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The solubility of supercritical CO₂ into pure water and synthetic Utsira porewater

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Saline Aquifer CO₂ Storage (SACS) Project
Commissioned Report CR/02/052N

BRITISH GEOLOGICAL SURVEY

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The solubility of supercritical CO₂ into pure water and synthetic Utsira porewater

C.A. Rochelle and Y.A. Moore

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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 SACS (Saline Aquifer CO₂ Storage) project. The SACS project aims to monitor and predict the behaviour of injected CO₂ in the Utsira Sand reservoir at the Sleipner field in the northern North Sea, using methods that include; time-lapse geophysics, modelling its subsurface distribution and migration, and simulating likely chemical interactions with the host rock.

This report aims to provide 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.

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Summary

This report describes work undertaken at the British Geological Survey (BGS) that forms part of the international SACS (Saline Aquifer CO₂ Storage) project. The SACS project aims to monitor and predict the behaviour of injected CO₂ in the Utsira Sand reservoir at the Sleipner field in the northern North Sea, using methods that include; time-lapse geophysics, modelling its subsurface distribution and migration, and simulating likely chemical interactions with the host rock. This report aims to provide a limited amount of 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 study was undertaken in the Hydrothermal Laboratory of the BGS, where a range of measurements were made using both synthetic Utsira porewater and distilled de-ionised water. The experimental conditions chosen were between 18-80°C and 8-12 MPa (80-120 bar), with most data generated at 37°C and 10 MPa (100 bar) – *in-situ* temperature and pressure at the injection point in the Utsira formation at Sleipner.

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 slightly lower than data from other studies. At 37°C and 10 MPa (100 bar), 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. Solubility values are lower than those obtained for distilled de-ionised water. At 37°C and 10 MPa (100 bar), measured solubility is in the order of 4.5 g of CO₂ per 100 g of solution.

1 Introduction

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

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

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 CO₂. This study focuses on hydrodynamic trapping, and in particular the quantity of CO₂ that can dissolve in formation water. This will be governed by factors such as; the *in-situ* pressure, the *in-situ* temperature, the composition of the formation water, and the degree of mixing between CO₂ and formation water.

In order to enhance the accuracy of storage calculations, and to construct accurate computer models of CO₂/ water/rock interactions, it is necessary to have data on the solubility of CO₂ and water. 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). The availability of literature data precludes the need for a detailed study into CO₂ solubility, but a limited number of experiments have been performed to:

- provide evidence for the solubility of CO₂ within the Utsira formation at Sleipner
- allow comparison of the results with extrapolations from previous experimental data

The conditions of importance within the Utsira formation at Sleipner are; 37°C, 10 MPa (100 bar, or approximately 100 atmospheres), and a porewater of approximately seawater salinity (Gregersen *et al.*, 1998, see Table 1). These conditions represent those at the injection point. After injection, the CO₂ will rise within the Utsira formation due to buoyancy (it has a density of approximately 0.7 compared to 1.0 for water), and it will experience a slight reduction in pressure. The experimental programme detailed in the following sections involves a range of pressures and temperatures centred around the *in-situ* injection conditions so that the influence of pressure and temperature on CO₂ solubility can be ascertained.

2 Literature data on CO₂ and its solubility in water

Under normal, ‘Earth surface’ conditions, CO₂ is a colourless and odourless gas, which is denser than air. It can also exist in another stable form at atmospheric pressure, namely ‘dry ice’. However, this white, ice-like solid requires temperatures below about -78.5°C to be stable (see Figure 1). Liquid CO₂ does not exist at atmospheric pressure. However, liquid CO₂ is stable at higher pressures, requiring a minimum of about 5.1 atmospheres pressure (approximately 5.2 MPa [5.2 bar]). The practicalities of CO₂ storage operations underground (namely that the CO₂ resides safely as a relatively dense phase) require the CO₂ to be ‘supercritical’. This means that the *in-situ* temperature and pressure are above those of the

‘critical point’ (31.1°C and 72.8 atmospheres (approximately 7.4 MPa [73.8 bar]) – see Figure 1). Beyond the critical point there is effectively no distinction between gas and liquid, there exists only a single fluid – a ‘supercritical fluid’.

