

SUMMARY REPORT

WORK AREA 3 - GEOCHEMISTRY

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This specific report is a summary of the geochemical work area of the SACS2 project. It will be included into the EU Final Technical Report of the Project.

1. Introduction

This specific report is a summary of the geochemical work carried out within the SACS/SACS2 project. Preliminary results were presented by Pearce *et al.* (2000) and Czernichowski-Lauriol *et al.* (2001).

The objective of the geochemical work within the SACS project was to determine the potential for chemical reactions between injected CO₂, formation water and the reservoir rock (Utsira sand), as these reactions may affect injection operations and long term CO₂ storage potential (Czernichowski-Lauriol *et al.*, 1996 a,b). For example, besides being trapped as a buoyant supercritical CO₂ 'bubble' (*physical trapping*), geochemical reactions with reservoir rock and formation water can trap the CO₂ as a dissolved phase (*solubility trapping*), as bicarbonate ions and complexes (*ionic trapping*), and carbonate minerals (*mineral trapping*), according to a terminology derived from Bachu *et al.* (1994). This can enhance the CO₂ storage capacity and have consequences on CO₂ migration or immobilisation.

A direct approach was used, based on laboratory experiments reacting samples of Utsira sand and formation water with CO₂ under simulated reservoir conditions for timescales up to 24 months. Work was divided into three tasks:

- determination of the initial state of water-rock interaction within the Utsira formation prior to CO₂ injection,
- laboratory experiments on actual Utsira material,
- numerical modelling for the interpretation of the experiments.

Such laboratory investigations are particularly useful for the study of shorter-term processes. Although limited in scale and timeframe, laboratory experiments have the advantage that they can help to identify the key geochemical reactions on actual rock material under actual reservoir conditions, which is very important as such reactions are known to be highly site-specific. They are also helpful to test the ability of geochemical codes to reproduce the experimental observations before using them to make long term predictions over experimental timescales up to thousands of years.

The geochemical partners involved in this study were two experimental groups (BGS and GEUS) and two modelling groups (BRGM and IFP). BRGM was co-ordinator of the geochemical work area.

2. Determination of the initial state of water-rock interaction within the Utsira formation prior to CO₂ injection

The objective of this task was to assess the 'baseline' conditions of mineralogy, fluid chemistry and water-rock interaction prior to CO₂ injection. Only with this information can changes due to the presence of CO₂ be assessed.

At the start of the SACS study only limited geochemical information and samples were available from the Utsira Sand. This included:

- A single (partial) analysis of Utsira formation water from the Oseberg field approximately 200 km north of Sleipner

- A 7 m core of Utsira Sand from the Sleipner field, well 15/9-A-23 (of which 1 m sections of frozen core supplied to the geochemists).

The core sample allowed for detailed mineralogical analyses and determination of transport properties. However, the core sample was heavily contaminated by drilling fluids, and no useable formation water sample could be obtained from it. Only one borehole terminates in the Utsira at Sleipner (the CO₂ injection borehole), and unfortunately no produced porewater samples were available from it.

Although there is a single analysis of Utsira porewater from the Oseberg field, it is limited by the lack of analyses of Al and Si. For predictive modelling, it was therefore necessary to assume that these elements were controlled by saturation with respect to specific minerals – in this case kaolinite and chalcedony.

However, during the study, a surface sample of formation water from the Brage field (also about 200 km north of Sleipner) was obtained (but without information on the gas phase) and analysed for a range of elements (including Al and Si). However, the sample was unpreserved (unfiltered and un-acidified) and the Al and Si analyses look problematic.

Figure 1 summarizes the geochemical data available at the time of the project. Despite this lack of information and samples, a reasonable assessment of baseline conditions within the Utsira sand was made by combining information from the Sleipner, Oseberg and Brage hydrocarbon fields, and through numerical modelling and the results of ‘blank’ experiments as mentioned later.

A roughly homogeneous porewater chemical composition throughout the Utsira formation was reasonably assumed. Direct measurements of Utsira fluid salinity are in agreement with this choice (in the range 33-43 g/l at the Sleipner, Grane, Oseberg and Brage fields). Then the decision of using the Oseberg analysis as representative of the Utsira formation is presently an acceptable compromise.

