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Geochemical interactions between supercritical CO_2 and the Midale Formation.

I: Introduction to fluid-rock interaction experiments

Reservoir Geosciences Programme
IEA Weyburn CO_2 Monitoring and Storage Project
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BRITISH GEOLOGICAL SURVEY

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Geochemical interactions between supercritical CO_2 and the Midale Formation.
I: Introduction to fluid-rock interaction experiments

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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 IEA Weyburn CO_2 Monitoring and Storage Project. This project aims to monitor and predict the behaviour of injected CO_2 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 aims to provide a description of the laboratory experimental techniques that are being applied at the British Geological Survey to investigate the reactions between CO_2 and various lithologies within the Midale formation. Later reports will detail the results of these experiments.

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The authors would also like to thank researchers at the University of Calgary for information on the baseline formation water chemistry of the Weyburn oil field.

Finally, the authors would like to thank staff at Saskatchewan Energy and Mines for their help in the selection of samples of core material from their extensive collection of borehole cores form the Weyburn oil field.

Contents

FIGURES

TABLES

Summary

This report describes work undertaken at the British Geological Survey (BGS) that forms part of the international IEA Weyburn CO_2 Monitoring and Storage Project. This project aims to monitor and predict the behaviour of injected CO_2 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 aims to provide a description of the laboratory experimental techniques that are being applied at the British Geological Survey to investigate the reactions between CO_2 and various lithologies within the Midale formation. Later reports will detail the results of these 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 CO_2 projects (e.g. during the JouleII CO_2 storage project [Holloway, 1996; Czernichowski-Lauriol *et al.*, 1996], and during the SACS project [Rochelle *et al.*, 2002]. This will hopefully allow for better intercomparison between the various studies.

The experiments will utilise actual Midale core material from the Weyburn oil field, together with synthetic formation waters based upon measured compositions of samples at the well-head. The experimental conditions chosen for the investigation cover those representative of in-situ conditions (approximately 60°C, 150 bar [15 MPa]), as well as conditions at the bottom of injection wells where pressures might reach approximately 250 bar [25 MPa]. Experiment durations are planned to range from one week to 6 months. Experiments will be pressurised with either nitrogen or carbon dioxide. The former will provide a ‘non reacting’ reference point from which to compare the more reactive experiments containing CO_2. However, it is hoped that they will also help to provide increased confidence in the understanding of the baseline conditions within the Midale formations prior to CO_2 injection.

1 Introduction

The IEA Weyburn CO_2 Monitoring Project is a collaborative investigation, involving geoscientists from North America and Europe (Moberg, 2001). It is studying the geological sequestration of CO_2 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 CO_2 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 (Figure 1a). 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 Mississipian age. The Midale Vuggy 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 CO_2 flood (Figure 1b).

Since 1964, water injection has been the preferred secondary recovery mechanism. The Midale Vuggy Beds proved more permeable than the overlying Midale Marly Beds and consequently the Midale Vuggy Beds have been saturated from the waterflood operation. However, recently installed CO_2-EOR operations are considered crucial to the future economic life of the oil field. It is hoped that the miscible CO_2 EOR operation will significantly extend the life of the Weyburn field by the production of 130 million barrels of incremental oil. Injection of CO_2 was commenced during September 2000. Initially, injection is in 17 patterns of nine wells each at the west end of the Weyburn Unit. This CO_2 flood will roll out south-eastwards until 75 patterns have been flooded. The CO_2 is a by-product of the coal gasification process and is supplied direct to Weyburn by the Dakota Gasification Company via a 330 km long pipeline from the Great Plains Synfuels Plant, Beulah, North Dakota, USA (Figure 1a) (for further details see Moberg [2001], and Malik and Islam [2000]).

During underground CO_2 storage operations in deep reservoirs, the CO_2 can be trapped in three main ways (with descriptors from Bachu *et al.*, 1994):

- as 'free' CO_2, most likely as a supercritical phase (physical trapping)
- dissolved in formation water (hydronamic trapping)
- precipitated in carbonate phases such as calcite (mineral trapping)

For CO_2-EOR operations, the CO_2 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 most important trapping mechanism. However, over time, hydrodynamic trapping and eventually mineral trapping will make significant contributions to the long-term containment of CO_2. This experimental study will focus on the reactions between CO_2, porewaters and rock within the Midale Formation. It therefore covers aspects related to both hydrodynamic trapping and mineral trapping.

2 Baseline information and samples

Although the overall IEA Weyburn CO_2 Monitoring and Storage Project will generate large quantities of information during its lifetime, the experimental geochemical programme will be constrained by the baseline data available at the start of the study. However, a key output of the experimental programme will be well-constrained test cases that can be used as 'benchmarks' for geochemical modelling activities, and hence increase confidence in the predictive capabilities of those codes. Although experiments will be run under conditions that are broadly applicable to the Weyburn field, 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

There is some uncertainty over the precise *in-situ* conditions within the oil-bearing rocks of the Weyburn field. In part, this is a consequence of only limited downhole pressure and temperature measurement. However, even if such parameters were routinely measured, they would only reflect *present-day* conditions, i.e. after nearly 50 years of oil production and 40 years of water injection. As a consequence, it may only be possible to *estimate* the original pressures and temperatures prior to oil extraction, as well as those that might occur some appreciable time after the field has ceased oil production.

The oil-bearing horizons exist some 1400 m below the ground surface. For a surface water table, this depth would equate to a hydrostatic pressure for pure water of approximately 14 MPa (140 bar). However, this would be very much a minimum pressure as many of the formations are filled with saline porewaters – being more dense that pure water. At the time of writing, the current understanding of realistic down-hole pressures suggests that they are in the order of 15-16 MPa (Gunter, pers. com.; Perkins, pers. com.). However, pressures in injection wells will be significantly higher than these (possibly up to 25 MPa [250 bar] [Riley, pers. com.]), and pressures in production wells will be significantly lower (possibly as low as 10 MPa [100 bar] [Riley, pers. com.]). Laboratory simulations of reactions within the Weyburn field could thus investigate a wide range of pressures. A knowledge of pressure conditions is important because higher pressures of CO_2 will cause increased CO_2 solubility, a larger decrease in pH (e.g. Toews *et al.*, 1995), and hence an increase in reactivity towards carbonate minerals. Although greater reactivity would make laboratory observations of any resulting changes easier, excessive reaction might make any such changes unrepresentative of the system under study. Also, the aim of this laboratory investigation is focussed primarily on the longer-term fate of the CO_2, rather than 'production' timescales.

Most experiments will therefore be undertaken at a pressure of approximately 15 MPa (150 bar) (i.e. conditions likely to exist in the field long after oil production has ceased). However, if time and resources permit, a few experiments will investigate conditions near the injection wells, and utilise pressures of approximately 25 MPa (250 bar).

Information about the exact *in-situ* temperatures within the Midale Marly are limited as per the pressure data mentioned above. However, data presented in Czernichowski-Lauriol *et al.* (2001) and mentioned by other members of the Canadian project team (Gunter, pers. com.; Perkins, pers. com.) suggest that 60°C is a reasonable approximation. Close to CO_2 injection wells however, temperatures could be somewhat lower because the CO_2 is at about 15°C as it enters the injection borehole. Running the laboratory experiments at higher temperatures would favour faster reactions, and allow for easier study. However, higher temperatures might also cause the formation of unrepresentative secondary phases (e.g. aragonite or even vaterite instead of calcite).

It was decided therefore, to conduct the experiments at temperatures that were representative of *in-situ* conditions (i.e. 60°C).

2.2 AQUEOUS FLUID COMPOSITION

The starting point for the experimental fluids is the data from the baseline fluid sampling exercise undertaken by the University of Calgary (Shevallier, pers. com.). This sampling exercise was undertaken prior to the injection of any CO_2. The data consists of analyses of 43 borehole fluid samples over the 'Phase 1' CO_2 injection area. (Table 1). The fluids sampled during this baseline sampling exercise came from a variety of different horizons depending on the position of the slotted liners within the boreholes.

In order to reduce the number of possible fluid compositions that are being used in this study, a subset was chosen. Inclusion in the later was based upon which boreholes had core material from approximately the same depth as the production interval (Pearce and Springer, 2001). This resulted in a subset of 4 fluid compositions (highlighted with an asterix in Table 1), which were then recalculated into 'recipes' to make up synthetic equivalents (see Tables 2-6). The recipes were calculated with an emphasis on matching the metallic ions and silica. Most metals were added as chloride salts. It is noteworthy that the recipe for the synthetic fluids are relatively rich in chloride compared to the analysis of the baseline fluid samples. Indeed, the baseline analyses appear to not be charge balanced, and about 9% low with respect to anions. At the time of writing this report it is not possible to say exactly why this charge imbalance should occur. However, depressurised samples (i.e. those that were actually analysed) may well have undergone significant changes in the speciation of their dissolved components – hence creating an apparent charge imbalance. Unfortunately, making up the synthetic porewaters necessitates a charge-balanced solution, which results in the experimental solutions having a slightly higher salinity than their realistic counterparts. Although not ideal, it should be born in mind that there is a considerable natural variation in fluid chemistry across the Weyburn oil field. In fact, the field lies at the boundary between two water types – one a more dilute water, the other a brine. As a consequence, there is a very large natural variation in salinity across the field – with measured chloride contents varying between 19650 mg l^{-1} and 60565 mg l^{-1} (see Table 1). This natural variation is greatly in excess of the differences between actual porewaters and their synthetic counterparts. Of the fluid compositions chosen for this study, three are approximately in the middle of the natural range of salinities, with the other representing more saline conditions (see compositions highlighted with an asterix in Table 1).

Within an underground CO_2 storage operation there will be regions of free CO_2 (e.g. a CO_2 'bubble', or CO_2 'fingers'), CO_2 dissolved in formation porewater and original formation porewater with no dissolved CO_2. It is likely therefore, that in different parts of the formation there will exist porewaters with a range of dissolved CO_2 concentrations. Within a relatively small experimental programme it is not possible to simulate all possible dissolved CO_2 concentrations. As a consequence, the two 'end-members' of the range have been chosen for investigation. The first of these is the 'CO_2-free' case where little 'induced' reaction is expected, and the second is the 'CO_2-saturated' case where maximum CO_2 is dissolved into the porewater (for a given pressure, temperature and salinity). It is anticipated that maximizing aqueous CO_2 concentrations will maximize the degree of fluid-rock reaction and provide a 'limiting case' for study. The 'CO_2-free' case will serve two important functions:

1) It will provide 'non-reacting' benchmarks with which to compare the results from the 'CO_2-saturated' experiments (i.e. it will allow artefacts related to the experimental techniques used to be discriminated from reactions due to the presence of CO_2).

2) It will increase confidence in our understanding of how close to equilibrium the baseline fluid samples are with the Weyburn rocks. For example, even relatively minor reaction will indicate non-equilibrium conditions, and hence possible flushing of original porewaters during relatively recent oil field (e.g. water flushing) operations.

2.3 SOLID SAMPLES

As detailed in Section 2.2 above, this study selected borehole cores that were associated with fluid analyses. Several cores were studied by BGS and GEUS staff at the core facility in Regina, Saskatchewan, run by Saskatchewan Energy and Mines (Pearce and Springer, 2001). Several boxes of core were shipped to GEUS for more detailed study and sub-sampling. For this study, it was decided to have one sample from the Midale Vuggy, two samples from the Midale Marly, and one sample from the Midale Evaporite. This would allow for most study to be focused on the Midale Marly (the main target horizon for CO_2 injection and oil recovery). However, the other samples allow investigation of CO_2-water-rock reactions in the underlying (vuggy) and overlying (evaporite) formations. A summary of information about the core samples used for this experimental study is presented in Table 7.

The solids were reacted in 3 forms within the experiments:

1) Granulated solid, as either 125-250 or 250-500 µm fractions with 'fines' removed by ultrasonic washing.
2) Powdered solid, <250µm fraction (i.e. 'fines' included).
3) Small columns or 'monoliths', of approximately 1 cm square section, approximately 4 cm long.

It is also proposed to study a very few pieces of borehole materials (provision of samples permitting). At the time of writing this report, no samples have been obtained. However, areas of particular interest will be the possible corrosion of steel liners within boreholes, and the borehole cement used to keep the liners in place. The engineered access points into the reservoir (boreholes) could provide fast return pathways for CO_2 to the surface. It is important therefore to investigate whether CO_2 will degrade them over prolonged timescales, and if so, suggest strategies for reducing such reaction. These solids are likely to be reacted as 'monoliths', though it is possible that granulated (fines removed) samples of borehole cement may also be reacted if resources permit.