Original experimental data for the solubility of supercritical CO₂ into aqueous solutions are limited over the range of pressure and temperature of relevance to the underground disposal of CO₂ in the Utsira at Sleipner. Indeed, most studies have concentrated on temperatures and pressures that are either too low or too high, or have used pure water (CO₂ solubility decreases with increasing salinity, e.g. Enick and Klara [1990]).

Ellis and Golding, (1963) do report CO₂ solubilities in pure water, and 0.5, 1 and 2 molal, NaCl solutions. However, the temperatures (170-335°C) and pressures (1-90 bar) of their study are some way outside the scope of the present investigation. They did, however, indicate that equilibrium between CO₂ and water can be obtained in under 24 hours. There are similar limitations to the Takenouchi and Kennedy (1965) dataset, which cover the range 150-450°C and 100-1400 bar (10-140 MPa) (though they do consider 0, 6 and 20 wt% NaCl solutions). Czernichowski-Lauriol *et al.* (1996) give CO₂ solubility data for a 0.55 M NaCl solution at 80°C and 200 bar.

The study by Kuk and Montagna (1983) gives 4 experimentally measured CO₂ solubilities in pure water at 100 and 150 atmospheres (approximately 10 and 15 MPa) pressure, and over a temperature range of 40-60°C. These results appear to have been obtained by gas chromatography measurements. Kuk and Montagna (1983) also report 6 experimental datapoints of Wiebe and Gaddy (1941) who also measured CO₂ solubilities in pure water at 100 and 150 atmospheres (approximately 10 and 15 MPa) pressure, but over a temperature range of 30-80°C. Suto *et al.* (2000) conducted experiments with distilled water and water pre-reacted with granite (<1000 mg l⁻¹ total dissolved solids) at 100-300°C and 10-30 MPa (100-300 bar). They also report a good assimilation of their solubility data with those from several previous studies.

It is apparent therefore, that there is a general lack of directly measured CO₂ solubility values in the pressure and temperature region of interest. However, extrapolation of the data from the above studies to 37°C and 10 MPa (100 bar), indicates that the solubility of CO₂ is likely to be in the order of 55 g for every kilogram of *pure* water. CO₂ solubility will decrease with increasing salinity. Enick and Klara (1990) suggest a pressure-insensitive relationship between salinity and CO₂ solubility. For seawater at 21°C, this appears to be in the order of 80% of that measured for deionised water. Data from Czernichowski-Lauriol *et al.* (1996) suggests a similar relationship. At 80°C and 200 bar, CO₂ solubility in 0.55 M NaCl solution is about 84% of that measured in distilled de-ionised water.

Other studies (van Eldik and Palmer, 1982), albeit at relatively low pressures, have also shown that 99% of dissolved CO₂ is as the dissolved gas rather than true carbonic acid. Thus, the reaction of primary interest during dissolution is:



Once formed, true carbonic acid could dissociate to form bicarbonate ions and protons (acidity):



The studies mentioned above typically used pure water in solubility measurements. However, in the Utsira Formation the CO₂ will be in contact with fluids of approximately seawater salinity. In order to provide data that are; comparable with previous studies, applicable to the

other experiments, and applicable to actual conditions at Sleipner, experiments were performed using both distilled de-ionised water (DDW) and synthetic Utsira porewater (SUP). These were used between a temperature range of 18-70°C and 8-12 MPa. A summary of the experiments conducted is given in Tables 2 and 3.

3 Experiments

3.1 STARTING MATERIALS

Three fluids were used in the experiments; CO₂ (as either a liquid or a supercritical phase) distilled de-ionised water and synthetic Utsira porewater.

3.1.1 CO₂

The CO₂ used in this study was sourced from high purity (99.99%) liquid CO₂ (Air Products, 4.5 Grade). This liquid CO₂ was obtained in a cylinder fitted with a dip tube and pressurised with 2000 psi (approximately 14 MPa [140 bar]) of helium. However, the actual experimental pressures were controlled by ISCO syringe pumps, which were 'zeroed' prior to each experiment. For experiments below 31.1°C, the pressure was sufficient for the CO₂ to be liquid. However, above this temperature (i.e. for most of the experiments) the CO₂ was a supercritical fluid.