Presently available data and geochemical modelling using the EQ3/6 (Wolery, 1995) and SCALE2000 (Azaroual *et al.*, 2002) codes were used to define:

- a typical in-situ porewater composition
- a typical mineralogical assemblage that controls initial fluid chemistry

However the scarcity of the data and the fact that the water analysis and the mineralogical description do not refer to the same location prevent from being able to do a precise and reliable assessment of the baseline geochemistry at Sleipner. The need for acquiring new data and samples is emphasized.

3. Laboratory experiments

The objective of this task was to identify the key geochemical reactions (direction, magnitude and rate) between injected CO₂, formation water and the reservoir rock (Utsira sand) at Sleipner, and provide test cases to improve the ability of geochemical modelling to make accurate predictions. Various sets of experiments were carried out reacting samples of Utsira sand and Synthetic Utsira Porewater with CO₂ under simulated reservoir conditions (37°C, 10 MPa) for timescales from a week to 24 months.

Both static batch experiments and dynamic coreflood experiments were used. Batch experiments can highlight the potential for reaction of samples of reservoir rock when in contact with CO₂ at reservoir temperature and pressure, over different timescales. Coreflood experiments are aimed at reproducing open systems where the rock is continuously flooded by porewater rich in injected CO₂, which represents more

closely actual reservoir conditions. They may elucidate inter-relationships between geochemical and hydrodynamic processes, and overall observable reaction may well be higher than in batch experiments.

Batch experiments were undertaken in pairs; one pressurised with CO₂ and a 'blank' pressurised with an inert gas, N₂. This is important to help distinguish purely-CO₂-related effects from any experimental artefacts, and thus increase confidence in the assessment of the geochemical impact of injected CO₂. The blank experiment was also useful for finding out how close the Synthetic Utsira Porewater was to equilibrium with the Utsira sand; in other words, the data from these experiments could help to compensate for the lack of information on baseline geochemistry at Sleipner.

3.1. CO₂ solubility measurements (37-70°C and 8-12 MPa)

A range of experimental measurements have been undertaken to provide CO₂ solubility data to help constrain geochemical modelling activities and to further our understanding of how much of the injected CO₂ will dissolve into the Utsira formation water. The experimental conditions chosen were between 18-80°C and 8-12 MPa, with most data generated at 37°C and 10 MPa (in-situ temperature and pressure in the Utsira formation at Sleipner). The approach taken was to equilibrate a stirred aqueous sample with a known pressure of CO₂, at a known temperature, for at least 24 hours.

There have been several previous experimental studies of CO₂ solubility in both pure water and seawater/brines (e.g. Ellis and Golding, 1963; Kuk and Montagna, 1983; Takenouchi and Kenedy, 1965) though the conditions that were used in many studies do not exactly represent the conditions at Sleipner (e.g. pressure, temperature, porewater composition etc). Therefore, a limited number of experiments have been performed on synthetic Utsira porewater (based upon a composition from the Oseberg field) and distilled de-ionised water to:

- Provide direct evidence for the solubility of CO₂ within the Utsira formation at Sleipner,
- Allow comparison of the results with extrapolations from previous experimental data.

Measured CO₂ solubility values in distilled de-ionised water follow trends that are similar to previous studies. However, at a more detailed level, the solubility values obtained were approximately 10% lower than expected. The exact reason for this reduction is not totally clear at this point, though it is possible that it may be due to the sensitivity of pure water to degassing prior to preservation. At 37°C and 10 MPa, measured solubility is in the order of 5.1 g of CO₂ per 100 g of water.

Measured CO₂ solubility in synthetic Utsira porewater is broadly in line with previous studies, though relevant literature data are very sparse. Solubility values are lower than those obtained for distilled de-ionised water. At 37°C and 10 MPa, measured solubility is in the order of 4.5 g of CO₂ per 100 g of solution.