2.4 GASES

Two gases were used in the experiments: CO_2 and N_2.

CO_2

The CO_2 used in this study is sourced from high purity (99.99%) liquid CO_2 (Air Products, 4.5 Grade). This liquid CO_2 is obtained in a cylinder fitted with a dip tube and pressurised with 2000 psi (approximately 14 MPa) of helium. However, the actual experimental pressure will be controlled by an ISCO syringe pump, which has its pressure transducer periodically 'zeroed' to minimise drift, and also checked against an externally calibrated Druck pressure transducer (see Table 8). The externally calibrated transducer had a deviation of not greater than ±0.03% in the range 0-4000 psi (0-270 bar [0-27 MPa]). As the liquid CO_2 is piped to the experiments in the ovens, the increase in temperature converts it into a supercritical state. Recorded pressures will be taken from the ISCO pump controller readout.

$\underline{N_2}$

The N_2 used in this study is obtained from BOC Gases and classified as 'oxygen free' (99.998% pure). It is delivered in a cylinder pressurised to 230 bar (23 MPa). However, the actual experimental pressure will be controlled by either; an ISCO syringe pump, or a single-stage regulator. The later can only be used for the lower pressure (150 bar [15 MPa]) experiments, whereas the ISCO pump will have to be used for the 250 bar (25 MPa) experiments. The ISCO pump has its pressure transducer periodically 'zeroed' to minimise drift, and also checked against an externally calibrated Druck pressure transducer (see comments above). Recorded pressures are taken from the ISCO pump controller readout if an ISCO pump is used. For experiments connected to a gas cylinder, recorded pressures are taken from an independent pressure transducer reading line pressure (see descriptions in the following sections).

3 Description of the experiments

3.1 EXPERIMENTAL EQUIPMENT

Laboratory experiments are being conducted within the Hydrothermal Laboratory of the British Geological Survey, Keyworth, UK. Two main approaches will be utilised during this study:

- Numerous low maintenance 'batch' experiments of variable durations up to 6 months.
- A pair of higher maintenance flowing 'column' experiments, having durations up to 6 months.

Prior to performing the experiments, it was necessary to consider the use of equipment that would perform well. Although dry supercritical CO_2 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 were made of stainless steel (e.g. steel types 316 and EN54) and were lined with PTFE (polytetrafluoroethene), high pressure tubing was made of either 316 stainless steel or PEEK™ (polyetheretherketone), O-ring seals were made of Viton®, high pressure columns were made of PEEK™ and pressurised sampling containers were made of titanium.

3.1.1 'Batch' equipment

In order to obtain a better understanding of rock-water-CO_2 interactions, 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. Indeed, it has also been used successfully in previous studies of CO_2-water-rock reaction (e.g. Czernichowski-Lauriol *et al.*, 1996; Gunter *et al.*, 1993; Rochelle *et al.*, 2002).

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

1) To study the evolution of porewater chemistry and solids mineralogy over time during CO_2-porewater-rock reaction. These can be achieved by either; setting up a series of identical experiments and terminating them at ever-increasing timescales, or periodic sampling of the same experiment. Both approaches are being used in

this study, although the latter only provides information on the *final* mineralogical composition. Evolving fluid chemistry is 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.

2) To investigate whether the synthetic porewaters used in the experiments are representative of realistic Midale porewaters at Weyburn. This is achieved by setting up an identical series of experiments to that described above, but this time using an inert gas (in this case nitrogen) rather than CO_2 as the pressurising medium. The Weyburn oil field has been subject to water flooding for many years, and it is possible that present day porewaters may not be in equilibrium with minerals in their host formations. If the starting synthetic porewater composition is broadly in equilibrium with the Midale rock sample, then very little change in fluid chemistry should be observed during the experiment. However, any dissolution or precipitation would indicate non-equilibrium conditions. These experiments will also serve as ‘blanks’ with which to compare the CO_2 experiments.

A schematic diagram of a typical ‘batch’ apparatus is shown in Figure 2. A combination of 100 ml and 150 ml vessels will be used depending on the amount of sample under study. Water saturated with CO_2 is relatively reactive, and this is especially so for saline fluids. For this reason PTFE (polytetrafluoroethylene) liners or ‘cups’ were used in all vessels.

Assembly of the apparatus involves first weighing out a sub-sample of dried Weyburn core into the PTFE liners, followed by an aliquot of synthetic Midale porewater. The fluid:rock mass ratio used in the experiments will vary depending on the actual experiment being undertaken. However, for many of the experiments (and especially those using granulated solids) a 10:1 porewater:solid mass ratio is likely to be used. Other experiments will use ‘monoliths’ of Midale core material to investigate reactions at the CO_2/porewater boundary. The monoliths will be mounted inside the vessels as shown in Figure 3.

For most experiments, the total volume of the solid and aqueous samples will fill about half the vessel. A small magnetic stirrer bead is then added, the liner placed into the appropriate steel vessel, fresh O-rings inserted into their grooves, and the lid securely fastened down. The vessel is then placed into a Gallenkamp PlusII thermostatically-controlled oven (accurate to better than ± 0.5°C) and connected to the appropriate pressure line.

The CO_2 will usually be supplied to the reactors from an ISCO 260D syringe pump running in ‘constant pressure’ mode. Inert nitrogen gas will usually be supplied via a gas bottle using a single-stage regulator, though a few (mainly higher pressure experiments) will also use an ISCO 260D syringe pump. 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 CO_2 experiments where the CO_2 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 ‘zerod’ to maintain accuracy, and will be checked periodically against an externally calibrated Druck pressure transducer (see Table 8, and comments in Section 2.4).

A maximum of 8 vessels can be accommodated per oven, though usually only half will be connected together at one time (i.e. 4 nitrogen experiments and 4 CO_2 experiments) (see schematic diagram in Figure 4). Pressure connections are placed at the top of the vessels so that aqueous fluids (denser than compressed nitrogen or supercritical CO_2) cannot move between vessels. This arrangement means that only a single pump or gas bottle is needed to maintain the system pressure. A *provisional* listing of the type of 'batch' experiments that will be undertaken during this study is given in Table 9.

Good mixing between CO_2, porewater and rock is achieved via the stirrer bead in each vessel. Although the base of the stainless steel pressure vessel is in the order of 1 cm thick, it still allows for good 'coupling' between a magnetic stirrer and the stirrer bead. However, stirring the experiments does present a dilemma. Lots of stirring would result in good mixing, but it could also mechanically degrade the solid sample. Conversely, little stirring would lessen any mechanical damage to the solid sample, but mixing would not be good. It was 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. Two minutes of stirring were used every 4 hours, which was controlled via an electronic time switch.

Previous studies (Toews *et al.*, 1995) indicate that stable CO_2 concentrations can be obtained in high pressure water-CO_2 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 batch experiments (weeks to months) and the relatively frequent stirring, it is reasonable to assume that the aqueous fluid within them will be saturated with CO_2 at the pressure and temperature of the experiment.

The 'blank' experiments pressurised by nitrogen were generally not controlled by a high precision pump, but instead utilised a regulator connected to a gas cylinder. Control of (single stage) regulators at the pressures used during this study can be somewhat coarse. However, the line pressure was monitored via a secondary pressure transducer. This was checked against the ISCO pump pressure transducer and found to agree to ±0.5 bar or better. Preliminary tests of the equipment seem to show that if care is taken, gas pressure can be controlled (by regulator) to within about 1% of the desired value.

3.1.2 'Column' equipment

These experiments will be aimed at understanding how the front of dissolved CO_2 (and associated chemical reactions) will propagate in an open system, and also to investigate the impact of mineral reaction kinetics on flowing systems. A schematic diagram the apparatus is shown in Figure 5. It is anticipated that it will consist of 3-4 lengths of PEEK tubing (each 50 cm long), making a total length of 1.5-2 m. Each column has an internal diameter of 0.7 cm, and will packed with a granulated sample (125-250 µm, fines removed) of Midale Marly (ideally sample BGS14A [see Tables 7 and 9], but the choice will depend on how much granulated material is available when the experiment starts). Previous experience suggests that it is likely to have an average porosity of approximately 40% (to be determined based on the difference between wet and dry weights, and assuming an overall solid density similar to calcite). The amount of solid material in each column will be recorded. Note that the grains of Midale Marly will be loosely packed into each column, and not compressed together by a strong confining force. This will mean that the sample grains will only experience a uniform pressure from the fluid flowing over them, and not anisotropic stresses as might be found *in-situ*. Although this arrangement is thus not a true representation of actual in-situ conditions, it is representative of the types of system that can be simulated with geochemical modelling packages (most of which do not incorporate geomechanical processes). Other parts of the overall Weyburn project will be conducting laboratory tests using anisotropic stresses (e.g. the tests being conducted by GEUS).

An experimental temperature of 60°C will be used. Although a higher temperature would speed up dissolution/precipitation reactions (and thus help form reaction fronts), it is thought that this might form unrepresentative secondary phases. Running at 60°C will also help comparisons with the batch experiments (see earlier sections) and field observations. The fluid used will be a synthetic porewater made up in the same way as that used for the batch experiments. It will be pre-saturated with CO_2 under the experimental conditions before being pumped into the column. A flow rate of 0.5 ml h^{-1} will be used throughout the experiments, and the sampling procedure will be similar to that used for batch experiments.

The fluid pressure will be monitored at the inlet and outlet of the column (via pressure transducers P_1 and P_2 in Figure 5). This will be done to investigate whether any pressure gradient exists across the column whilst the CO_2-rich porewater flows through it. Given the likely high porosity and permeability of the columns, a significant pressure gradient is not expected. However, if one is observed, any changes in it during the experiment might be due to mineral dissolution/precipitation that alters permeability.

4 Sampling and analysis

4.1 SAMPLING PROCEDURE

The sample handling procedure will be similar for both batch and column experiments. However, the methods by which the pressurised samples are actually taken are slightly different.

For each set of experiments, samples from both CO_2-pressurised and N_2-pressurised experiments are treated in the same way. However, different sets of experiments will use one of two slightly different sampling methods:

1) For samples of limited volume (e.g. the multiple samples taken from the experiments using <250 µm solids – see Table 9), the procedure will involve degassing straight into a sterile syringe. The samples will then be treated as detailed in Section 4.2.2.
2) All other experiments will use high-pressure sampling as they are less constrained by fluid volumes.

High pressure sampling 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 CO_2 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 the sample, then the gas-rich aqueous sample withdrawn into a titanium floating piston sampler (internal volume of approximately 22 ml) (see Figure 6). In order to prevent degassing, this will be done under constant pressure conditions. This will be achieved by isolating all the other 'batch' experiments, and using the gas pressurising pump (or cylinder) to maintain constant pressure conditions. The de-ionised water on the non-sample end of the floating piston will be either; withdrawn via a pump, or allowed to slowly drip out via a needle valve. Degassing can also minimised by sampling the fluid slowly. Previous experience shows that too rapid sampling is likely to result in a localised reduction in pressure and hence possible degassing (this is especially so within the fine pores of the filter shown in Figures 2 and 3).

Sampling of the column equipment is more straightforward, in that the fluid flow is diverted into the pressurised Ti sampler until it is full (probably within a few tens of hours given likely flow rates) (see Figure 5). The Ti sampler can then be isolated from the flow system and the fluids extracted as per the batch samples.

For most of the batch and both of the column experiments, the samples for straightforward cation and anion analysis will be degassed and vented into a suitable vessel during the opening of the titanium sampler. The samples will then be treated as detailed in Section 4.2.2. However, some samples are likely to 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). The basis behind this, is to convert all dissolved carbon species (e.g. HCO_3^-, $CO_{2(aq)}$ and H_2CO_3) to carbonate (CO_3^{2-}) by increasing the pH to hyperalkaline conditions:

$$HCO_3^- + OH^- \Rightarrow CO_3^{2-} + H_2O \qquad [1]$$

$$CO_{2(aq)} + 2\,OH^- \Rightarrow CO_3^{2-} + H_2O \qquad [2]$$

$$H_2CO_3 + 2\,OH^- \Rightarrow CO_3^{2-} + 2\,H_2O \qquad [3]$$

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 sufficient fluid sample is obtained, as much as possible of the remaining fluid inside the vessel will also be removed (also at pressure). This is to minimise the potential for carbonate mineral precipitation as a result of the solution degassing (basically this would be an artefact of sampling). However, previous experience has indicated that such degassing results in carbonate precipitation only after several hours. Consequently, for solution samples that are taken and preserved in a matter of a few tens of minutes, such precipitation is not thought to represent a significant problem.