3.1.2 Distilled de-ionised water

The water used was produced in a two-step process, distillation, followed by passage through ion-exchange cartridges. It had a conductance better than 16 µS cm⁻¹. Distilled de-ionised water was used in this study to compare results with previous studies. Pure water also represents a limiting case, in that it has a maximum solubility for CO₂ compared to saline fluids.

3.1.3 Synthetic Utsira porewater

At the start of the experimental programme it was decided to make up a single, 25 l stock solution of synthetic Utsira porewater (SUP), and that this would be used for all the experiments. The 'recipe' for this is given in Table 4, and was based upon the only analysis of the Utsira porewater available at the start of the study - from the Oseberg field some 200 km north of Sleipner (Gregersen *et al.*, 1998). This synthetic porewater was close to seawater composition and was used in the majority of the experiments. Three analyses of the initial solution were made, and these averaged to give a representative composition (see Appendix I) of the starting fluid for the experiments.

It is noteworthy that the Utsira is a relatively shallow formation. Porewaters within deep aquifers or associated with hydrocarbon fields (Abbotts, 1991) could be significantly more saline than the SUP used in these experiments. The effect of higher salinity would be to lower the concentration of dissolved CO₂ in solution and hence possibly reduce the amount of CO₂/rock reaction (see Enick and Klara, 1990).

As a quality assurance check, it was also decided to periodically analyse the stock solution that was kept in the laboratory. Data for this are given in Appendix I. Most analytes show uniform concentrations over time (within analytical uncertainties). However, values for bicarbonate concentration do decrease over the 2 years of the experimental programme, possibly as a result of slow conversion to CO₂ and loss to the atmosphere. This is not considered an important aspect for the experimental programme as bicarbonate concentrations

change radically once a high pressure of CO₂ is applied to the synthetic porewater in the experiments.

3.2 APPARATUS AND EXPERIMENTAL METHODOLOGY

The approach used in this study is essentially the same as that used for CO₂ solubility experiments reported previously (Czernichowski-Lauriol *et al.*, 1996). The basic idea is to allow an aqueous fluid sample to react with a known pressure of CO₂ at a fixed temperature (generally above room temperature). A sub-sample of the aqueous phase is then withdrawn and preserved at the experimental pressure, but at room temperature. The sample is then depressurised and analysed for total dissolved carbon. A key aspect of this approach, is that preservation of the sample prevents CO₂ loss by degassing during depressurisation.

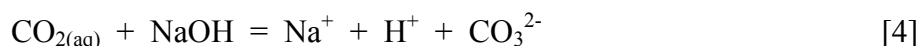
The equipment consists of a stainless steel pressure vessel with Viton O-ring pressure seals, containing a PTFE (polytetrafluoroethylene) sample container (Figure 2). Two sizes of otherwise identical pressure vessels were used in this study, having volumes of either 100 ml or 150 ml. During assembly, a sample of either distilled de-ionised water or synthetic Utsira porewater was placed into the PTFE container (filled to approximately ²/₃ full), together with a magnetic stirrer bead. The top of the pressure vessel was then securely tightened down, and pressure tubing connected. The whole assembly was then placed on top of a magnetic stirrer inside a Gallenkamp PlusII fan-assisted oven that could be maintained to within ± 0.5°C. Although the base of the stainless steel pressure vessel was in the order of 1 cm thick, it still allowed for good ‘coupling’ between the magnetic stirrer and the stirrer bead. Consequently, the aqueous solution was well mixed and was in good contact with overlying supercritical CO₂. Previous tracer tests (Czernichowski-Lauriol *et al.*, 1996) have shown that this method of stirring can result in mixing in under 5 seconds. Rapid mixing is desirable so that concentration gradients do not develop at the surface of the aqueous phase due to the rapid solution of CO₂.

A known pressure of CO₂ was then admitted to the reactor using a high pressure ISCO 260D syringe pump. This pump was set to ‘constant pressure’ mode such that it automatically injected or withdrew CO₂ as necessary. This minimised the impact of any leaks of CO₂ from the reactors or pipework. The fluid phase was stirred periodically. Previous work (Ellis and Golding, 1963; Stewart and Munjal, 1970; Czernichowski-Lauriol *et al.*, 1996) indicated that at least 24 hours should have passed between changing the experimental conditions and sampling the aqueous phase. This procedure helped ensure that a stable dissolved CO₂ concentration could be achieved. However, other studies (Toews *et al.*, 1995) have indicated that stable CO₂ concentrations can be obtained in high pressure water-CO₂ experiments within timescales as short as 30 minutes.