3.2. CO₂ reaction with Utsira sand (37°C and 10 MPa, 70°C and 10 MPa, 1 week to 2 years duration)

A range of experiments have been conducted in either 'batch' and 'flow through' equipment to react samples of Utsira sand from Sleipner with a synthetic Utsira porewater based upon a composition from the Oseberg field. A schematic diagram of the batch reactor is presented on Figure 2. The experimental conditions chosen were mainly 37°C and 10 MPa (in-situ temperature and pressure in the Utsira formation at Sleipner), though some experiments were run at 70°C and 10 MPa to enhance the rates of reaction. Durations ranged from one week to two years. Experiments were pressurised with either nitrogen or carbon dioxide. The former provided a 'non reacting' reference point from which to compare the more reactive experiments containing CO₂. However, they also helped provide confidence in the baseline conditions within the Utsira formation

prior to CO₂ injection. The CO₂ experiments provided direct information on how CO₂ reacted with the Utsira sand and its porewater.

Most of the observed reactions were deduced from fluid chemical changes associated mainly with dissolution of primary minerals. Overall however, observed CO₂-water-rock reactions have resulted in relatively little dissolution of the Utsira sand.

Batch experiments at 37°C and pressurised by N₂ showed relatively few changes in aqueous chemistry relative to the starting fluid. To a first approximation therefore, the initial assumption that the Utsira porewater from the Oseberg field was similar to the Utsira porewater at Sleipner would appear to have been valid. However, closer inspection of the data reveals some differences that will help refine models of the original geochemical 'baseline' at Sleipner.

Batch experiments at 37°C and pressurised by CO₂ show the impact that storage operations will have on the porewater chemistry. Dissolution of carbonate phases led to large increases in concentrations of Group II metals (and in particular Ca, Sr and Fe). This process appears to have been relatively rapid, and for the 10:1 fluid:rock ratio batch experiments, was essentially complete after 2 months of reaction. Dissolution of silicate minerals was a much slower process, and was still ongoing (though at a reduced rate) after 2 years of reaction. As SiO₂ concentrations increased faster for the CO₂ experiments than for the 'blank' experiments, this suggests that the dissolution of silicate or aluminosilicate minerals is enhanced by CO₂.

In spite of the observed changes in solution chemistry, which suggests mineral dissolution (and in particular a Ca-carbonate phase), mineralogical analysis provided little evidence that any such reactions occurred. Pitting and corrosion features are observed on all the main detrital components of the sand (quartz, feldspar and Ca-carbonate bioclasts), with apparently equal prominence in both the samples reacted in a CO₂-rich environment and those from the N₂ 'blanks'. These features are therefore taken to represent primary features of the Utsira Sand. Furthermore, it is possible to find both lightly and highly corroded bioclasts within the same sample from either CO₂-reacted experiments or blank experiments. This indicates that observed changes in fluid chemistry must be attributable to mineral dissolution reactions whose extent is lost within the 'noise' of natural mineralogical variation within the sand.

The 10-month duration coreflood experiment did not bring additional information. Although reproducing a more-reactive open system and although carried out at 70°C approximately twice the actual in-situ temperature to enhance the mineral reaction rates, no mineralogical changes have been observed as any reactions which have occurred in response to exposure to CO₂ appear to be below the resolution of the SEM analytical technique.

The experiments appear to show that the Utsira sand is only likely to undergo limited reaction with the injection of CO₂. Most of the observed reactions involve dissolution of a carbonate phase (much of which is probably shell fragments), half of which was observed to dissolve over a 2 year period under in-situ conditions (37°C, 10 MPa). However, sand porosity is approximately 40%, and as carbonates only constitute 3.9% of the total rock volume, dissolution of half of them will not change overall porosity by a large degree. There was no direct evidence for the formation of appreciable quantities of secondary precipitates during the timescales of the experiments.

3.3. Detailed investigations on changes of mineralogical and petrophysical properties of Utsira sand in contact with CO₂ (37°C and 10 MPa, 2-4 weeks duration)

Analysis of core material from the Utsira sand has been undertaken to characterize mineralogical and petrophysical properties before and after reaction with CO₂-saturated formation water. Most experiments

were performed as short term (2-4 weeks) dynamic flooding tests at overburden or reservoir conditions, 10 MPa net effective stress, 10 MPa pore pressure and 37 °C. The analytical programme involved the following characterization:

- Mineralogy before and after reaction with CO₂-saturated formation water
- Surface properties before and after reaction with CO₂-saturated formation water
- Porosity measurements on sandpacks and frozen samples
- Porosity at overburden pressure and pore volume compressibility
- Gas and liquid permeability at overburden pressure

In the CO₂ reaction experiments, Ca seems to be the most reactive element due to dissolution of carbonate shell fragments in the sand. The mineralogical study showed a significant drop in sample surface area after reaction with CO₂-saturated formation water due to dissolution of these carbonate shells. A special study with AFM (atomic force microscope) did not reveal any dissolution-precipitation processes taking place for the main minerals quartz and mica in the Utsira sand. Cation exchange capacity remained unchanged for the CO₂ reacted samples, presumably because no reaction occurred in the clay fraction.

