point the samples of reacted caprock will be extracted.
- 3) *Intact piece of Utsira caprock partially exposed to damp CO₂*. The aim of these experiments will be to study possible changes in caprock mineralogy and ‘gross’ physical properties in the presence of *free* CO₂. The samples of Utsira caprock will be constrained within non-reacting holders/‘cups’ (probably made of titanium) so that only the end faces will be exposed to excess free CO₂. By placing the samples in holders it is hoped that they will be less likely to undergo possible disintegration. If a reasonably tight fit in the holders is achieved, then it is also hoped that reaction fronts (probably diffusion-controlled) may be observed away from the end surfaces exposed to CO₂. The overall lifetime of the experiments is likely to be in the order of 2-3 years, at which point the samples of reacted caprock will be extracted.
- 4) *Intact piece of Utsira caprock partially exposed to CO₂-saturated synthetic porewater*. The aim of these experiments is as above, but they will focus on *dissolved* CO₂. The equipment set-up will be very similar to the above experiments, but this time the caprock sample will be immersed in CO₂-saturated synthetic porewater. The overall lifetime of the experiments is also likely to be in the order of 2-3 years, at which point the samples of reacted caprock will be extracted.

All of the above experiments will use the same types of pressure vessels, only their internal layout will differ. When filled, all vessels will be placed into thermostatically controlled incubator (accurate to better than $\pm 0.5^{\circ}\text{C}$) and connected to the appropriate pressure line (Figure 3).

For experiments of type (1) and (2) above, a known quantity of disaggregated Utsira caprock will be added into the PTFE liners, followed by an aliquot of synthetic caprock porewater. At the time of writing this report (early September 2002) it is envisaged that a 10:1 porewater:solid mass ratio is likely to be used. The volume of the solid and aqueous samples is likely to fill about half of each vessel (see Figure 2). A small magnetic stirrer ‘bead’ will be added to each experiment to ensure solid and fluids are well mixed. Assembly of each vessel will involve placing the PTFE liner into the appropriate steel vessel, a fresh O-ring being inserted into its groove, a dip tube/filter assembly being fitted, and the lid of the vessel securely fastened down.

Good mixing between CO₂, porewater and disaggregated caprock will be achieved via the stirrer bead in each vessel. Although the bases of the stainless steel pressure vessels are in the order of 1 cm thick, this still allows for good ‘coupling’ between a magnetic stirrer and the stirrer bead. However, stirring the experiments does present a dilemma. Vigorous and continuous stirring would result in good mixing, but it could also mechanically degrade the solid sample. Conversely, little stirring would keep the sample relatively pristine, but mixing

would not be good and concentration gradients could result. It has been decided to adopt a compromise between these two extremes, and have several short periods of stirring a day, with a stirring speed just high enough to agitate any granular material. It is likely that two minutes of stirring will be used every 4 hours, which will be controlled via an electronic time switch.

Previous studies (Toews *et al.*, 1995) indicate that stable dissolved CO₂ concentrations can be obtained in high pressure water-CO₂ experiments within timescales as short as 30 minutes, though slightly longer timescales of just a few hours may be more realistic (Ellis and Golding, 1963; Stewart and Munjal, 1970; Czernichowski-Lauriol *et al.*, 1996). However, given the relatively long duration of the SACS-TFE batch experiments (months to years) and the relatively frequent stirring, it is reasonable to assume that the aqueous fluid within the experiments will be saturated with CO₂ at the pressure and temperature of the experiment.

For potential experiments of type (3) and (4) described above, a known quantity of intact Utsira caprock (\pm confining holder) will be placed into the PTFE liners. This will be placed above, or submerged within, an aliquot of synthetic caprock porewater (Figure 4). The purpose of the synthetic porewater in the type (3) experiments is not to react with the caprock sample, but to dampen the pressurising gas. A small magnetic stirrer ‘bead’ will be added to each experiment to ensure that the synthetic porewater and pressurising gas are well mixed. Assembly of each vessel will be similar to experiments of type (1) and (2) above, but no dip tube/filter assembly will be fitted.

All of the above experiments (types 1-4) will be accommodated in a single incubator (see schematic diagram in Figure 3). Pressure connections will be placed at the top of the vessels so that aqueous fluids (denser than compressed nitrogen or CO₂) cannot move between vessels. This arrangement means that only a single pump (for CO₂) and gas bottle (for N₂) are needed to maintain the system pressure.

The CO₂ for all the experiments (types 1-4) will usually be supplied to the experiments from an ISCO 260D syringe pump running in ‘constant pressure’ mode. Inert nitrogen gas will be supplied via a gas bottle using a single-stage regulator. The ISCO pumps are particularly useful for the ‘batch’ experiments, as they automatically adjust themselves for changes in gas volume. This is especially useful at the start of the CO₂ experiments where the CO₂ is first being warmed (increasing in volume) and dissolving in the porewater (decreasing in volume). The ISCO computerised controllers can allow pressure control to within 0.1 bar. The integral pressure transducer on the ISCO pump will be regularly ‘zeroed’ to maintain accuracy, and will be checked periodically against an externally calibrated pressure transducer.