Sampling of the aqueous phase was achieved by means of a ‘dip tube’ (see Figure 2). This ensured that only the aqueous phase (and not the CO₂ phase) was sampled. The CO₂-saturated aqueous sample was withdrawn from the oven along ¹/₈ inch diameter PEEK (polyetheretherketone) pressure tubing. This resulted in a cooling of the sample to room temperature (approximately 20°C). This was advantageous, in that the solubility of CO₂ increases at lower temperatures (e.g. Kuk and Montagna, 1983). Consequently, the cooled aqueous solution was below saturation with CO₂, and hence less prone to degassing. After flushing the pipework with a few ml of sample, the CO₂-rich aqueous sample was then withdrawn into a titanium ‘floating piston’ sampling vessel previously part filled (approximately 50%) with 4M NaOH solution. The other end of the floating piston sampler was filled with distilled de-ionised water, which was slowly removed to allow the CO₂-rich aqueous solution to mix with the 4M NaOH solution. Removal of the distilled de-ionised

water was achieved by either; bleeding it out slowly through a needle valve, or drawing it out via a second ISCO syringe pump. This second pump was set at a withdrawal rate of 5 ml per minute. This arrangement of pumps and sampler ensured that the relatively delicate and costly syringe pumps were contacted by only dry CO₂ or pure water. This minimised the potential for corrosion and subsequent loss of performance of the pumps.

Stabilisation of the dissolved CO₂ was achieved by reacting it with 4M NaOH solution at room temperature and at the experimental pressure:



Other carbon species (such as HCO₃⁻ and H₂CO₃) are also converted to CO₃²⁻. As long as the NaOH is present in excess, the CO₃²⁻ will remain stable. The two solutions were allowed to react for approximately 5 minutes, and then depressurised without generation of CO₂ gas. Analysis for CO₃²⁻ gave a measurement of total dissolved carbon, most of which will have been in the form of CO_{2(aq)} (van Eldik and Palmer, 1982). Addition of the 4M NaOH solution caused a dilution of the CO₂-rich solution. This was corrected for, by calculating a dilution factor based upon measured Cl⁻ content (for experiments using synthetic Utsira porewater) or measured Na content (for experiments using distilled de-ionised water) - see Section 3.4.

Although the above procedure worked well, great care had to be taken on sampling to prevent pressure reduction, and as a consequence degassing. Degassing would result in the formation of bubbles that may cause the floating piston sampler to not fill completely with liquid. The impact of this would be that a smaller than expected sample would be taken, which would result in an underestimation of the quantity of CO₂ in solution. Key potential locations for degassing are any points in the flow system where fluid flow might be restricted. An important one of these is the filter at the base of the dip tube (see figure 2 and later sections).

3.3 ANALYTICAL PROCEDURE

3.3.1 Instrumentation

Analyses of the alkaline preserved samples were performed by titration on a Radiometer VIT90 Video Titrator with ABU93 Triburette and SAM90 Sample Station. Measurements of pH were made using a Radiometer pHG200 pH electrode with a REF200 reference electrode.

3.3.2 Calibration of pH

Calibration was performed using Whatman high-resolution pH buffers. For samples of pH less than 10, calibration was carried out using pH 4 and 10 buffers, and checked using a pH 7 buffer. For samples of pH greater than 11.5, calibration was carried out using pH 7 and 13 buffers, and checked using a pH 10 buffer. The ambient laboratory temperature was measured using a mercury-in-glass thermometer and the exact pH at that temperature was manually entered immediately prior to calibration.

3.3.3 Titration

Either 0.01 mol l⁻¹ (0.02N) or 0.5 mol l⁻¹ (1N) sulphuric acid was used as titrant against 2.0 ml or 1.0 ml of samples of pH less than 10 and greater than 11.5 respectively. The pH of the analytical sample was monitored as a function of volume of titrant added and the titration was allowed to proceed until a pH of less than 2 was achieved.