Unconfined room condition measurements of preserved samples from a 0.9 meter deep frozen core section showed a mean porosity of 41.5% for the Utsira sand. When confining pressure equal to ~900 meter TVD is applied to the samples, the porosity is reduced to approx. 38-39%. This is the depth from which the present core was cut. A best estimate of the porosity reduction and pore volume compressibility was obtained. It was observed that unconsolidated samples do not keep a solid form during overburden experiments. Water acts as a lubricant and even long time after confining pressure has been posed on the sample, grains re-arrange which means small changes in bulk and pore volume. Thus small changes in volume due to dissolution of minerals by CO₂ saturated water cannot be discriminated from grain re-arrangement in tests of unconsolidated sediments. Packing of the sand and fines migration is by far the most important phenomena affecting the measured permeability, even overshadowing the effect of confining pressure. After repeated testing of many samples it was found that the gas and Klinkenberg corrected gas permeability for the tested Utsira sand core section is within the range 1.5-2.5 D. The liquid permeability is lower at 1-1.5 D, mainly due to fines migration.

4. Numerical modelling of the experiments

Geochemical and reaction-transport models were used to interpret the experimental data by considering thermodynamic, kinetic and transport processes. Comparison of experimental and modelling results is also a way to validate the numerical models on experimental tests cases before using them to make predictions. As a result, increased confidence in our understanding of chemical reactions induced by CO₂ and in the validity of numerical tools is expected.

4.1. Description of the numerical codes used

Several ‘off the shelf’ and ‘custom-made’ geochemical codes were used for this study:

- EQ3/6 (Wolery, 1995), an international reference code for geochemical modelling of water-rock interactions, version 7.2b, thermodynamic database data0.com.R2. It is a general purpose code that may take into account up to about 80 chemical elements, 900 aqueous species, 900 minerals and 80 gas species.
- SCALE2000, a geochemical code built at BRGM (Azaroual et al., 2002), which takes into account the effect of pressure (10 MPa at Sleipner) on thermodynamic constants and uses the Pitzer formalism for the calculation of activity coefficients in high salinity brines. It was specially developed using the

ALLAN/NEPTUNIX tool to deal with carbonate scaling in oil-gas production operations. It takes into account a limited number of components, i.e. key components: 15 chemical elements, 17 minerals and 2 gas species (CO₂, H₂S). However aluminium is not considered in SCALE2000.

- UTSIRA simulator, a Specific Chemical Simulator (SCS) developed by BRGM for the SACS project using the ALLAN/NEPTUNIX code generator system (Kervévan et Baranger, 1998; Fabriol and Czernichowski-Lauriol, 1992; Czernichowski-Lauriol *et al.*, 1992). It is a code dedicated to the modelling of CO₂-water-rock interactions within the Utsira formation. As a consequence, it takes into account the identified key processes which can be described by a limited number of components: 11 chemical elements, 32 aqueous reactions involving 42 relevant dissolved species, 9 minerals and CO₂ as a gas phase. The thermodynamic database was constructed from the EQ3/6 database. As a SCS only includes relevant reaction mechanisms, the calculation-time is notably reduced compared to that of general chemical modelling software that take into account the wide range of chemical processes likely to occur in natural systems. This computational efficiency allows to perform reactive transport modelling by coupling a SCS to a flow and transport model.
- MARTHE+UTSIRA, a coupled reaction-transport code developed by BRGM for the SACS project by coupling the UTSIRA chemical simulator to the flow and transport code MARTHE used for modelling groundwater flow in porous media (Thiery, 1990; Czernichowski-Lauriol *et al.*, 1995; Kervévan *et al.*, 1998).
- DIAPHORE, a reaction-transport code which was developed by IFP for the modelling of water-rock interactions during diagenesis of oil reservoirs (Le Gallo *et al.*, 1998; Brosse *et al.*, 2000 ; Brosse *et al.*, in press). This code has its own thermodynamic database compiled from various references in the literature. It can account for a wide range of components.