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, from time to time, it may 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

4.2.1.1 BATCH EXPERIMENTS

On opening a batch pressure vessel, its PTFE liner containing the (hopefully only slightly damp) sample of reacted solid will be removed. The powdered or granular solid will then be washed 3 times in de-ionised water (using approximately 10-20 ml each time). The sample will be allowed to settle for about 5 minutes between washings in order to maintain as much fine material as possible. A final wash of acetone (again using approximately 10-20 ml) will be used to remove traces of water. The sample will then be allowed to dry at approximately 60°C. Once dry, the sample will placed in an airtight container prior to mineralogical analysis.

4.2.1.2 COLUMN EXPERIMENTS

On completion of the column experiments, the entire column assembly (several linked 50 cm columns) will be flushed with isopropyl alcohol - in order to displace the synthetic formation water. This will be done to minimise salt formation when the columns are dried and prepared for mineralogical analysis (previous experience has shown that this might obscure observations of subtle mineralogical features). Prior to analysis, each column will sliced up into several sections (each likely to be approximately 2-4 cm long), and the reacted solid removed and dried.

4.2.2 Fluid samples

For most of the experiments, two types of samples will 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 CO_2 by preservation with excess alkaline solution, but the resulting mixture is relatively less straightforward to analyse.

4.2.2.1 DEPRESSURISATION SAMPLE

After depressurisation/discharge from the Ti pressure sampler, 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 12 ml) of this sample will be placed into a polystyrene tube and acidified with 1% (i.e. in the order of 0.12 ml) 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 the filtered sample (in the order of 4 ml) will be taken and placed in a polyethylene tube for analysis of anions by ion chromatography (IC). This latter sample may also need to be diluted to minimise carbonate mineral precipitation. Samples will be stored in a fridge (at about 5°C) prior to analysis.

4.2.2.2 ALKALI PRESERVED SAMPLE

This will involve first filling the Ti floating piston sampler (see Figure 6) approximately half full of 4M NaOH solution - the alkali conditions ensuring that all dissolved C species (mainly $CO_{2(aq)}$, H_2CO_3 and HCO_3^-) will be converted into CO_3^{2-}. 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 – for example due to the precipitation of either portlandite ($Ca(OH)_2$) or calcite ($CaCO_3$):

$$Ca^{2+} + 2\,OH^- \Rightarrow Ca(OH)_2 \qquad [4]$$

$$Ca^{2+} + CO_{2(aq)} + 2\,OH^- \Rightarrow CaCO_3 + H_2O \qquad [5]$$

The precipitate may be very fine. If it does form, the solution will probably be left for several hours to allow it to settle. Mineralogical analysis of the precipitate will identify if significant $CaCO_3$ is present (and as a consequence, whether this needs to be taken into account in calculating total dissolved carbon concentrations).

The relatively clear sample fluid can then be filtered 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 CO_2 (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 (± some minor) cations using inductively coupled plasma - optical emission spectroscopy (ICP-OES), and for all major (± 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 which 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 applied. This technique effectively monitors the colour change of an aqueous pH indicator solution (e.g. bromophenol blue) using a UV-visible spectrometer. Although this technique is 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 analysed, typical detection limits and associated analytical errors are given in Table 10. 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. Conclusions

An experimental study is being undertaken to react CO_2 with samples of Midale rocks from the Weyburn oil field and synthetic formation waters based upon measured compositions. The aim of this study is to investigate the potential for CO_2-porewater-rock interaction in the Weyburn oil field. 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 either ‘batch’ and ‘flow through’ equipment at pressures between 150 and 250 bar (approximately 15 to 25 MPa) and a temperatures of 60°C. Durations of the experiments are likely to range from one week to six months. 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.

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Figure 1 a) Location of the Weyburn oilfield and the route of the CO_2 pipeline.

b) Diagram illustrating how a miscible CO_2-EOR flood produces incremental oil; at Weyburn, the depth to the reservoir unit is *c*. 1400 m.

(from Riding *et al.*, 2002).

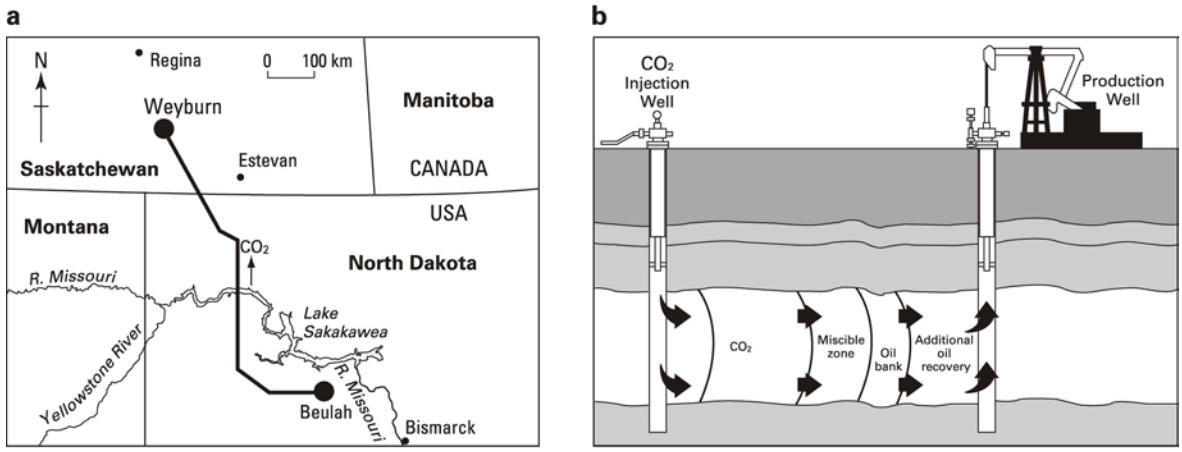


Figure 2 Schematic diagram showing a typical batch reactor.

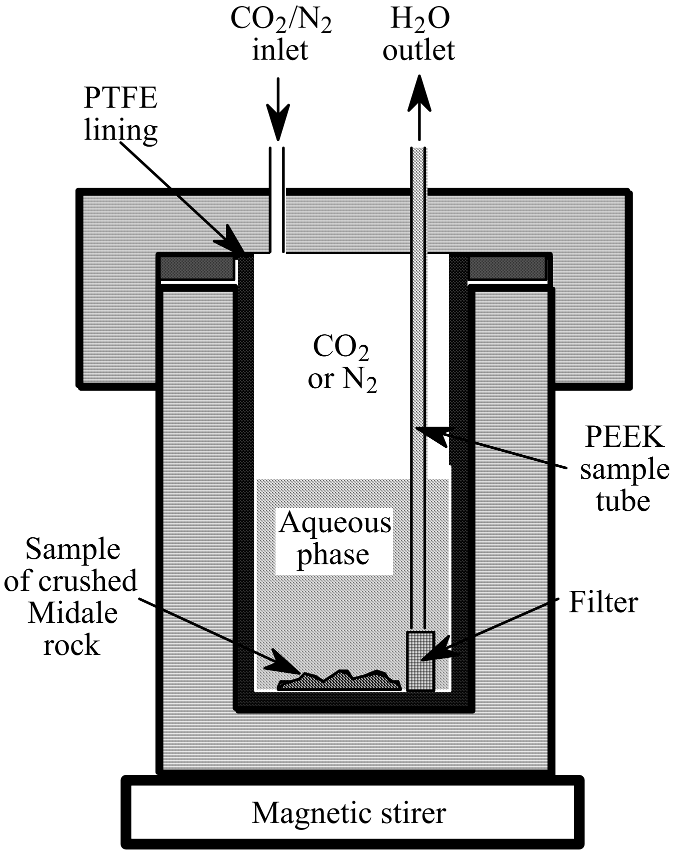


Figure 3 Schematic diagram showing how rock monoliths are mounted onto the 'dip tube' assembly.

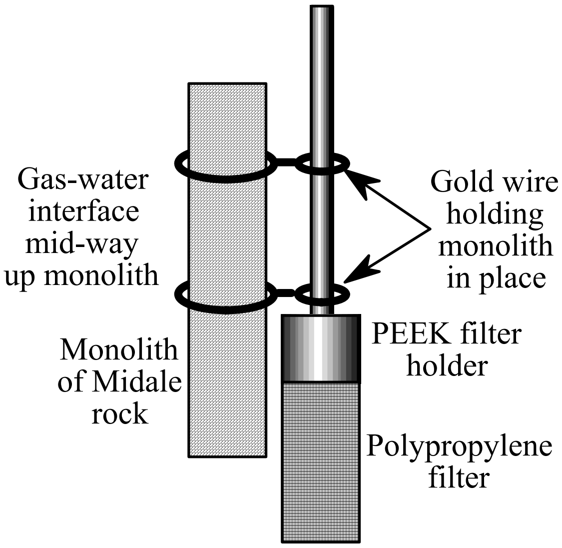


Figure 4 Schematic diagram showing the typical layout for a series of batch experiments.

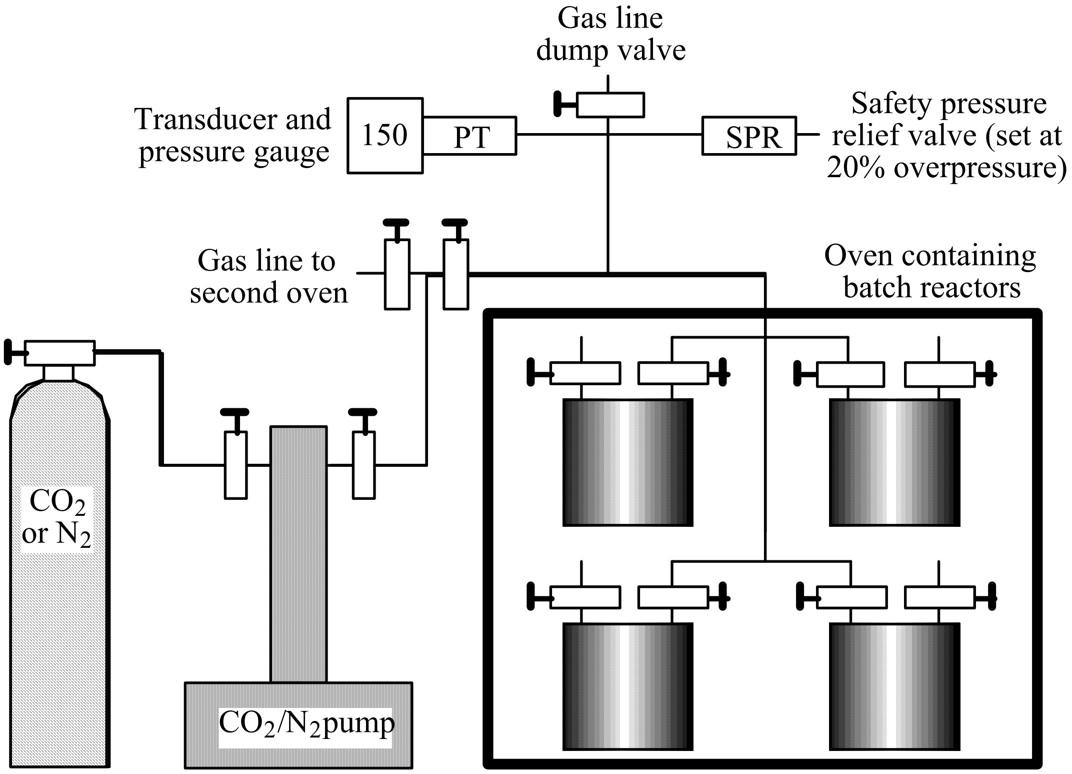


Figure 5 Simplified schematic of column experiment layout.