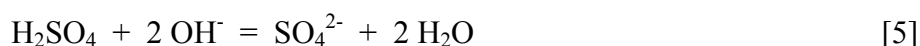
3.3.4 Results

The software automatically identified any equivalence points by examining the derivative curve of pH versus titrant volume. Addition of a small volume of titrant caused a large change in pH at an equivalence point, and thus the equivalence point was identified as a peak on the derivative curve.

Samples having an initial pH > ~11.5

For these samples it was assumed that the concentration of bicarbonate ions in the sample was negligible and that the alkalinity was dominated by hydroxide ions or by hydroxide and carbonate ions. One, two or three equivalence points may be observed, depending on whether the relative concentrations of these two ions allowed resolution of their equivalence points.

a) For samples where one equivalence point was observed at pH ~8.5, this was assumed to represent neutralisation of hydroxyl ions:



In this case, it was assumed that the concentration of carbonate ions in solution is too low to be determined. If the sample volume is denoted as V_s , the total volume of titrant added to each equivalence point is denoted as V_1, V_2 , etc, and the sulphuric acid titrant molarity is denoted as M_a , then:

$$[\text{OH}^-] \text{ mg l}^{-1} = \frac{17007.37 \times M_a \times 2 \times V_1}{V_s} \quad [6]$$

b) For samples where three equivalence points are observed, the first at pH ~8.5 was assumed to represent neutralisation of hydroxyl ions, the second at pH ~7.5 represented the carbonate/hydrogen carbonate end point:



and the third at pH ~4.5 represented the hydrogen carbonate/carbonic acid end point:



Since the HCO_3^- was wholly derived from the CO_3^{2-} , the previous two equations may be combined to give:



If the total volume of titrant added to each equivalence point is denoted as V_1, V_2 and V_3 respectively and the sample volume and sulphuric acid titrant molarity are denoted as before then:

$$[\text{OH}^-] \text{ mg l}^{-1} = \frac{17007.37 \times M_a \times 2 \times V_1}{V_s} \quad [10]$$

$$[\text{CO}_3^{2-}] \text{ mg l}^{-1} = \frac{60009.35 \times M_a \times (V_3 - V_1)}{V_s} \quad [11]$$

c) For samples where two equivalence points were observed, the first at pH ~8.5 was assumed to be a combined $\text{OH}^-/\text{CO}_3^{2-}$ equivalence point and the second at pH ~4.5 was assumed to be an equivalence point due to HCO_3^- formed by titration of the CO_3^{2-} . If the sample volume, the sulphuric acid titrant molarity and the total volume of titrant added to each equivalence point are denoted as before, then:

$$[\text{OH}^-] \text{ mg l}^{-1} = \frac{17007.37 \times M_a \times 2 \times (V_2 - (2 \times (V_2 - V_1)))}{V_s} \quad [12]$$

$$[\text{CO}_3^{2-}] \text{ mg l}^{-1} = \frac{60009.35 \times M_a \times (V_2 - V_1)}{V_s} \quad [13]$$

Samples having an initial pH <~10

For these samples it was assumed that the concentration of OH^- in the sample was negligible and that alkalinity was dominated by the carbonate equilibrium system. One or two equivalence points may be observed depending on whether CO_3^{2-} only, HCO_3^- only or a mixture of these two ions were present in the sample.

a) For samples where one equivalence point was observed at pH ~4.5 it was assumed that only HCO_3^- was present in the sample. The software automatically calculated the alkalinity, expressed as $\text{mg l}^{-1} \text{HCO}_3^-$, to the equivalence point observed, assuming a sample volume of 2 ml.

b) For samples where two equivalence points were observed, the first at pH ~8.5 was assumed to be a CO_3^{2-} equivalence point and the second at pH ~4.5 was assumed to be an equivalence point due to the HCO_3^- formed by titration of the CO_3^{2-} and any HCO_3^- present in the original sample. If the sample volume was denoted as V_s , the total volume of titrant added to each equivalence point is denoted as V_1 and V_2 respectively and the sulphuric acid titrant molarity is denoted as M_a , then:

$$[\text{CO}_3^{2-}] \text{ mg l}^{-1} = \frac{60009.35 \times M_a \times 2 \times V_1}{V_s} \quad [14]$$

$$[\text{HCO}_3^-] \text{ mg l}^{-1} = \frac{61017.1 \times M_a \times 2 \times (V_2 - (2 \times V_1))}{V_s} \quad [15]$$