All the geochemical calculations deal with thermodynamic equilibrium, thermodynamic disequilibrium and reaction kinetics. The geochemical codes have their own thermodynamic datafiles as described above. However, kinetic data usually have to be supplied by the user.

4.2. Modelling constraints and assumptions

One of the main difficulty in geochemical modelling is to choose a simplified rock mineralogical composition representative of the natural system to be modelled. This complexity is even increased in the SACS project as three distinct mineralogical studies have been carried out by SINTEF, GEUS and BGS on Utsira core fragments from well 15/9-A-23, as they have all identified a great variety of minerals, and as comparison between these analyses is not straightforward possibly because of the spatial heterogeneity of the Utsira formation. Then several mineralogical assemblages were tested during the modelling.

The main features of the conceptual model are described below:

- the chemical system was restricted to: Na, K, Ca, Mg, Cl, SO₄, HCO₃, CO₃, CO₂, Si, Al, H₂O;
- redox reactions were not taken into account;
- the CO₂ experiments were modelled at a constant CO₂ pressure of 10 MPa, which corresponds to a CO₂ fugacity of 52 at 37°C and 66.5 at 70°C, according to the formula given by Duan *et al.* (1992);
- different mineral assemblages were tested including up to 10 minerals, among quartz, chalcedony, calcite, kaolinite, dis-dolomite, albite, anorthite, muscovite, K-feldspar, Ca-montmorillonite, K-montmorillonite, Na-montmorillonite;
- Reaction kinetics for these minerals were compiled and assessed from the literature at 37°C and 70°C.

4.3. Modelling results

The modeling confirms that the main observed changes in fluid chemistry are associated mainly with the dissolution of minerals. Ion-exchange processes on clays, which may be suspected to affect the behaviour of Na, K, Ca and Mg concentrations, do not seem to be significant in the experiments. However such processes might play a role in the increase in K in some of the experiments. As the original Utsira sand sample was heavily contaminated with drilling fluid (rich in K), some reverse K ion exchange reactions may sometimes occur, although care was taken during starting material preparation to remove as much of the drilling fluid as possible.

The main reaction observed from the analytical data in the batch and coreflood experiments at 37 and 70°C and confirmed by geochemical modelling is the fast dissolution of carbonate phases (calcite and probably shell fragments) in presence of pressurised CO₂. However this mineral is not fully dissolved at the end of the CO₂ experiments. As the Utsira sand porosity is approximately 40% and as the carbonate minerals constitute 3.9% of the total rock volume, overall porosity will be little affected by the partial dissolution of calcite.

Geochemical modelling confirms that the reactions corresponding to the dissolution of silicate or aluminosilicate minerals involve small amounts of dissolved matter and are minor with respect to the carbonate dissolution in the CO₂ experiments. This is not surprising given the low solubility of the aluminosilicate minerals. Moreover, these reactions are generally much slower. In this context, mineralogical analyses cannot provide evidence that any such reactions occur and overall porosity of the Utsira sand formation will be very little modified by these processes.

According to the experimental data and modelling results, the presence of a significant amount of CO₂ seems to slightly increase the dissolution of K-feldspar and kaolinite (lower pH) and the dissolution rate for K-feldspar and chalcedony. This last mineral probably controls the dissolved silica in the CO₂ experiments at 37 and 70°C whereas in the blank experiments, it remains under-saturated with respect to the solution because of a slower dissolution rate.

As an illustration, the behaviour of dissolved calcium and silica in the blank and CO₂ experiments at 37°C is presented on Figure 3, with comparison of the analytical and modelling results. The modelling curves present the best fits obtained after a series of sensitivity studies on:

- the solubility of calcite ($\Delta\log K = -0.3$, which enters the uncertainty range of the determination of this thermodynamic constant),
- the CO₂ fugacity (from 52 to 45 to better fit with the measured total inorganic carbon),
- the kinetic constants of mineral dissolution (for instance for chalcedony, calculations were tested from the standard value of $5 \cdot 10^{-17}$ mol/cm²/s in all the experiments to a slower value of $3 \cdot 10^{-17}$ mol/cm²/s for the blank experiment at 37°C to account for the slower kinetics observed in the blank experiment compared to the CO₂ experiment).
- the mineralogical assemblage selected for the modelling, as explained in 4.2.