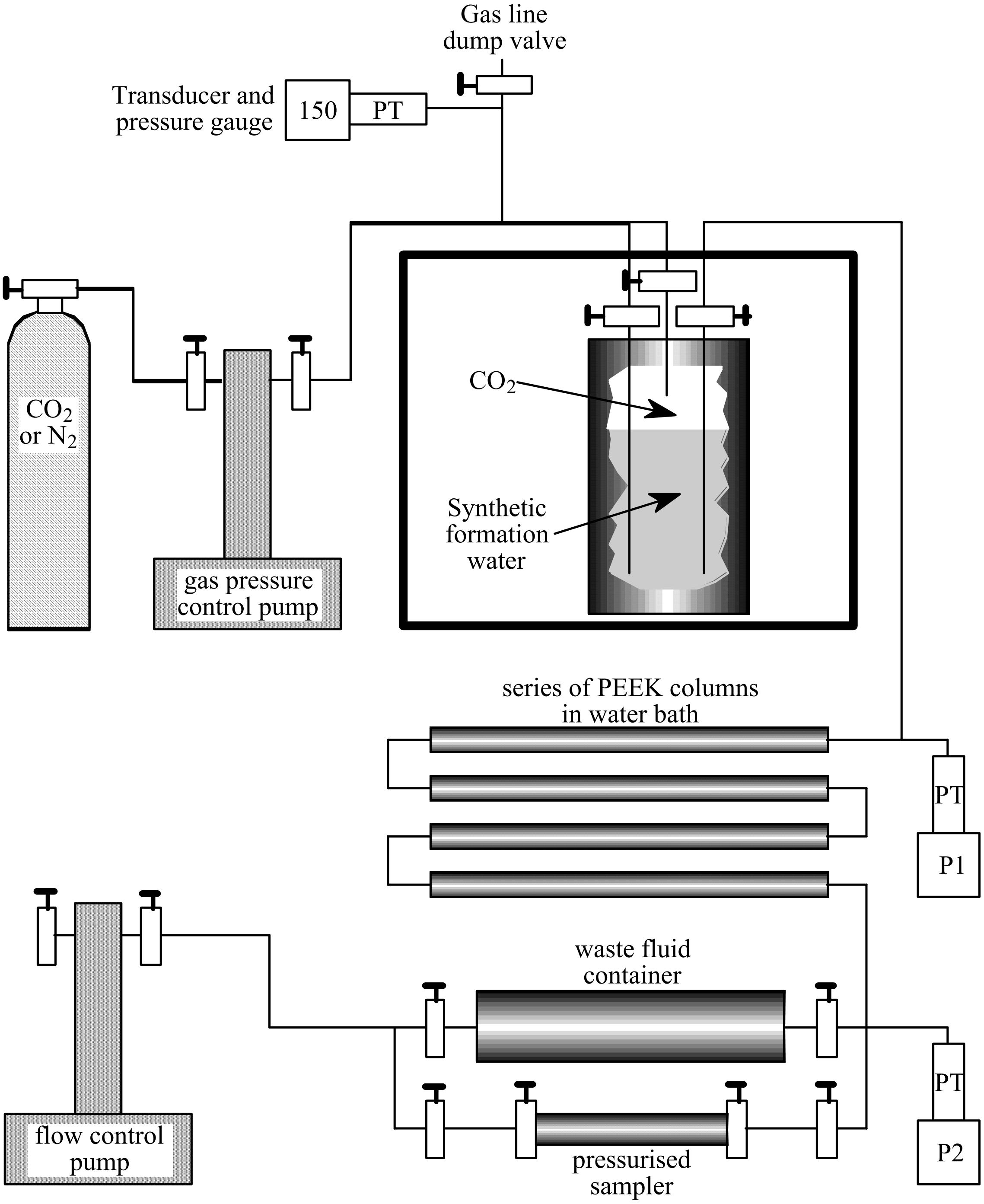


Figure 6 Schematic diagram showing the sampling of a batch reactor.

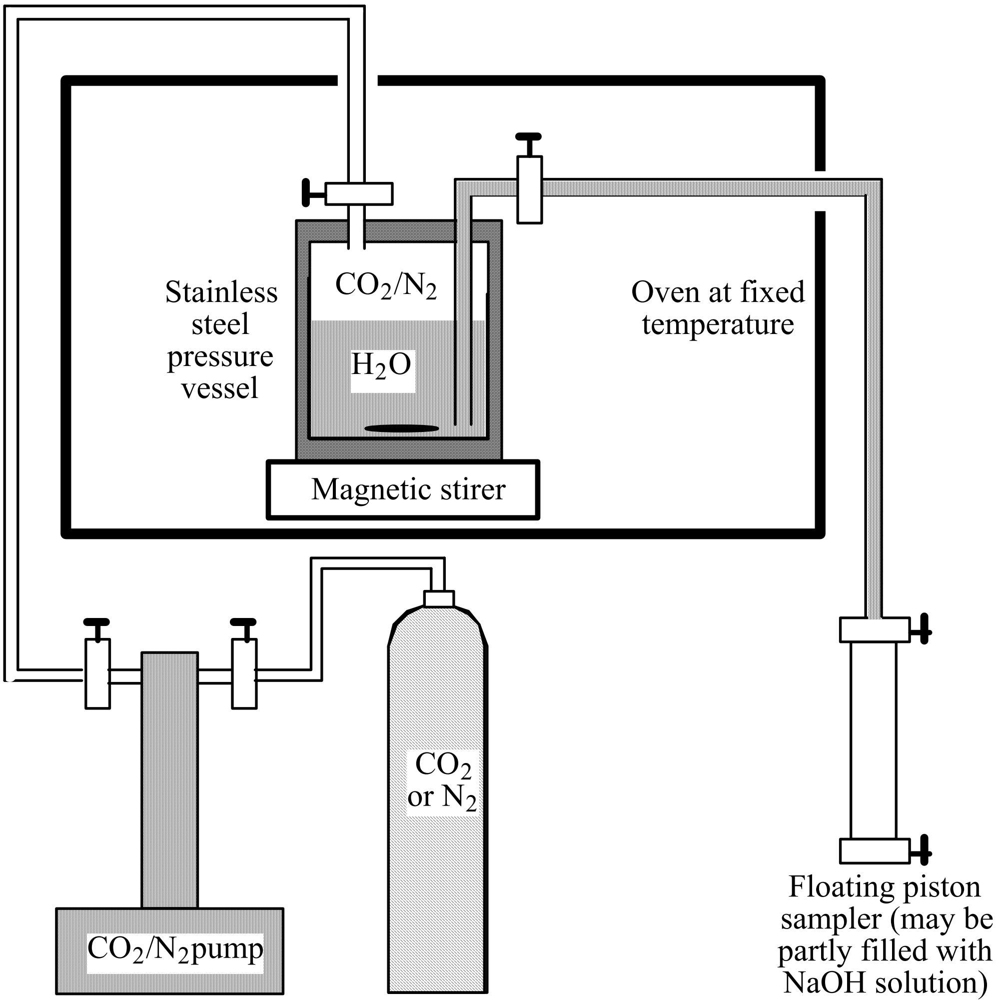
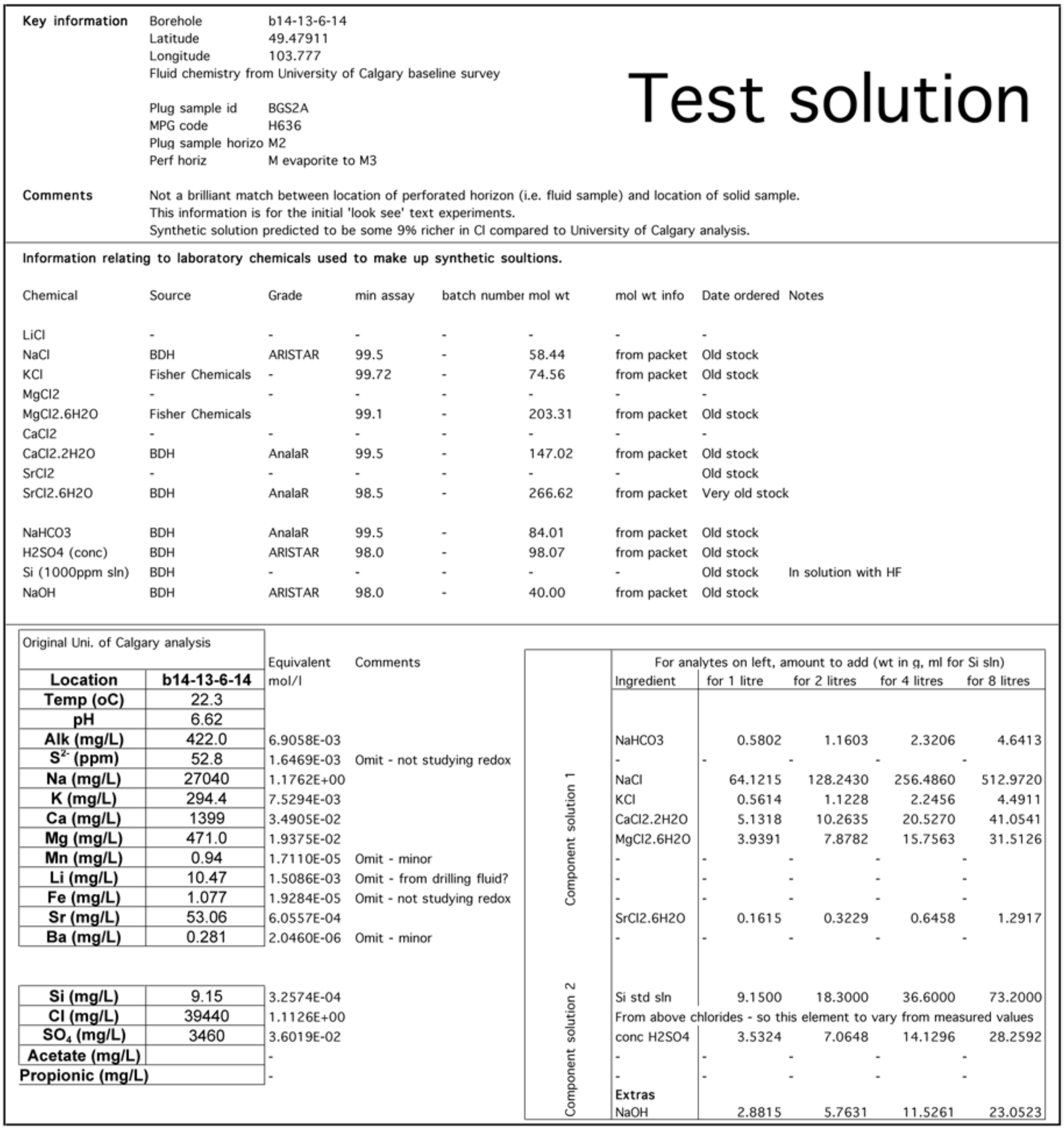


Table 1 Summary of analyses of preliminary baseline fluid sampling survey (Shevalier pers. comm.). Key fluids are marked with an asterisk.