The ‘blank’ experiments pressurised by nitrogen will utilise a regulator connected to a gas cylinder. Control of (single stage) regulators at the pressures that will be used during this study can be somewhat coarse. However, the line pressure will be monitored via a secondary pressure transducer, and this will be checked against an externally calibrated pressure transducer. Past experience with the equipment indicates that if care is taken, gas pressure can be controlled (by regulator) to within about 1 bar of the desired value.

4 Sampling and analysis

4.1 SAMPLING PROCEDURE

4.1.1 Experiments using samples of disaggregated Utsira caprock

The sample handling procedure will be similar to that used previously (Rochelle *et al.*, 2002). Samples from both CO₂-pressurised and N₂-pressurised experiments are treated in the same way. In essence, this will involve withdrawing a sample of gas-saturated aqueous fluid up the dip tube shown in Figure 2, and along ¹/₈ inch diameter PEEK (polyetherethylketone) pressure tubing and out of the oven. This results in a cooling of the sample to room temperature (approximately 20°C). This is advantageous, in that gas solubilities generally increase at lower temperatures (e.g. for CO₂ see Kuk and Montagna, 1983), and so problems due to degassing are likely to be reduced. The pipe work to the sampler will be flushed initially with a few ml of sample, then the (gas-rich) aqueous sample withdrawn into either; a titanium floating piston sampler, or a syringe (see Figure 5). If it is deemed necessary that degassing be prevented, sampling will be done under constant pressure conditions using the titanium floating piston sampler. Whichever method of sampling is used, the sample will be taken slowly (over a few minutes) to prevent degassing within the internal filter assembly. Too rapid sampling may also enhance possibly clogging of the filter by fine material.

It is possible that some samples will be taken for the analysis of total dissolved carbon. This will involve reacting some of the gas-rich solution with NaOH solution at the experimental pressure (previous experience has shown that 4 molar NaOH works well [Czernichowski-Lauriol *et al.*, 1996; Rochelle and Moore, 2002; Rochelle *et al.*, 2002]). The basis behind this approach is to convert all dissolved carbon species (e.g. HCO₃⁻, CO_{2(aq)} and H₂CO₃) to carbonate (CO₃²⁻) by increasing the pH to hyperalkaline conditions:



If the pH is high enough, these equations lie so far to the right that depressurisation does not cause significant loss of carbon through the formation of CO_{2(g)}.

Once a sufficient number of samples have been obtained (over a period of several months), as much as possible of the remaining fluid inside the vessel will be removed. The rationale behind this is to minimise the potential for carbonate mineral precipitation as a result of the solution degassing (this would be an artefact of sampling). The (hopefully only slightly) damp solid will then be depressurised slowly by venting the pressurising gas. This process is likely to take 5-10 minutes.

4.1.2 Experiments using samples of intact Utsira caprock

These experiments are simpler to sample than those described above, in that possibly just a single fluid sample will be taken at the end of each experiment. When an experiment is complete, it will be depressurised slowly and carefully by venting the pressurising gas. If depressurisation is faster than the rate at which gas can escape from the intact sample, then damage to the sample may result. At the time of writing this report (early September 2002) it is not clear exactly how slowly this process will have to be done (though it may have to be over several days). It is hoped that short-term tests as part of CO2STORE will provide the necessary information prior to the termination of the long-term experiments.

4.2 PREPARATION OF EXPERIMENTAL PRODUCTS

The following sub-sections describe the most likely sample handling procedures that will be used during the study. However, it may also be necessary to use slightly different methodologies, and any such differences will be noted in subsequent reports. Differing approaches may be necessary, for example, to preserve unexpected run products (e.g. delicate precipitates), or to preserve fluid samples for less usual analyses (e.g. trace heavy metals).

4.2.1 Solid products

On opening a batch pressure vessel, its PTFE liner containing the sample of reacted solid will be removed. In the case of the disaggregated material, it is likely to be split into several subsamples depending on the type of analysis required. These subsamples could include; washed, unwashed, air dried and freeze dried. Once dry, the samples are likely to be placed into an airtight container prior to mineralogical analysis.

4.2.2 Fluid samples

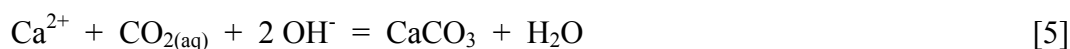
For the experiments utilising disaggregated Utsira caprock, two types of samples may be taken. One will involve depressurisation (and hence loss of dissolved gases), but the solution is relatively straightforward to analyse. The other involves capture of dissolved CO₂ by preservation with excess alkaline solution, but the resulting mixture is relatively less straightforward to analyse.