Although the modelling suggests the possibility of precipitation of several aluminosilicate minerals such as muscovite, illite, smectites, Al-hydroxides or aluminocarbonates such dawsonite, no direct evidence for the formation of appreciable quantities of secondary precipitates was detected. However, kinetic factors, energy barriers or nucleation problems may prevent the formation of such minerals in the conditions and timescales of the experiments.

5. Conclusions

Despite the scarcity on data and samples for fluid chemistry and mineralogical investigations, a reasonable assessment of baseline conditions within the Utsira sand was made by combining information from the

Sleipner, Oseberg and Brage hydrocarbon fields. However, the need for acquiring new data and samples was emphasized. Without a full description of the baseline conditions, it is less reliable to make predictions about how the system will evolve once CO₂ is injected.

An experimental study has been undertaken to react samples of Utsira sand from Sleipner with a synthetic CO₂-saturated Utsira porewater. A range of experiments have been conducted in either 'batch' and 'flow through' equipment at a pressure of 10 MPa and temperatures of either 37°C or 70°C. Durations ranged from one week to two years. These have revealed changes in fluid chemistry associated mainly with dissolution of primary minerals. However, direct evidence from mineralogical observations has never been possible despite the high water-rock ratio used for these experiments (10:1), their relatively long duration (up to 2 years) and the higher temperature (70°C) used for some of them. This is because changes were below the resolution of the analytical technique or below the natural mineralogical variation within the sand.

Modelling of the experiments has shown that for most of the major elements, the predicted trends in fluid chemistry were in reasonable agreement with the experimental observations. However, further sensitivity calculations would be helpful to better understand the complexity of the geochemical system by considering four types of uncertainties: on experimental handling, on analytical measurements, on natural sample heterogeneity, and on modelling parameters.

This study appears to show that observed CO₂-water-rock reactions have resulted in relatively little dissolution of the Utsira sand. Most reaction occurred with carbonate phases (shell fragments), but these were a very minor proportion (about 3%) of the overall solid material. Silicate and aluminosilicate minerals showed only slow, and minor reaction. In terms of geochemical reactions, the Utsira sand would appear to be a good reservoir for storing CO₂. However further studies are needed to assess the long term storage behaviour within the Utsira formation, and investigate the reactivity of CO₂ with the impermeable rocks (caprocks) above the Utsira formation.

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Figure 1: Baseline geochemical data from the Utsira Formation available during the SACS project