Sample	Location	Temp (°C)	pH	Concentrations (mg/L)															
				Alk	S_2^-	Na	K	Ca	Mg	Mn	Li	Fe	Sr	Ba	Si	Cl	SO_4	Acetate	Propionic
1	12-23-6-14	28.2	6.76	864.6	686.2	13770	225.2	945	421.1	0.25	4.641	0.8090	15.43	1.066	24.47	19665	3625		
2	2-26-6-14	32.9	6.43	439.0	273.6	20700	488.4	1495	272.1	0.40	10.44	1.606	80.61	1.027	18.85	34250	3330	6.64	
3	12-25-6-14	23.0	6.75	519.8	284.2	14990	143.9	1122	196.9	0.10	3.782	0.5198	31.40	1.581	18.06	24150	3695		3.875
4	b8-18-6-13	21.7	6.45	395.8	168.2	29740	363.7	1571	709.9	0.55	11.22	1.705	40.71	1.618	18.07	44920	3245		
5	14-12-6-14	31.5	6.81	419.6	144.5	21720	552.4	1539	487.6	nd	11.67	1.654	76.28	1.961	14.79	36710	3680		
6	b2-13-6-14	26.6	6.68	398.3	145.6	22890	565.4	1687	274.6	0.46	11.49	1.971	92.56	0.310	12.47	35495	3460		
7	b8-17-6-13	20.3	6.50	277.0	66.1	35410	710.3	1696	862.8	0.49	11.55	1.514	44.22	0.184	17.30	55830	2895		
8	8-20-6-13	22.1	6.20	342.9	90.2	27580	365.4	1476	206.6	0.03	9.173	0.8202	43.31	0.317	15.12	39545	3395	5.15	4.43
9	14-20-6-13	23.2	6.66	308.3	69.2	25030	400.4	1406	330.7	0.17	9.992	0.9291	53.35	0.370	13.57	37000	3320	7.71	1.55
10	b14-8-6-13	25.4	6.88	391.1	34.6	35000	451.8	1388	234.7	0.20	14.14	0.9021	62.02	0.285	12.71	47200	3265		
11	d14-7-6-13	24.3	6.85	371.6	138.4	34990	746.1	1552	1096.0	0.70	15.42	1.588	45.70	0.047	11.98	53400	3150	5.09	
12	d8-7-6-13	30.2	6.57	358.8	123.6	27730	337.3	1559	157.2	0.08	10.54	0.8094	84.07	0.171	10.32	42315	3595		
13	d14-6-6-13	30.3	6.84	710.5	17.2	29730	322.7	1373	1248.0	0.49	18.66	2.477	31.76	0.202	13.72	51800	3045	6.09	5.14
14 *	14-1-6-14	23.6	6.34	493.4	121.6	40850	588.7	1319	687.9	0.56	24.30	2.563	44.38	0.262	6.86	60565	3105	19.72	
15	2-12-6-14	29.1	6.49	414.6	100.2	18960	382.3	1530	345.5	0.41	10.51	1.175	68.97	0.258	13.58	30025	3625		
16	d8-12-6-14	32.6	6.79	386.9	49.3	29550	584.1	1615	971.6	1.05	11.26	1.669	39.39	0.179	9.23	46375	3690		
17	11-1-6-14	29.2	6.64	66.3	87.4	28710	400.4	1647	679.3	0.69	11.28	1.485	36.27	0.194	11.00	44100	3205		
18	d14-11-6-14	37.6	6.50	389.3	103.5	29200	512.7	1760	796.2	0.39	10.68	1.512	35.64	0.261	10.71	45000	3175		
19 *	12-11-6-14	24.0	6.47	537.8	169.3	24570	269.0	1296	476.0	nd	30.90	1.425	45.65	0.276	19.23	37855	3900		
20	2-10-6-14	24.8	6.61	578.5	203.7	26070	268.9	1158	220.9	0.17	10.42	0.8050	65.19	0.384	12.40	44100	3850		
21	14-2-6-14	30.6	6.78	232.7	77.5	29630	611.2	1592	818.8	0.59	11.68	1.522	41.42	0.036	11.01	43875	3565		
22	2-24-6-14	28.5	6.94	476.6	88.8	25070	434.5	1318	641.4	0.40	8.998	1.603	31.95	0.021	19.31	37555	3485		
23	8-13-6-14	29.6	6.73	407.3	40.7	35860	427.9	1452	242.7	0.34	11.70	0.8106	79.38	0.071	16.94	51720	3455	7.14	
24	12-19-6-13	31.1	7.08	437.9	60.8	21540	359.6	1138	689.2	0.52	6.884	1.130	23.22	0.142	9.99	31645	3755		
25	2-30-6-13	30.6	6.85	388.3	117.8	22510	123.5	1138	862.6	0.31	3.106	1.405	24.47	0.059	14.01	34960	3445	5.85	
26	8-25-6-14	26.0	6.92	353.1	45.5	12220	128.4	1008	148.9	0.05	3.103	0.6376	42.00	0.066	16.65	20635	3665	7.86	2.76
27	14-30-6-13	24.1	6.88	359.3	52.6	16140	107.4	1096	169.1	0.24	3.427	0.7041	60.26	0.029	14.90	26000	3605	8.025	4.65
28	8-36-6-14	23.3	7.30	264.8	23.5	19940	345.7	1416	216.4	0.38	9.191	1.243	88.50	0.013	18.32	30815	3670	14.66	2.54
29	8-30-6-13	24.0	6.92	510.9	35.2	21500	218.4	1178	174.4	0.09	4.596	0.6465	89.01	0.092	12.64	31745	3685		4.33
30	12-20-6-13	28.6	6.63	298.6	67.0	30070	558.9	1432	988.6	0.43	10.64	1.441	37.51	0.150	11.35	45480	3690	5.13	
31	10-17-6-13	25.2	6.58	390.0	19.1	34180	584.9	1504	877.7	0.44	12.22	2.020	39.26	0.023	11.80	51200	3790	5.57	
32	8-19-6-13	22.4	7.00	335.9	13.4	23020	389.7	1195	565.1	0.35	8.512	1.398	29.01	0.011	11.17	34320	3350	6.04	1.55
33	5-36-6-14	19.9	6.93	302.9	25.0	19820	162.9	1049	458.0	0.36	4.019	1.089	27.64	nd	13.68	30225	3605	9.88	
34	34																		
35	12-26-6-14	29.1	6.79	550.4	283.9	22100	193.5	1166	312.1	0.08	6.048	0.4906	86.96	nd	9.25	32610	2995		
36	14-23-6-14	17.1	6.40	704.2	133.5	11280	181.4	1110	286.3	0.07	5.359	0.5191	62.89	nd	11.28	19650	3290		
37	37																		
38	14-14-6-14	20.9	6.77	602.1	44.7	24830	298.1	1402	315.7	0.55	8.687	1.220	30.05	nd	7.46	36570	3385	4.90	
39 *	d8-23-6-14	33.5	7.00	470.7	188.6	24750	404.0	1359	538.5	0.47	8.696	1.377	39.11	nd	11.99	36880	3320	15.465	5.12
40	2-23-6-14	21.2	6.81	605.1	354.3	22560	364.6	1141	660.0	0.33	30.90	1.283	29.18	nd	8.99	33960	3330		
41 *	b14-13-6-14	22.3	6.62	422.0	52.8	27040	294.4	1399	471.0	0.94	10.47	1.077	53.06	0.281	9.15	39440	3460		
42	b13-18-6-13	26.5	6.57	367.0	152.4	30660	395.6	1782	780.2	0.46	12.16	1.450	46.70	0.293	7.41	43705	3600	17.27	1.95
43	d14-18-6-13	19.5	6.31	437.1	182.9	19920	393.0	1238	224.7	0.39	10.52	1.494	79.68	0.011	11.96	32875	3650	8.50	2.23

Table 2 Initial recipe for making up a synthetic equivalent of the porewater from well b14-13-6-14 (as highlighted in Table 1) for the preliminary test experiments.



Key information

Key information	Borehole	b14-13-6-14
	Latitude	49.47911
	Longitude	103.777
	Fluid chemistry from University of Calgary baseline survey	
	Plug sample id	BGS2A
	MPG code	H636
	Plug sample horizo	M2
	Perf horiz	M evaporite to M3

Test solution

Comments

Not a brilliant match between location of perforated horizon (i.e. fluid sample) and location of solid sample.
This information is for the initial 'look see' text experiments.
Synthetic solution predicted to be some 9% richer in Cl compared to University of Calgary analysis.

Information relating to laboratory chemicals used to make up synthetic soultions.

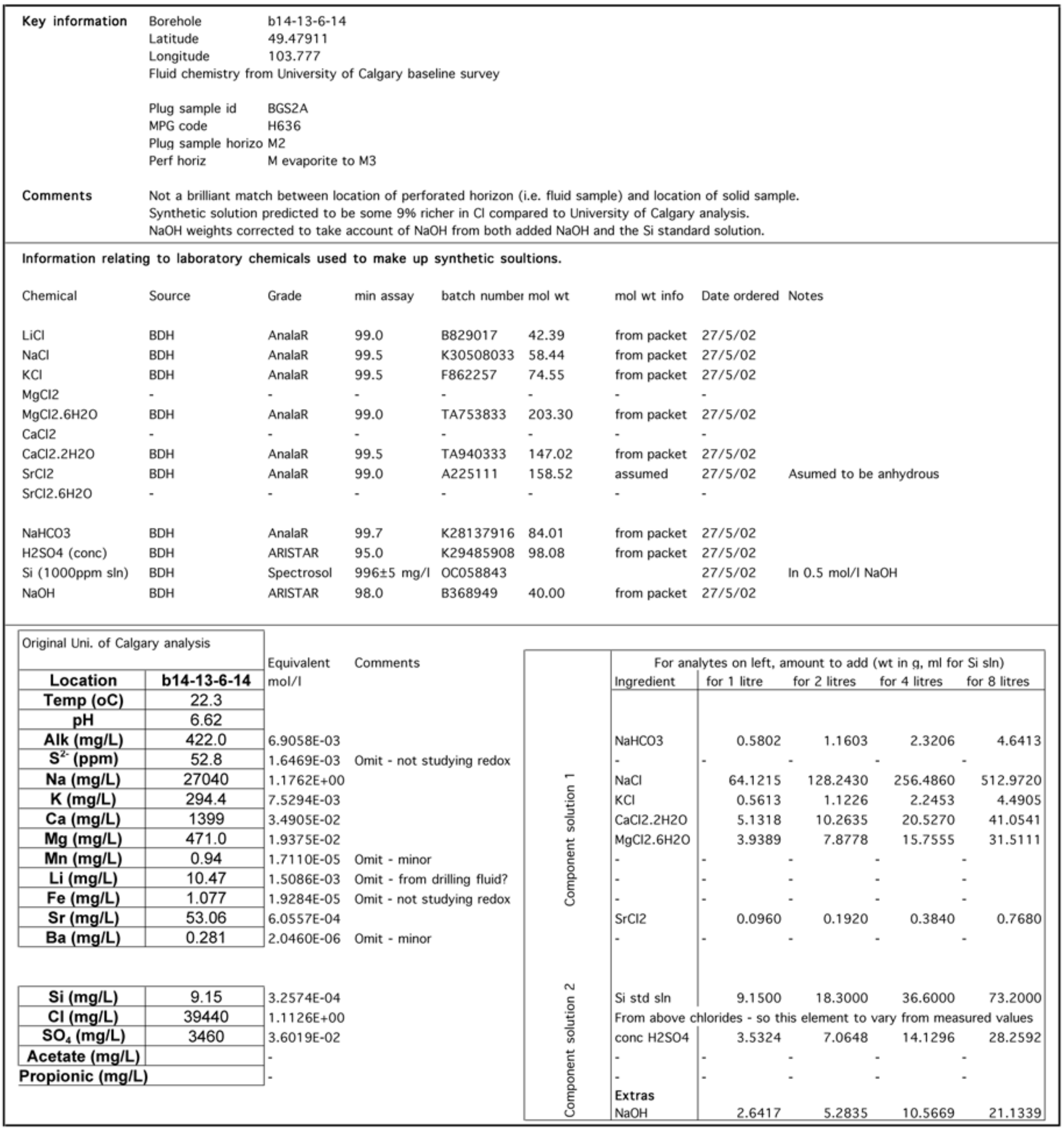
Chemical	Source	Grade	min assay	batch number	mol wt	mol wt info	Date ordered	Notes
LiCl	-	-	-	-	-	-	-	
NaCl	BDH	ARISTAR	99.5	-	58.44	from packet	Old stock	
KCl	Fisher Chemicals	-	99.72	-	74.56	from packet	Old stock	
MgCl2	-	-	-	-	-	-	-	
MgCl2.6H2O	Fisher Chemicals		99.1	-	203.31	from packet	Old stock	
CaCl2	-	-	-	-	-	-	-	
CaCl2.2H2O	BDH	AnalaR	99.5	-	147.02	from packet	Old stock	
SrCl2	-	-	-	-	-	-	Old stock	
SrCl2.6H2O	BDH	AnalaR	98.5	-	266.62	from packet	Very old stock	
NaHCO3	BDH	AnalaR	99.5	-	84.01	from packet	Old stock	
H2SO4 (conc)	BDH	ARISTAR	98.0	-	98.07	from packet	Old stock	
Si (1000ppm sln)	BDH	-	-	-	-	-	Old stock	In solution with HF
NaOH	BDH	ARISTAR	98.0	-	40.00	from packet	Old stock	

Original Uni. of Calgary analysis

Location	**b14-13-6-14**	Equivalent mol/l	Comments
Temp (oC)	22.3		
pH	6.62		
Alk (mg/L)	422.0	6.9058E-03	
S^{2-} (ppm)	52.8	1.6469E-03	Omit - not studying redox
Na (mg/L)	27040	1.1762E+00	
K (mg/L)	294.4	7.5294E-03	
Ca (mg/L)	1399	3.4905E-02	
Mg (mg/L)	471.0	1.9375E-02	
Mn (mg/L)	0.94	1.7110E-05	Omit - minor
Li (mg/L)	10.47	1.5086E-03	Omit - from drilling fluid?
Fe (mg/L)	1.077	1.9284E-05	Omit - not studying redox
Sr (mg/L)	53.06	6.0557E-04	
Ba (mg/L)	0.281	2.0460E-06	Omit - minor
Si (mg/L)	9.15	3.2574E-04	
Cl (mg/L)	39440	1.1126E+00	
SO_4 (mg/L)	3460	3.6019E-02	
Acetate (mg/L)		-	
Propionic (mg/L)		-	

	For analytes on left, amount to add (wt in g, ml for Si sln)				
	Ingredient	for 1 litre	for 2 litres	for 4 litres	for 8 litres
Component solution 1	NaHCO3	0.5802	1.1603	2.3206	4.6413
	-	-	-	-	-
	NaCl	64.1215	128.2430	256.4860	512.9720
	KCl	0.5614	1.1228	2.2456	4.4911
	CaCl2.2H2O	5.1318	10.2635	20.5270	41.0541
	MgCl2.6H2O	3.9391	7.8782	15.7563	31.5126
	-	-	-	-	-
	-	-	-	-	-
	-	-	-	-	-
	SrCl2.6H2O	0.1615	0.3229	0.6458	1.2917
	-	-	-	-	-
Component solution 2	Si std sln	9.1500	18.3000	36.6000	73.2000
	From above chlorides - so this element to vary from measured values				
	conc H2SO4	3.5324	7.0648	14.1296	28.2592
	-	-	-	-	-
	-	-	-	-	-
	Extras				
	NaOH	2.8815	5.7631	11.5261	23.0523

Table 3 Modified recipe for making up a synthetic equivalent of the porewater from well b14-13-6-14 (as highlighted in Table 1).