Depressurisation sample

After depressurisation, each of the reacted fluids will be split into several sub-samples. A sub-sample of 1 ml will be taken for immediate analysis of pH. Another sub-sample will be taken using a polythene syringe and filtered using a 0.2 µm 'Anotop'® nylon syringe filter. A volume (in the order of 4-8 ml) of this sample will be placed into a polystyrene tube, diluted with a similar volume of distilled de-ionised water, and acidified with 1% of concentrated 'ARISTAR'® nitric acid. This will be analysed subsequently for major and trace cations by inductively coupled plasma - optical emission spectroscopy (ICP-OES). A further aliquot of this filtered sample (in the order of 2-4 ml) will be taken and placed in a polystyrene tube, diluted with a similar volume of distilled de-ionised water, and analysed for anions by ion chromatography (IC). Samples will be stored in a fridge (at about 5°C) prior to analysis.

Alkali preserved sample

This will involve first filling a titanium floating piston sampler (see Figure 5) approximately half full of 4M NaOH solution - the alkali conditions ensuring that all dissolved C species (mainly CO_{2(aq)}, H₂CO₃ and HCO₃⁻) will be converted into CO₃²⁻. The remainder of the sampler volume is then filled with gas-rich sample fluid at the experimental pressure. After standing for approximately 10 minutes (with occasional shaking) the sample will be depressurised. Previous experience shows that well-collected samples undergo with minimal degassing at this stage. However, previous experience has also shown that samples rich in dissolved Ca may go 'cloudy' when mixed with NaOH – probably due to the precipitation of either portlandite (Ca(OH)₂) or calcite (CaCO₃):



At the time of writing this report (early September 2002) work is underway to assess the relative contribution of both of the above solids to the precipitate. If calcite is found to be a major component in the precipitate, then this will need to be taken into account when

calculating the total amount of carbon in the aqueous phase within the experiment. The precipitate may be very fine and hard to filter. If it does form, the solution will probably be left for several hours to allow it to settle. The relatively clear sample fluid can then be filtered easily using a 0.2 μm ‘Anotop’[®] nylon syringe filter and placed into a polystyrene tube. It will then be stored in a fridge (at about 5°C) prior to analysis by titration against sulphuric acid. This analysis will provide a determination of total dissolved inorganic carbon, of which approximately 99% is likely to be dissolved CO₂ (van Eldik and Palmer, 1982).

Dilution factors between gas-saturated synthetic porewater and 4M NaOH solution are calculated based on measured Cl⁻ content of the synthetic formation water and the mixed synthetic formation water/4M NaOH solution - the 4M NaOH solution effectively containing none of this element.

4.3 ANALYTICAL TECHNIQUES

Standard methods of analysis of solid and liquid samples will be employed in this study. In brief, appropriate fluid samples will be taken for chemical analysis of major (\pm some minor) cations using inductively coupled plasma - optical emission spectroscopy (ICP-OES), and for all major (\pm some minor) anions using ion chromatography (IC). Other types of analyses will be used as necessary (e.g. inductively coupled plasma - mass spectroscopy (ICP-MS) for trace cations). Mineralogical analyses will utilise standard techniques that are likely to include; conventional optical microscopy, scanning electron microscopy (SEM), X-ray diffraction (XRD), and electron probe micro analysis (EPMA).

pH measurements will be made on cooled and depressurised samples using an Orion[®] 900A pH meter calibrated using Whatman[®] NBS traceable buffers at pH 7, 10 and 13. However, if practicable (constrained by time and sample volume) another technique may also be applied. This effectively monitors the colour change of an aqueous pH indicator solution (e.g. bromophenol blue) using a UV-visible spectrometer. Although somewhat more complex than conventional methods, it has the advantage that it can be used at elevated temperatures and pressures (Toews *et al.*, 1995; Faanu, 2001), and so can provide an indication of *in-situ* pH. Determination of pH is based upon calibration against known citric acid/NaOH pH buffers.

Details of elements/species that might be analysed for, their typical detection limits, and their associated analytical errors are given in Table 2. The errors are based on long-term internal quality control standards. However, there are a couple of points that are worth noting:

- 1) The actual detection limit of any element/species will depend on whether the sample had to be diluted prior to analysis. For example, the *apparent* detection limit of a particular analyte for a sample diluted by a factor of 10, will be 10 times *greater* than for an undiluted sample.
- 2) The uncertainty (error) associated with a single analytical datum will depend upon how close that value is to the detection limit for that analyte. For example, a useful ‘rule of thumb’ is as follows:

Nearness to detection limit	Degree of uncertainty/error
<10x detection limit	>10%
~10x detection limit	10%
~10-100x detection limit	5-10%
>100x detection limit	<5%

5 Possible future experiments

The experimental study detailed above aims to study geochemical processes and reactions occurring over months to a few years. The experiments will be initiated under the SACS-TFE project, but will be terminated and sampled under the CO2STORE project. By starting the experiments early, it is hoped that they can be studied over timescales not possible within just the CO2STORE project. It is planned that other, shorter-term, experiments will be undertaken as part of the CO2STORE project. Although the focus of these future projects is still to be finalised, it is useful to outline possible experiments and what they might address. The following list briefly describes some possible future experiments:

- 1) *Disaggregated Utsira caprock + synthetic porewater (short-timescales)*. The aim of these experiments would be to study possible changes in fluid chemistry and caprock mineralogy in the presence of *dissolved* CO₂. The experiments would maximise the rate of fluid-rock reaction to give an indication of likely long-term steady-state conditions. Changes in fluid chemistry could be monitored on a weekly interval. The overall lifetime of the experiments could be in the order of a few months, at which point the samples of reacted caprock would be extracted. These ‘batch’ experiments would provide shorter-timescale data to those conducted under the SACS-TFE project, and the combined dataset should dovetail together to give information on processes occurring over a few days to a few years.
- 2) *Intact piece of Utsira caprock partly exposed to dry CO₂*. The aim of these experiments would be to study possible changes in ‘gross’ physical properties in the presence of *free* CO₂. In particular, shrinkage phenomena could be studied as a result of dehydration by dry CO₂. The experiments would utilise a disc of Utsira caprock contained within a high pressure ‘view cell’ so that visual observations of the caprock could be made. The overall lifetime of the experiments is likely to be in the order of a few months, at which point the samples of reacted caprock will be extracted.
- 3) *Disaggregated Utsira caprock + synthetic porewater (high temperatures)*. The aim of these experiments would be similar to (1) above. However, geochemical reactions may be slow at *in-situ* temperatures, and these may hinder the study of reaction processes. Heating the experiments would increase reaction rates, and would allow the temperature dependence of the reactions to be studied. However, care would be needed during interpretation of the results in case unrepresentative secondary phases formed during the experiment.
- 4) *Pure mineral separates*. It may be necessary to understand the reaction mechanisms of a particular mineral or minerals in greater detail (e.g. if of particular importance). Samples of pure mineral could be obtained (not necessarily from the Utsira caprock, but from elsewhere in the world) and reacted under a variety of conditions. Detailed analysis of reaction products could provide information on reaction mechanisms, rates of reaction, and possibly long-term steady-state conditions.

6 Conclusions

An experimental study is being undertaken to react CO₂ with samples of Utsira caprock from the Sleipner field and synthetic formation waters. The aim of this study is to investigate the potential for CO₂-porewater-caprock interaction above the stored CO₂. Quantitative data will be produced relating to the direction, rate and magnitude of any reactions. It is hoped that this will help predictive modelling exercises by providing well-constrained test cases with which to compare the models.

A range of experiments are being conducted in 'batch' equipment at a pressure of 8 MPa (80 bar) and at a temperature of 30°C. Durations of the experiments are likely to range from several months to a few years. This report describes the experiments, and typical procedures for setting them up and sampling them. Deviations from these methods will be noted in future reports, which will also detail the results from various of the experiments.

References

- Atkins, P.W. (1982). *Physical Chemistry* (2nd edition), Oxford University Press, Oxford, UK, ISBN 0-19-855151-7, 1095p.
- Bachu, S., Gunter, W.D. and Perkins, E.H. (1994). Aquifer disposal of CO₂: hydrodynamic and mineral trapping. *Energy Conversion and Management*, 35, 269-279.
- Czernichowski-Lauriol, I., Sanjuan, B., Rochelle, C., Bateman, K., Pearce, J. and Blackwell, P. (1996). Area 5: Inorganic Geochemistry, Chapter 7 in 'The underground disposal of carbon dioxide' (S. Holloway ed.). Final report for the CEC, contract number JOU2-CT92-0031. Published by the British Geological Survey.
- Ellis, A.J. and Golding, R.M. (1963). The solubility of carbon dioxide above 100°C in water and in sodium chloride solutions. *American Journal of Science*, 261, 47-60.
- Faanu, A. (2001). Spectroscopic determination of pH. MSc project report, University of Nottingham.
- Gunter, W.D., Perkins, E.H., Bachu, S., Law, D., Wiwchar, B., Zhou, Z. and McCann, T.J., 1993. Aquifer disposal of CO₂-rich gases. Alberta Research Council report, C-1993-5.
- Kuk, M.S. and Montagna, J.C. (1983). Solubility of oxygenated hydrocarbons in supercritical carbon dioxide. In: 'Chemical Engineering at Supercritical Fluid Conditions', Ann Arbor Science, Ann Arbor, MI, USA, 101-111.
- Pitzer, K.S. (1991). *Activity Coefficients in Electrolyte Solutions* (2nd edition), CRC Press Inc., Boca Raton, Florida, USA, ISBN 0-8493-5415-3, 542p.
- Rochelle, C.A., Bateman, K. and Pearce, J.M. (2002). Geochemical interactions between supercritical CO₂ and the Utsira formation: an experimental study. British Geological Survey Commissioned Report (commercial-in-confidence), CR/02/060, 57 p.
- Rochelle, C.A. and Moore, Y.A. (2002). The solubility of CO₂ into pure water and synthetic Utsira porewater. British Geological Survey Commissioned Report, CR/02/052. 23 pp.
- Schremp, F.W., and Roberson, G.R., 1975. Effect of supercritical carbon dioxide (CO₂) on construction materials. *Soc. of Petroleum Engineers Journal*, June edition, p. 227-233.
- Sloan, E.D. Jr. (1998). *Clathrate Hydrates of Natural Gases*, (2nd edition), Marcel Dekker Inc., New York, ISBN 0-8247-9937-2, 697p.
- Stewart, P.B. and Munjal, P.K. (1970). The solubility of carbon dioxide in pure water, synthetic sea water and synthetic sea-water concentrates at -5 to 25°C and 10 to 45 atm pressure. *Journal of Chemical Engineering Data*, 15(1), 67-71.
- Toews, K.L., Shroll, R.M. and Wai, C.M. (1995). pH-defining equilibrium between water and supercritical CO₂. Influence on SFE of organics and metal chelates. *Analytical Chemistry*, 67, 4040-4043.
- van Eldik, R. and Palmer, D.A. (1982). Effects of pressure on the kinetics of the dehydration of carbonic acid and the hydrolysis of CO₂ in aqueous solution. *Journal of Solution Chemistry*, 11(5), 339-346.