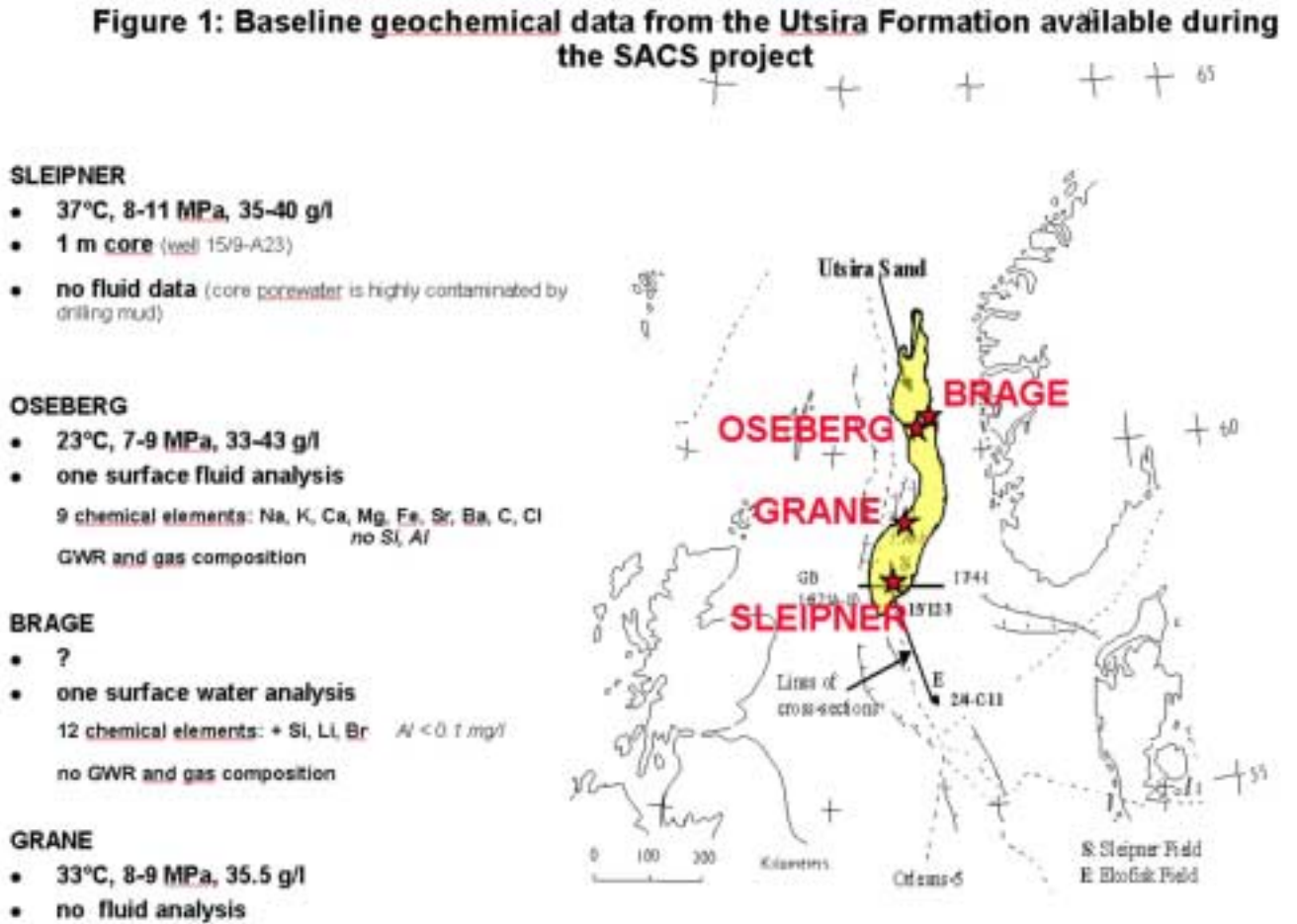


Figure 2: Schematic diagram of the batch reactor used for SACS experiments

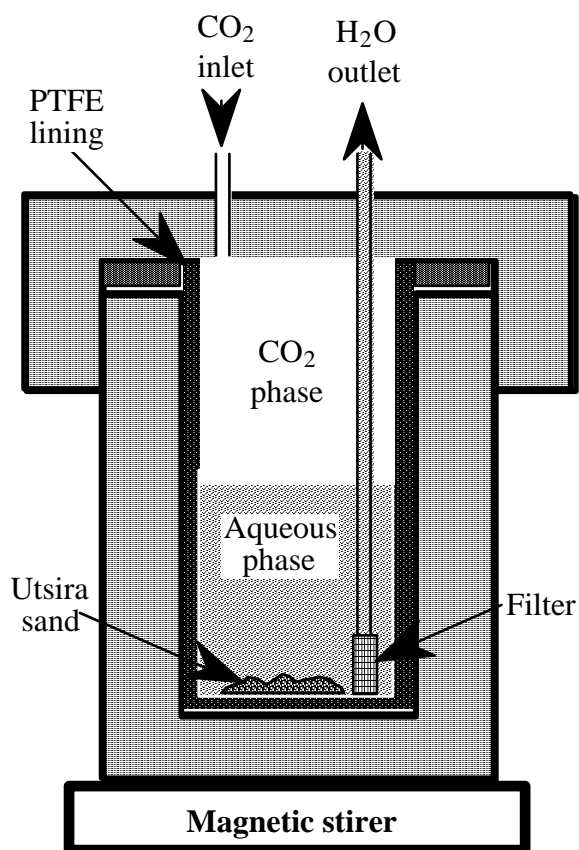


Figure 3: Behaviour of dissolved Ca and Si concentrations during the SACS batch experiments reacting Utsira sand with CO₂ at reservoir temperature and pressure (37°C, 10 MPa).
 CO₂ experiment : pressurised with CO₂ Blank experiment: pressurised with N₂