Key information

Borehole	b14-13-6-14
Latitude	49.47911
Longitude	103.777
Fluid chemistry from University of Calgary baseline survey	
Plug sample id	BGS2A
MPG code	H636
Plug sample horizo	M2
Perf horiz	M evaporite to M3

Comments

Not a brilliant match between location of perforated horizon (i.e. fluid sample) and location of solid sample.
Synthetic solution predicted to be some 9% richer in Cl compared to University of Calgary analysis.
NaOH weights corrected to take account of NaOH from both added NaOH and the Si standard solution.

Information relating to laboratory chemicals used to make up synthetic soultions.

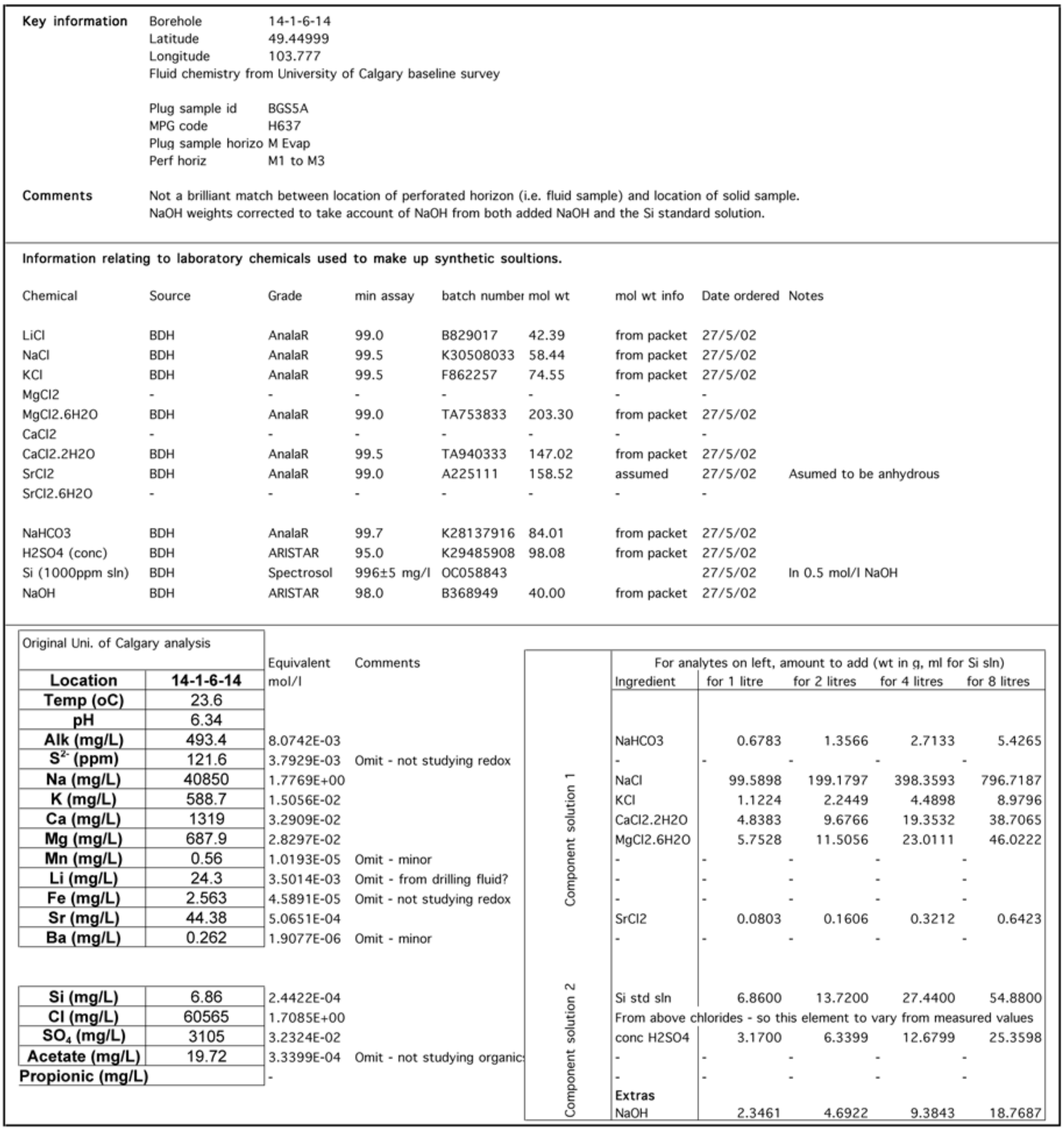
Chemical	Source	Grade	min assay	batch number	mol wt	mol wt info	Date ordered	Notes
LiCl	BDH	AnalaR	99.0	B829017	42.39	from packet	27/5/02	
NaCl	BDH	AnalaR	99.5	K30508033	58.44	from packet	27/5/02	
KCl	BDH	AnalaR	99.5	F862257	74.55	from packet	27/5/02	
MgCl2	-	-	-	-	-	-	-	
MgCl2.6H2O	BDH	AnalaR	99.0	TA753833	203.30	from packet	27/5/02	
CaCl2	-	-	-	-	-	-	-	
CaCl2.2H2O	BDH	AnalaR	99.5	TA940333	147.02	from packet	27/5/02	
SrCl2	BDH	AnalaR	99.0	A225111	158.52	assumed	27/5/02	Asumed to be anhydrous
SrCl2.6H2O	-	-	-	-	-	-	-	
NaHCO3	BDH	AnalaR	99.7	K28137916	84.01	from packet	27/5/02	
H2SO4 (conc)	BDH	ARISTAR	95.0	K29485908	98.08	from packet	27/5/02	
Si (1000ppm sln)	BDH	Spectrosol	996±5 mg/l	OC058843			27/5/02	In 0.5 mol/l NaOH
NaOH	BDH	ARISTAR	98.0	B368949	40.00	from packet	27/5/02	

Original Uni. of Calgary analysis

Location	b14-13-6-14	Equivalent mol/l	Comments
Temp (oC)	22.3		
pH	6.62		
Alk (mg/L)	422.0	6.9058E-03	
S^{2-} (ppm)	52.8	1.6469E-03	Omit - not studying redox
Na (mg/L)	27040	1.1762E+00	
K (mg/L)	294.4	7.5294E-03	
Ca (mg/L)	1399	3.4905E-02	
Mg (mg/L)	471.0	1.9375E-02	
Mn (mg/L)	0.94	1.7110E-05	Omit - minor
Li (mg/L)	10.47	1.5086E-03	Omit - from drilling fluid?
Fe (mg/L)	1.077	1.9284E-05	Omit - not studying redox
Sr (mg/L)	53.06	6.0557E-04	
Ba (mg/L)	0.281	2.0460E-06	Omit - minor
Si (mg/L)	9.15	3.2574E-04	
Cl (mg/L)	39440	1.1126E+00	
SO_4 (mg/L)	3460	3.6019E-02	
Acetate (mg/L)		-	
Propionic (mg/L)		-	

	For analytes on left, amount to add (wt in g, ml for Si sln)				
	Ingredient	for 1 litre	for 2 litres	for 4 litres	for 8 litres
Component solution 1	NaHCO3	0.5802	1.1603	2.3206	4.6413
	-	-	-	-	-
	NaCl	64.1215	128.2430	256.4860	512.9720
	KCl	0.5613	1.1226	2.2453	4.4905
	CaCl2.2H2O	5.1318	10.2635	20.5270	41.0541
	MgCl2.6H2O	3.9389	7.8778	15.7555	31.5111
	-	-	-	-	-
	-	-	-	-	-
	-	-	-	-	-
	SrCl2	0.0960	0.1920	0.3840	0.7680
	-	-	-	-	-
Component solution 2	Si std sln	9.1500	18.3000	36.6000	73.2000
	From above chlorides - so this element to vary from measured values				
	conc H2SO4	3.5324	7.0648	14.1296	28.2592
	-	-	-	-	-
	-	-	-	-	-
	Extras				
	NaOH	2.6417	5.2835	10.5669	21.1339

Table 4 Recipe for making up a synthetic equivalent of the porewater from well 14-1-6-14 (as highlighted in Table 1).



Key information	Borehole	14-1-6-14
	Latitude	49.44999
	Longitude	103.777
	Fluid chemistry from University of Calgary baseline survey	
	Plug sample id	BGS5A
	MPG code	H637
	Plug sample horizo	M Evap
	Perf horiz	M1 to M3
Comments	Not a brilliant match between location of perforated horizon (i.e. fluid sample) and location of solid sample. NaOH weights corrected to take account of NaOH from both added NaOH and the Si standard solution.	

Information relating to laboratory chemicals used to make up synthetic soultions.