Figure 1 Phase diagram for CO₂ (based upon Atkins, 1982).

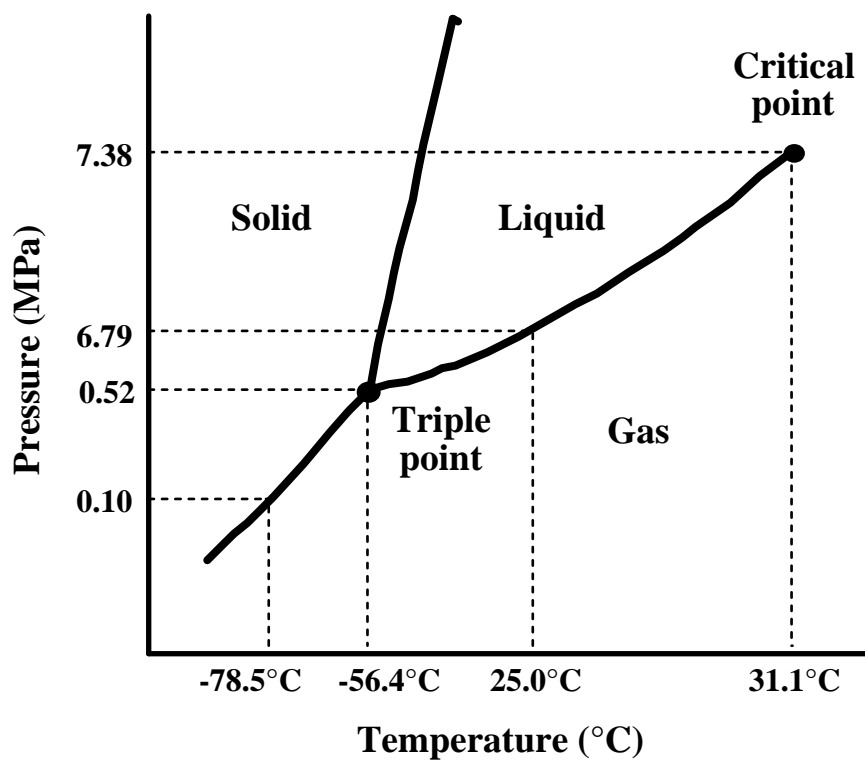


Figure 2a Schematic diagram showing a new design batch reactor that will be used for CO₂-porewater-caprock experiments.

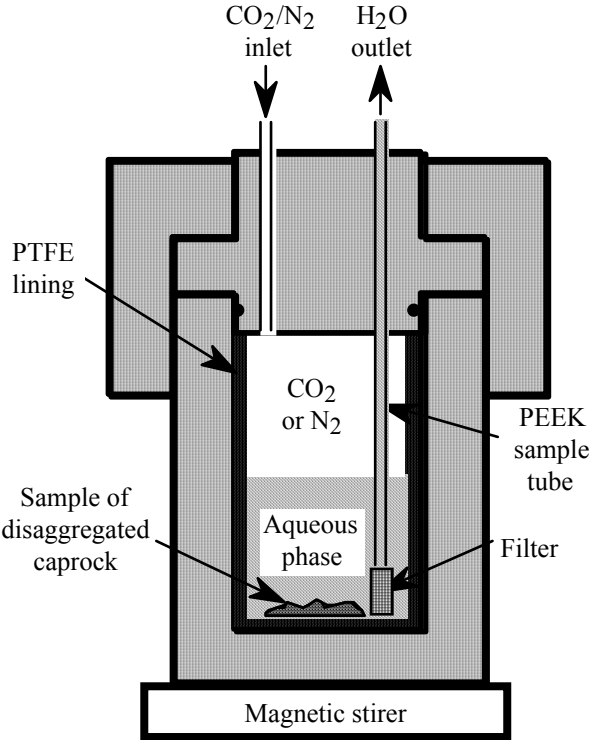


Figure 2b Comparison schematic diagram showing a typical batch reactor used for previous experimental studies with Utsira sand (see Rochelle *et al.*, 2002).