3.3.5 Quality Control

Two quality control standards were used. For the samples of pH greater than 11.5, a quality control standard containing 2 mol l^{-1} of hydroxyl ions and 0.5 mol l^{-1} of carbonate ions was prepared by dissolving 40.00 g of BDH AnalaR[®] sodium hydroxide and 26.4472 g of BDH AnalaR[®] sodium carbonate in 500 ml of deionised water. For the samples of pH less than 10, a quality control standard containing 200 mg l^{-1} bicarbonate was prepared by dissolving 0.2754 g of BDH AnalaR[®] grade sodium bicarbonate in 1000 ml of deionised water. The relevant QC standards were analysed at the start and finish of the analytical run and after not more than every ten samples.

3.4 DATA MANIPULATION

During sampling, stabilisation of the dissolved CO_2 was achieved by reacting it with an excess of 4M NaOH solution at the experiments pressure (see equation [4]). If the NaOH is present in excess, the dissolved CO_2 will be trapped as carbonate (CO_3^{2-}) rather than bicarbonate (HCO_3^-). This is useful, as the CO_3^{2-} will remain stable during depressurisation, and so CO_2 gas will not be lost to the atmosphere. The solution can then be analysed by potentiometric titration.

The 'raw' analytical data for the experimental solution/NaOH solution mixture reported CO_3^{2-} concentrations in mg l^{-1} . However, these values need to be corrected for dilution due to the NaOH. For the synthetic Utsira porewater (SUP) experiments the dilution factor was calculated by assuming that all Cl^- was derived from the SUP. By knowing the starting and final Cl^- concentration, the dilution factor could be calculated. Similarly, for the experiments using distilled de-ionised water (DDW), the dilution factor was calculated by assuming that all Na was derived from the NaOH.

Example calculation for SUP case:

Cl⁻ concentration in SUP starting fluid = 18659 mg l⁻¹

Measured Cl⁻ concentration in preserved (SUP/NaOH) sample = 8738 mg l⁻¹

Therefore CO₂-rich SUP makes up $(8738 / 18659) \times 100 = 46.8\%$ of the mixture

In other words, times diluted = $100 / 46.8$ or $18659 / 8738 = 2.14$

If measured CO₃²⁻ concentration in the preserved (SUP/NaOH) sample = 24916 mg l⁻¹,
then the equivalent corrected CO₃²⁻ concentration = 53206 mg l⁻¹

Example calculation for DDW case:

Na⁺ concentration in 4M NaOH = 106228 mg l⁻¹

Measured Na⁺ concentration in preserved (SUP/NaOH) sample = 59795 mg l⁻¹

Therefore NaOH solution makes up $(59759 / 106228) \times 100 = 56.3\%$ of the mixture

Consequently the DDW sample makes up 43.7% of the mixture

In other words, times diluted = $100 / 43.7 = 2.29$

If measured CO₃²⁻ concentration in the preserved (SUP/NaOH) sample = 19704 mg l⁻¹,
then the equivalent corrected CO₃²⁻ concentration = 45078 mg l⁻¹

The experiments were conducted at between 8-12 MPa (80-120 bar) and 18-70°C. However, they were sampled at room temperature and between 8-12 MPa (80-120 bar). It would be possible to apply corrections to account for changes in solution volume due to temperature changes using isobaric expansivity functions (and similarly any pressure changes using isothermal compressibility functions). Whether such correction is needed can be scoped by considering the case of pure water.