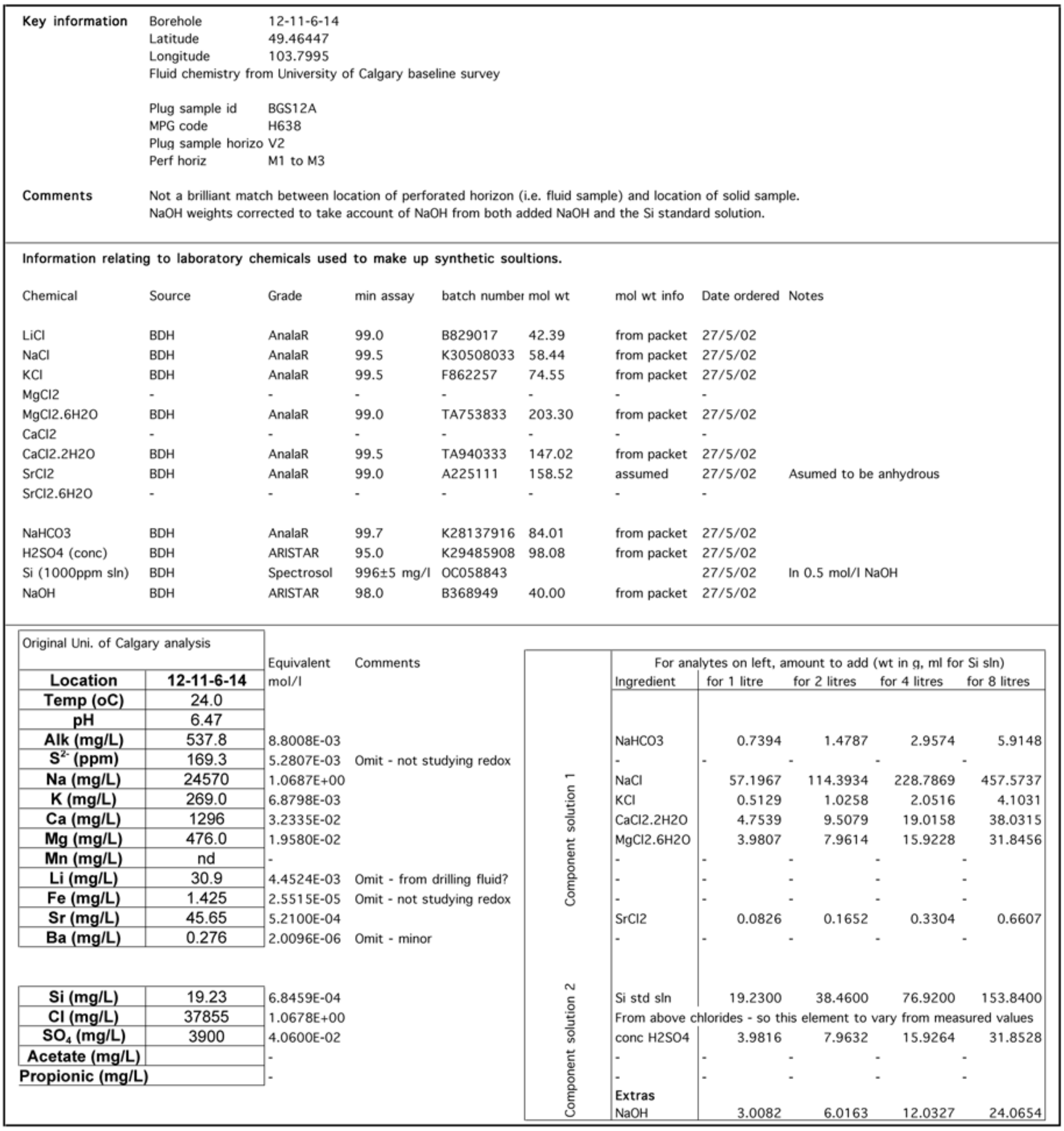
Chemical	Source	Grade	min assay	batch number	mol wt	mol wt info	Date ordered	Notes
LiCl	BDH	AnalaR	99.0	B829017	42.39	from packet	27/5/02	
NaCl	BDH	AnalaR	99.5	K30508033	58.44	from packet	27/5/02	
KCl	BDH	AnalaR	99.5	F862257	74.55	from packet	27/5/02	
MgCl2	-	-	-	-	-	-	-	
MgCl2.6H2O	BDH	AnalaR	99.0	TA753833	203.30	from packet	27/5/02	
CaCl2	-	-	-	-	-	-	-	
CaCl2.2H2O	BDH	AnalaR	99.5	TA940333	147.02	from packet	27/5/02	
SrCl2	BDH	AnalaR	99.0	A225111	158.52	assumed	27/5/02	Asumed to be anhydrous
SrCl2.6H2O	-	-	-	-	-	-	-	
NaHCO3	BDH	AnalaR	99.7	K28137916	84.01	from packet	27/5/02	
H2SO4 (conc)	BDH	ARISTAR	95.0	K29485908	98.08	from packet	27/5/02	
Si (1000ppm sln)	BDH	Spectrosol	996±5 mg/l	OC058843			27/5/02	In 0.5 mol/l NaOH
NaOH	BDH	ARISTAR	98.0	B368949	40.00	from packet	27/5/02	

Original Uni. of Calgary analysis

Location	**14-1-6-14**	Equivalent mol/l	Comments
Temp (oC)	23.6		
pH	6.34		
Alk (mg/L)	493.4	8.0742E-03	
S^{2-} (ppm)	121.6	3.7929E-03	Omit - not studying redox
Na (mg/L)	40850	1.7769E+00	
K (mg/L)	588.7	1.5056E-02	
Ca (mg/L)	1319	3.2909E-02	
Mg (mg/L)	687.9	2.8297E-02	
Mn (mg/L)	0.56	1.0193E-05	Omit - minor
Li (mg/L)	24.3	3.5014E-03	Omit - from drilling fluid?
Fe (mg/L)	2.563	4.5891E-05	Omit - not studying redox
Sr (mg/L)	44.38	5.0651E-04	
Ba (mg/L)	0.262	1.9077E-06	Omit - minor
Si (mg/L)	6.86	2.4422E-04	
Cl (mg/L)	60565	1.7085E+00	
SO_4 (mg/L)	3105	3.2324E-02	
Acetate (mg/L)	19.72	3.3399E-04	Omit - not studying organic
Propionic (mg/L)		-	

	For analytes on left, amount to add (wt in g, ml for Si sln)				
	Ingredient	for 1 litre	for 2 litres	for 4 litres	for 8 litres
Component solution 1	NaHCO3	0.6783	1.3566	2.7133	5.4265
	-	-	-	-	-
	NaCl	99.5898	199.1797	398.3593	796.7187
	KCl	1.1224	2.2449	4.4898	8.9796
	CaCl2.2H2O	4.8383	9.6766	19.3532	38.7065
	MgCl2.6H2O	5.7528	11.5056	23.0111	46.0222
	-	-	-	-	-
	-	-	-	-	-
	-	-	-	-	-
	SrCl2	0.0803	0.1606	0.3212	0.6423
	-	-	-	-	-
Component solution 2	Si std sln	6.8600	13.7200	27.4400	54.8800
	From above chlorides - so this element to vary from measured values				
	conc H2SO4	3.1700	6.3399	12.6799	25.3598
	-	-	-	-	-
	-	-	-	-	-
	Extras				
	NaOH	2.3461	4.6922	9.3843	18.7687

Table 5 Recipe for making up a synthetic equivalent of the porewater from well 12-11-6-14 (as highlighted in Table 1).



Key information		
	Borehole	12-11-6-14
	Latitude	49.46447
	Longitude	103.7995
	Fluid chemistry from University of Calgary baseline survey	
	Plug sample id	BGS12A
	MPG code	H638
	Plug sample horizo	V2
	Perf horiz	M1 to M3

Comments Not a brilliant match between location of perforated horizon (i.e. fluid sample) and location of solid sample.
NaOH weights corrected to take account of NaOH from both added NaOH and the Si standard solution.

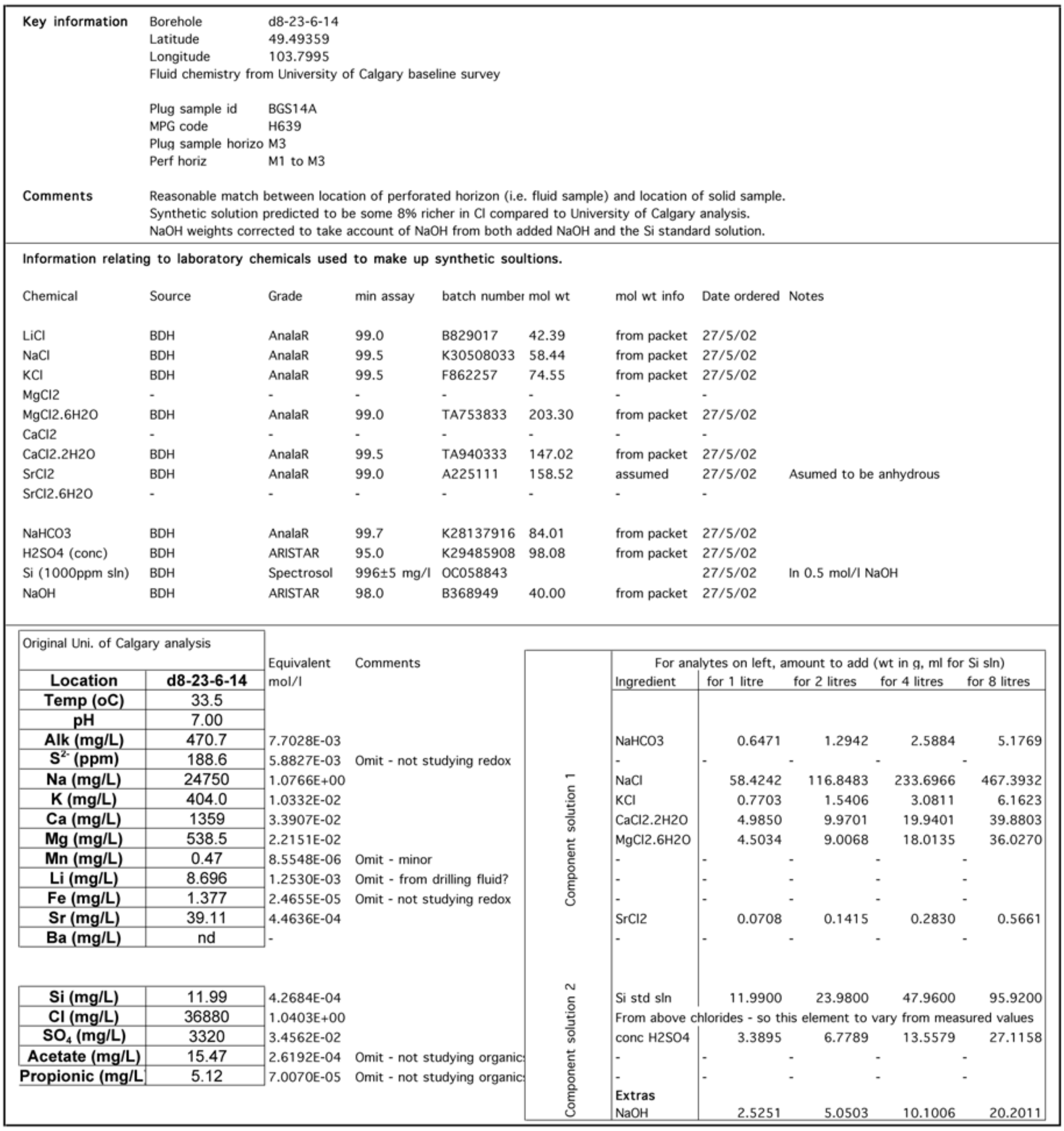
Information relating to laboratory chemicals used to make up synthetic soultions.

Chemical	Source	Grade	min assay	batch number	mol wt	mol wt info	Date ordered	Notes
LiCl	BDH	AnalaR	99.0	B829017	42.39	from packet	27/5/02	
NaCl	BDH	AnalaR	99.5	K30508033	58.44	from packet	27/5/02	
KCl	BDH	AnalaR	99.5	F862257	74.55	from packet	27/5/02	
MgCl2	-	-	-	-	-	-	-	
MgCl2.6H2O	BDH	AnalaR	99.0	TA753833	203.30	from packet	27/5/02	
CaCl2	-	-	-	-	-	-	-	
CaCl2.2H2O	BDH	AnalaR	99.5	TA940333	147.02	from packet	27/5/02	
SrCl2	BDH	AnalaR	99.0	A225111	158.52	assumed	27/5/02	Asumed to be anhydrous
SrCl2.6H2O	-	-	-	-	-	-	-	
NaHCO3	BDH	AnalaR	99.7	K28137916	84.01	from packet	27/5/02	
H2SO4 (conc)	BDH	ARISTAR	95.0	K29485908	98.08	from packet	27/5/02	
Si (1000ppm sln)	BDH	Spectrosol	996±5 mg/l	OC058843			27/5/02	In 0.5 mol/l NaOH
NaOH	BDH	ARISTAR	98.0	B368949	40.00	from packet	27/5/02	

Original Uni. of Calgary analysis		Equivalent	Comments
Location	**12-11-6-14**	mol/l	
Temp (oC)	24.0		
pH	6.47		
Alk (mg/L)	537.8	8.8008E-03	
S^{2-} (ppm)	169.3	5.2807E-03	Omit - not studying redox
Na (mg/L)	24570	1.0687E+00	
K (mg/L)	269.0	6.8798E-03	
Ca (mg/L)	1296	3.2335E-02	
Mg (mg/L)	476.0	1.9580E-02	
Mn (mg/L)	nd	-	
Li (mg/L)	30.9	4.4524E-03	Omit - from drilling fluid?
Fe (mg/L)	1.425	2.5515E-05	Omit - not studying redox
Sr (mg/L)	45.65	5.2100E-04	
Ba (mg/L)	0.276	2.0096E-06	Omit - minor
Si (mg/L)	19.23	6.8459E-04	
Cl (mg/L)	37855	1.0678E+00	
SO_4 (mg/L)	3900	4.0600E-02	
Acetate (mg/L)		-	
Propionic (mg/L)		-	

	For analytes on left, amount to add (wt in g, ml for Si sln)				
	Ingredient	for 1 litre	for 2 litres	for 4 litres	for 8 litres
Component solution 1	NaHCO3	0.7394	1.4787	2.9574	5.9148
	-	-	-	-	-
	NaCl	57.1967	114.3934	228.7869	457.5737
	KCl	0.5129	1.0258	2.0516	4.1031
	CaCl2.2H2O	4.7539	9.5079	19.0158	38.0315
	MgCl2.6H2O	3.9807	7.9614	15.9228	31.8456
	-	-	-	-	-
	-	-	-	-	-
	-	-	-	-	-
	SrCl2	0.0826	0.1652	0.3304	0.6607
	-	-	-	-	-
Component solution 2	Si std sln	19.2300	38.4600	76.9200	153.8400
	From above chlorides - so this element to vary from measured values				
	conc H2SO4	3.9816	7.9632	15.9264	31.8528
	-	-	-	-	-
	-	-	-	-	-
	Extras				
	NaOH	3.0082	6.0163	12.0327	24.0654

Table 6 Recipe for making up a synthetic equivalent of the porewater from well d8-23-6-14 (as highlighted in Table 1).