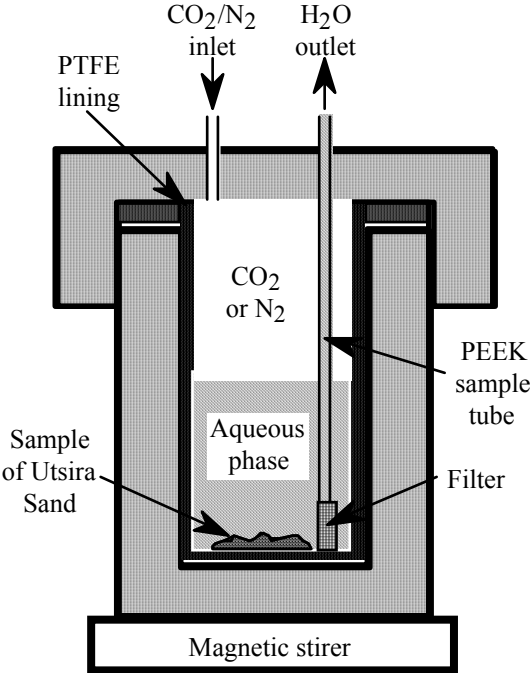


Figure 3 Schematic diagram showing the typical layout for a series of batch experiments.

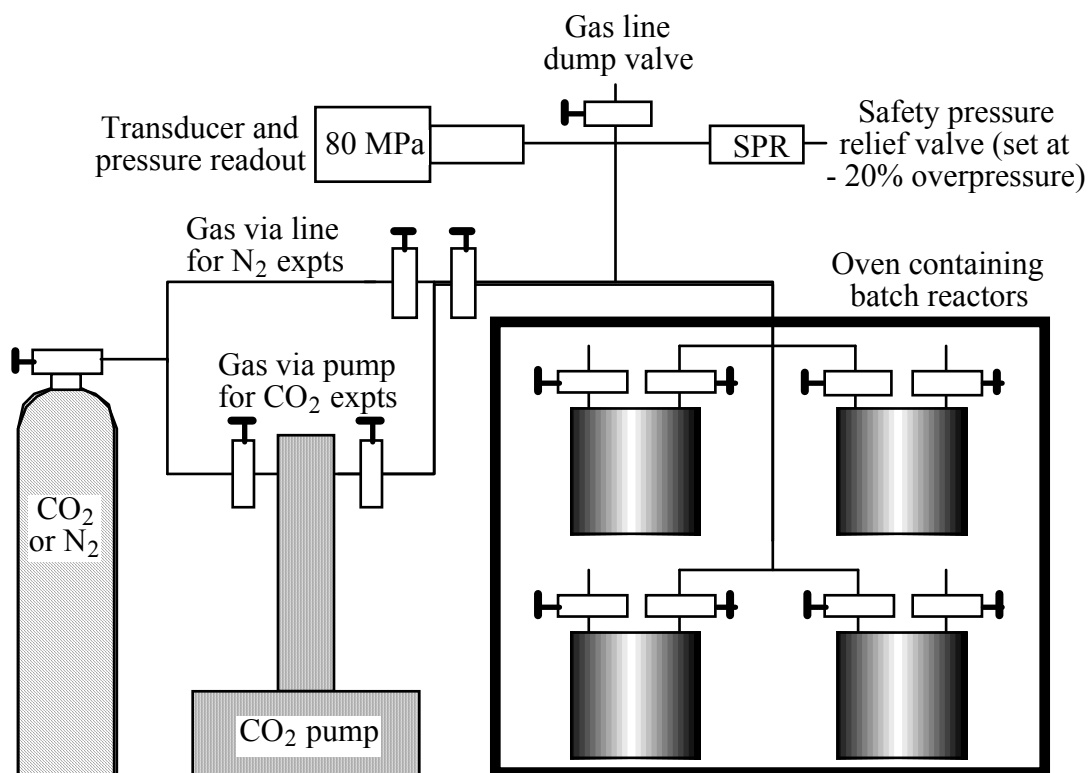


Figure 4 Schematic diagram showing a typical batch reactor used for studying the impact of ‘damp’ CO₂ on intact samples of caprock. Note that the CO₂-saturated synthetic porewater experiments are similar, but the caprock sample is covered by the aqueous phase.