Key information

Borehole	d8-23-6-14	
Latitude	49.49359	
Longitude	103.7995	
Fluid chemistry from University of Calgary baseline survey		
Plug sample id	BGS14A	
MPG code	H639	
Plug sample horizo	M3	
Perf horiz	M1 to M3	

Comments

Reasonable match between location of perforated horizon (i.e. fluid sample) and location of solid sample.
Synthetic solution predicted to be some 8% richer in Cl compared to University of Calgary analysis.
NaOH weights corrected to take account of NaOH from both added NaOH and the Si standard solution.

Information relating to laboratory chemicals used to make up synthetic soultions.

Chemical	Source	Grade	min assay	batch numbe	mol wt	mol wt info	Date ordered	Notes
LiCl	BDH	AnalaR	99.0	B829017	42.39	from packet	27/5/02	
NaCl	BDH	AnalaR	99.5	K30508033	58.44	from packet	27/5/02	
KCl	BDH	AnalaR	99.5	F862257	74.55	from packet	27/5/02	
MgCl2	-	-	-	-	-	-	-	
MgCl2.6H2O	BDH	AnalaR	99.0	TA753833	203.30	from packet	27/5/02	
CaCl2	-	-	-	-	-	-	-	
CaCl2.2H2O	BDH	AnalaR	99.5	TA940333	147.02	from packet	27/5/02	
SrCl2	BDH	AnalaR	99.0	A225111	158.52	assumed	27/5/02	Asumed to be anhydrous
SrCl2.6H2O	-	-	-	-	-	-	-	
NaHCO3	BDH	AnalaR	99.7	K28137916	84.01	from packet	27/5/02	
H2SO4 (conc)	BDH	ARISTAR	95.0	K29485908	98.08	from packet	27/5/02	
Si (1000ppm sln)	BDH	Spectrosol	996±5 mg/l	OC058843			27/5/02	In 0.5 mol/l NaOH
NaOH	BDH	ARISTAR	98.0	B368949	40.00	from packet	27/5/02	

Original Uni. of Calgary analysis		Equivalent	Comments		For analytes on left, amount to add (wt in g, ml for Si sln)				
Location	d8-23-6-14	mol/l			Ingredient	for 1 litre	for 2 litres	for 4 litres	for 8 litres
Temp (oC)	33.5								
pH	7.00								
Alk (mg/L)	470.7	7.7028E-03		Component solution 1	NaHCO3	0.6471	1.2942	2.5884	5.1769
S^{2-} (ppm)	188.6	5.8827E-03	Omit - not studying redox		-	-	-	-	-
Na (mg/L)	24750	1.0766E+00			NaCl	58.4242	116.8483	233.6966	467.3932
K (mg/L)	404.0	1.0332E-02			KCl	0.7703	1.5406	3.0811	6.1623
Ca (mg/L)	1359	3.3907E-02			CaCl2.2H2O	4.9850	9.9701	19.9401	39.8803
Mg (mg/L)	538.5	2.2151E-02			MgCl2.6H2O	4.5034	9.0068	18.0135	36.0270
Mn (mg/L)	0.47	8.5548E-06	Omit - minor		-	-	-	-	-
Li (mg/L)	8.696	1.2530E-03	Omit - from drilling fluid?		-	-	-	-	-
Fe (mg/L)	1.377	2.4655E-05	Omit - not studying redox		-	-	-	-	-
Sr (mg/L)	39.11	4.4636E-04			SrCl2	0.0708	0.1415	0.2830	0.5661
Ba (mg/L)	nd	-			-	-	-	-	-
Si (mg/L)	11.99	4.2684E-04		Component solution 2	Si std sln	11.9900	23.9800	47.9600	95.9200
Cl (mg/L)	36880	1.0403E+00			From above chlorides - so this element to vary from measured values				
SO_4 (mg/L)	3320	3.4562E-02			conc H2SO4	3.3895	6.7789	13.5579	27.1158
Acetate (mg/L)	15.47	2.6192E-04	Omit - not studying organic		-	-	-	-	-
Propionic (mg/L	5.12	7.0070E-05	Omit - not studying organic		-	-	-	-	-
					Extras				
					NaOH	2.5251	5.0503	10.1006	20.2011

Table 7 General information about the solid samples used in this study (data from Pearce and Springer (2001) and Springer (pers. comm.).

Well and selected core stick information

Well	Latitude	Longitude	Date drilled	Core number	Box Number		Depth		Deposit. Type	Perf. horizon
						base (m)	interval (m)	top (m)		
14-13-6-14W2	49.479112	103.777038	1956	1	7	1404.15	0.67	1403.48	Intershoal	M. evap. to M3
14-1-6-14W2	49.449992	103.777038	1958	1	5	1439.20	1.43	1437.77	Shoal	M1 to M3
12-11-6-14W2	49.464468	103.799454	1957	1	8	1426.89	1.13	1425.76	Shoal	M1 to M3
B8-23-6-14W2	49.493589	103.799454	1991	1	10	1399.36	1.42	1397.94	Intershoal	M1 to M3

Core sample information

Well	Plug no.	Rock type	Plug orient.	Plug diam. (mm)	Plug depth (m)	Gas perm. (mD)	Porosity (%)	Grain dens. (g cc^{-1})	Comment	Approx. Cl content of pore water (mg l^{-1})
14-13-6-14W2	BGS2A	M. Marly	Vertical	54	1403.54	7.40	29.3	2.85		39440
14-1-6-14W2	BGS5A	M. Evaporite	"	"	1437.91	0.03	8.02	2.86		60565
12-11-6-14W2	BGS12A	M. Vuggy	"	"	1426.85	56.81	15.21	2.71	Frac. Perm.	37855
B8-23-6-14W2	BGS14A	M. Marly	"	"	1398.30	8.94	28.38	2.81		36880
B8-23-6-14W2	BGS14B	M. Marly	***	***	1398.50	NA	28.10	2.82		36880

NA = data not available
*** = 2 pieces of whole core were used for this sample rather than a plug

Table 8 Comparison of pressure transducer outputs between those used in the lab and a Druck PTX 610 transducer having external calibration. Note that the ISCO 260D pressure control pump is within 1.5% of the externally-calibrated transducer, and that the secondary pressure transducers give readings virtually identical to the ISCO 260D pump.

Approximate pressure (bar)	**Primary calibration Druck PTX 610 transducer (psi)**	**ISCO 260D syringe pump reading (psi)**	**Readout difference (%)**	**ISCO 260D syringe pump reading (bar)**	**Batch equipment Secondary pressure transducer readings (bar)**			
					PT11 (CO2 expts)	PT12 (N2 expts)	PT13 (N2 expts)	PT14 (CO2 expts)
0	0	0	0.0	0	0	0	0	0
14	198	200	1.0	20	20	20	20	20
28	396	400	1.0	40	40	40	40	40
41	589	600	1.8	60	60	60	60	60
55	786	800	1.8	80	80	80	80	80.5
69	985	1000	1.5	100	100	100	100.5	100.5
83	1180	1200	1.7	120	120	120	120.5	120.5
97	1377	1400	1.6	140	140	140	141	140.5
110	1575	1600	1.6	160	160	160	161	160
124	1771	1800	1.6	180	180	180	181	180
138	1968	2000	1.6	200	200	200	200	200
152	2166	2200	1.5	220	220	220	220	220
165	2363	2400	1.5	240	240	240	240	240
179	2560	2600	1.5	260	259.5	259.5	260	260
193	2756	2800	1.6	280	279.5	279.5	280	280
207	2953	3000	1.6	300	299.5	299.5	300	300
221	3149	3200	1.6	320	319.5	319.5	320	320
234	3347	3400	1.6	340	340	340	340	340
248	3544	3600	1.6	360	360	360	360	360
262	3740	3800	1.6	380	380	380	380	380
276	3937	4000	1.6	400	400	400	400	400

Table 9 Preliminary listing of possible experiments that it is hoped to complete during the study (T = initial test experiments, Y = main experiments, P = possible experiments if resources permit).

Sample type	**ID number**	**State**	**Duration**	**Run conditions (all at 60°C)**					
				~150 bar				~250 bar	
				Batch - CO2	Batch - N2	Column - CO2	Column - N2	Batch - CO2	Batch - N2
Midale Marly	**BGS2A (HTL 134)**	250-500µm	1 w	T	T	-	-	-	-
			3 w	T	T	-	-	-	-
			6 w	T	T	-	-	-	-
			8 w	T	T	-	-	-	-
		<250 µm	8 w	T	T	-	-	Y	Y
		Monolith	12 w	P	P	-	-	P	P
	BGS14A (HTL 137)	250-500µm	2 w	Y	P	-	-	-	-
			4 w	Y	Y	-	-	-	-
			8 w	Y	P	-	-	-	-
			12 w	Y	Y	-	-	-	-
		<250 µm	8 w	Y	Y	-	-	Y	Y
			6 m	Y	Y	-	-	-	-
		125-250 µm	6 m	-	-	Y	Y	-	-
		Monolith	2 w	Y	Y	-	-	-	-
			4 w	Y	Y	-	-	-	-
			8 w	Y	Y	-	-	-	-
			12 w	Y	Y	-	-	-	-
Midale Evaporite	**BGS5A (HTL 135)**	250-500µm	2 w	Y	Y	-	-	-	-
			4 w	Y	Y	-	-	-	-
			8 w	Y	Y	-	-	-	-
			12 w	Y	Y	-	-	-	-
		<250 µm	8 w	Y	Y	-	-	Y	Y
			6 m	Y	Y	-	-	-	-
		Monolith	2 w	Y	Y	-	-	-	-
			4 w	Y	Y	-	-	-	-
			8 w	Y	Y	-	-	-	-
			12 w	Y	Y	-	-	-	-
Midale Vuggy	**BGS12A (HTL 136)**	250-500µm	2 w	Y	Y	-	-	-	-
			4 w	Y	Y	-	-	-	-
			8 w	Y	Y	-	-	-	-
			12 w	Y	Y	-	-	-	-
		<250 µm	8 w	Y	Y	-	-	Y	Y
			6 m	Y	Y	-	-	-	-
		Monolith	4 w	Y	Y	-	-	-	-
			8 w	Y	Y	-	-	-	-
			12 w	Y	Y	-	-	-	-
Borehole cement		250-500µm	12 w	Y	Y	-	-	Y	Y
		<250 µm	8 w	P	P	-	-	P	P
		Monolith	12 w	Y	Y	-	-	P	P
Borehole steel		Monolith	12 w	Y	Y	-	-	Y	Y

Table 10 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	7.2×10^{-5}	10
Na	0.35	7	3.0×10^{-4}	<5
K	0.5	10	2.6×10^{-4}	<5
Mg	0.01	0.2	8.2×10^{-6}	<5
Ca	0.1	2	5.0×10^{-5}	<5
Sr	0.002	0.04	4.6×10^{-7}	<5
Ba	0.002	0.04	2.9×10^{-7}	<5
Mn	0.002	0.02	3.6×10^{-7}	5-10
Total Fe	0.01	0.2	3.6×10^{-7}	5-10
Cr	0.002	0.04	7.7×10^{-7}	10
Al	0.01	0.1	3.7×10^{-6}	10
Total P	0.01	0.1	3.2×10^{-6}	10
Total S	0.25	2.5	7.8×10^{-5}	5-10
Si	0.075	0.75	2.7×10^{-5}	5-10
SiO_2	0.16	1.6	2.7×10^{-5}	5-10
Cl^-	0.1	2	5.6×10^{-5}	<5
Br^-	0.03	6	7.5×10^{-5}	5
NO_3^-	0.04	0.8	1.3×10^{-5}	5-10
SO_4^{2-}	0.3	60	6.3×10^{-4}	10
HCO_3^-	22	22	3.6×10^{-4}	5
CO_3^{2-}	22	22	3.6×10^{-4}	<5
TOC	1	3.6	3.0×10^{-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%.