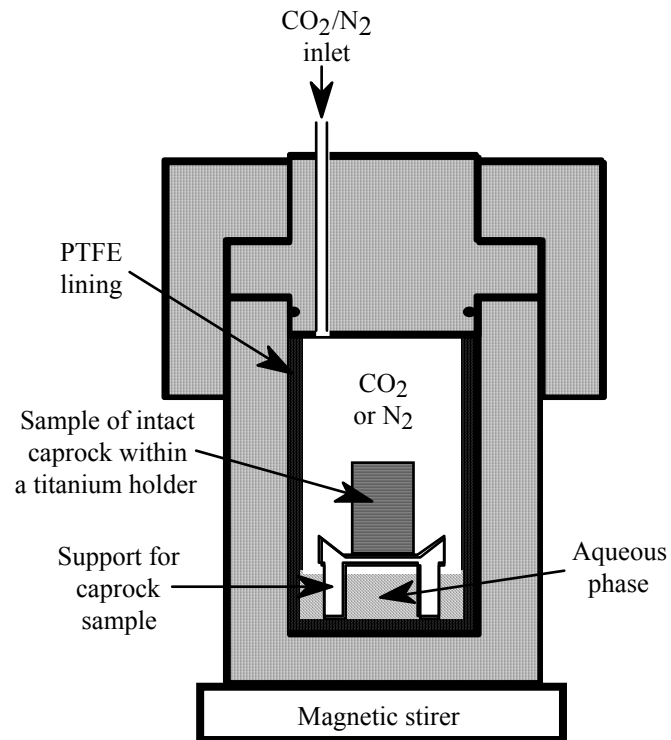


Figure 5 Schematic diagram showing the typical method of sampling aqueous fluids from a batch reactor.

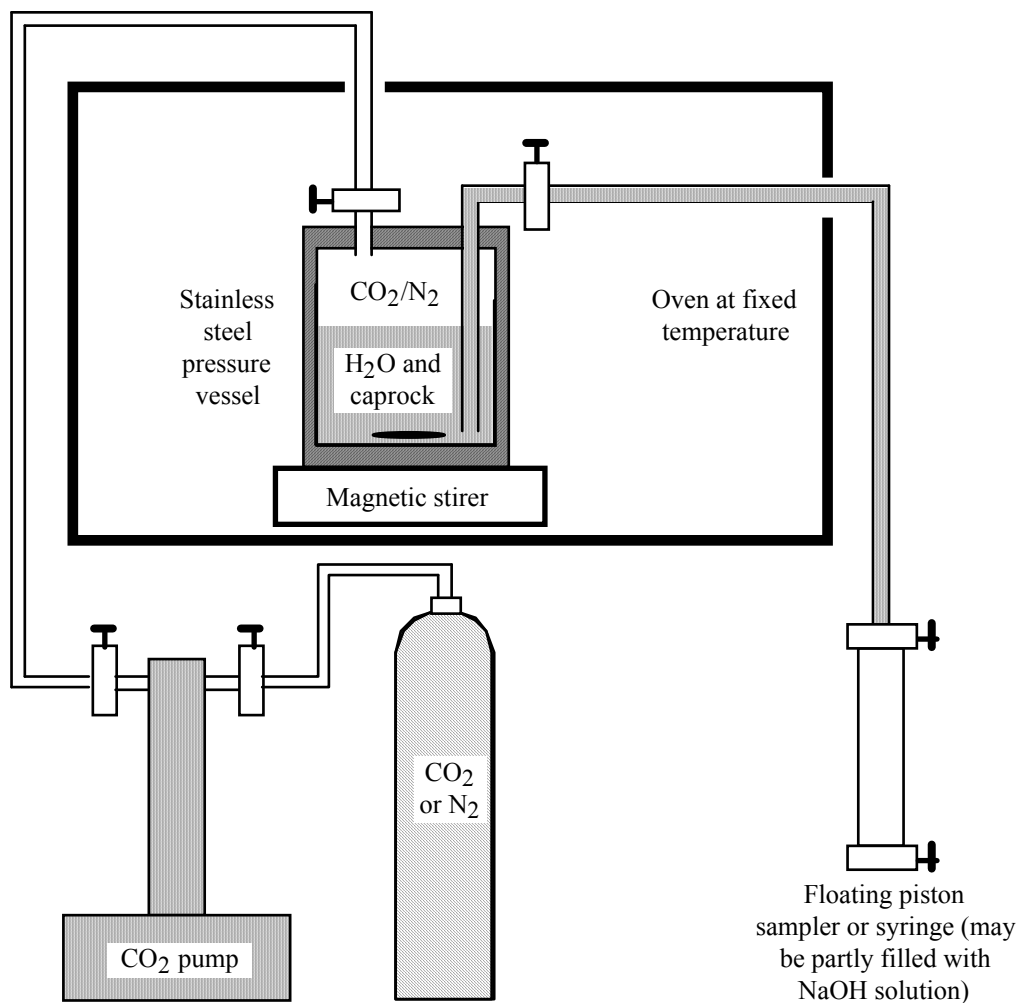


Table 1 'Recipe' used for making synthetic Utsira porewater. It was called 'Synthetic Utsira Porewater 2', or 'SUP2' for short.

Compound	Weight of compound added (g) per litre of distilled, de-ionised water	
	Recipe	Actually added
KCl	0.3966	0.3966
CaCl ₂ .2H ₂ O	1.5627	1.5627
MgCl ₂ .6H ₂ O	5.2693	5.2685
SrCl ₂ .6H ₂ O	0.0304	0.0305
BaCl ₂ .2H ₂ O	0.0009	0.0009
NaHCO ₃	0.7880	0.2157 *
FeCl ₃ .6H ₂ O	0.0097	0.0097 **
NaCl	25.8676	25.8679

- * A weighing error appears to have resulted in slightly less NaHCO₃ being added than was in the recipe. However, the impact of this is thought to be very minor given that vastly more Na was added as NaCl, and that the dissolved inorganic carbon concentration (i.e. primarily CO_{2(aq)} and HCO₃) will change rapidly in the experiments through reaction with shell fragments and excess high pressure CO₂.
- ** After the solution had been standing for a while, a yellow/brown precipitate was observed at the bottom of the container. It is thought that this was a Fe^{III}-phase precipitate, and the solution was filtered to remove it. As a consequence, the total dissolved Fe concentration may well have been less than was originally aimed for.

Table 2 Information on the 4 samples of Utsira caprock sent to the BGS.

Drilled (uncorrected) depth (metres)		Vertical depth below sea level (metres)	Use
Top of core	Bottom of core		
906.00	906.20	784.0	Porewater (\pm slight possibility of disaggregated sample for use in geochemistry experiments), mineralogy, petrology.
907.40	907.60	785.0	Block for gas transport experiments, blocks for geochemistry experiments, mineralogy, petrology.
908.80	909.00	786.2	Some for porewater extraction, the rest to be left intact for possible use at a later date.
910.20	910.40	787.3	Porewater (+ disaggregated sample for geochemistry experiments), block for gas transport experiments mineralogy, petrology.

Table 3 Listing of a range of possible analytes, instrument detection limits, likely detection limits given likely dilution factors, and an estimation of uncertainty (note that other analytes will probably be studied, and these will be detailed in later reports).

Analyte	Detection limits (instrument)# (mg l ⁻¹)	Likely detection limits #		Likely percentage ± uncertainty †
		mg l ⁻¹	mol l ⁻¹	
Li	0.025	0.5	7.2 x 10 ⁻⁵	10
Na	0.35	7	3.0 x 10 ⁻⁴	<5
K	0.5	10	2.6 x 10 ⁻⁴	<5
Mg	0.01	0.2	8.2 x 10 ⁻⁶	<5
Ca	0.1	2	5.0 x 10 ⁻⁵	<5
Sr	0.002	0.04	4.6 x 10 ⁻⁷	<5
Ba	0.002	0.04	2.9 x 10 ⁻⁷	<5
Mn	0.002	0.02	3.6 x 10 ⁻⁷	5-10
Total Fe	0.01	0.2	3.6 x 10 ⁻⁷	5-10
Cr	0.002	0.04	7.7 x 10 ⁻⁷	10
Al	0.01	0.1	3.7 x 10 ⁻⁶	10
Total P	0.01	0.1	3.2 x 10 ⁻⁶	10
Total S	0.25	2.5	7.8 x 10 ⁻⁵	5-10
Si	0.075	0.75	2.7 x 10 ⁻⁵	5-10
SiO ₂	0.16	1.6	2.7 x 10 ⁻⁵	5-10
Cl ⁻	0.1	2	5.6 x 10 ⁻⁵	<5
Br ⁻	0.03	6	7.5 x 10 ⁻⁵	5
NO ₃ ⁻	0.04	0.8	1.3 x 10 ⁻⁵	5-10
SO ₄ ²⁻	0.3	60	6.3 x 10 ⁻⁴	10
HCO ₃ ⁻	22	22	3.6 x 10 ⁻⁴	5
CO ₃ ²⁻	22	22	3.6 x 10 ⁻⁴	<5
TOC	1	3.6	3.0 x 10 ⁻⁴	5

Limits of quantification can be described in more than one way. Firstly there is the actual instrument limit for an 'ideal' dilute solution. However, more concentrated solutions (i.e. saline porewaters) have to be diluted prior to analysis as high concentrations of total dissolved solids cause analytical problems. Dilution causes an effective worsening of the detection limits. During this study, samples are likely to be diluted 10x or 20x prior to analysis.

† Illustrative uncertainties considered 'typical' for the concentration ranges likely to be found in this study. Concentrations <10x the detection limit have uncertainties ≥10%, concentrations >10x the detection limit have uncertainties typically ≤5%.

NA Not applicable, as element was below the detection limit.