For a small change in temperature (Atkins, 1982):

$$\Delta V \approx \alpha V \Delta T \quad [16]$$

where:

ΔV = change in volume of the system

α = isobaric expansivity

V = volume

ΔT = change in temperature

For a notional 1000 ml of water, a temperature change of 70 to 20°C, and $\alpha = 2.0678 \times 10^{-4} \text{ K}^{-1}$ (Weast, 1972/1973):

$\Delta V \approx 10.3 \text{ cm}^3$ volume decrease (i.e. approximately 1.0%)

For a notional 1000 ml of water, a temperature change of 37 to 20°C, and $\alpha = 2.0678 \times 10^{-4} \text{ K}^{-1}$ (Weast, 1972/1973):

$\Delta V \approx 3.5 \text{ cm}^3$ volume decrease (i.e. approximately 0.4%)

Similarly, for a small change in pressure (Atkins, 1982):

$$\Delta V \approx -K V \Delta p \quad [17]$$

where:

ΔV = change in volume of the system

K = isothermal compressibility

V = volume

Δp = change in pressure

For a notional 1000 ml of water, a pressure change of 100 to 1 bar (approximately 10 to 0.1 MPa), and $K = 45.1819 \times 10^{-6} \text{ bar}^{-1}$ (Weast, 1972/1973):

$$\Delta V \approx 4.6 \text{ cm}^3 \text{ volume increase (i.e. approximately 0.5\%)}$$

It is assumed that the experimental solutions will behave in a similar way to pure water, and so depressurising and cooling the solution will result in volume changes of less than 1% (assuming no degassing). This change is considered relatively small compared to uncertainties introduced by the sampling or analytical processes. Consequently, compressibility and expansivity corrections have *not* been applied to the results.

4 Results

Specific comments on the results are mentioned in the following sections. However, it is worth re-iterating a couple of points alluded to earlier. Firstly, an apparent reduction in CO_2 concentration can easily happen if pressure reduction occurred during sampling. Consequently, where there have been several analyses (i.e. for individual samples having undergone similar conditions), the one with the highest concentration will be more representative of the actual concentration in the experiment. Although care was taken to minimise reductions in pressure, these could occur when opening valves to equilibrate pressures in the sampling line, or too fast a sampling flow rate through the in-line filter.

However, it is also possible to have excess CO_2 in the extracted sample if breakthrough of supercritical CO_2 occurred (i.e. with this being drawn into the dip tube rather than the aqueous fluid). Normally however, this problem was straightforward to identify during sampling, as it resulted in excessive gas being released when the pressurised sampler was removed from the sampling line.

Samples that were obviously unrepresentative (mainly those with large excesses of CO_2) were discarded prior to analysis, and are thus not recorded.

The errors assumed for the data were set at $\pm 0.05 \text{ mol l}^{-1}$ (2200 mg l^{-1} as CO_2). These are much larger than the analytical errors, but were set so as to account for 'equipment handling' variations during sampling. Larger variations caused by obvious sampling problems (as noted above) were apparent from trends in the data, and caused rejection of suspect data.

4.1 SOLUBILITY OF CO_2 IN DISTILLED DE-IONISED WATER

The experiments were conducted in two phases. The first, larger phase utilised a filter at the end of the dip tube inside the pressure vessel. In the second phase this dip tube was removed. The results of the experiments are presented in Table 2 and are also plotted on Figures 3-7.

Several observations can be made from the data:

- CO_2 solubility in distilled de-ionised water increases with decreasing temperature
- CO_2 solubility in distilled de-ionised water generally increases with increasing pressure
- there is a fair amount of scatter in the data

For most of the data, the general solubility trends observed for pressure and temperature are in line with previous studies (e.g. Kuk and Montagna, 1983; Wiebe, 1941; Wiebe and Gaddy, 1941). However, there is more scatter in the data than might have been expected. It is possible that a certain degree of degassing could have occurred during sampling, especially when the

filter was in place at the end of the sampling ‘dip tube’ (‘series 1’ data in Figures 3-7). This would have occurred if there were too much of a pressure decrease across the filter. Samples collected without a filter (‘series 2’ data in Figures 3-7) do tend to give higher solubility values. If some degassing was occurring, then the data should represent minimum solubilities, as gas formation would tend to reduce the volumes of the sample taken. Although the number of experimental data points at a given pressure is variable, the upper bound to the data for each pressure does appear to map out a linear relationship between solubility and temperature (see comments below).

It is worth noting that scatter of data below the expected solubility was more apparent for pure water than for synthetic Utsira porewater (see below). It is possible that this may just be an artefact due to ‘operator error’. It is also possible, that the higher solubility of CO₂ in dilute solutions makes them more prone to degassing. However, it could also be that dilute solutions have a faster rate of gas release should any slight depressurisation occur (though this is somewhat speculative at the moment, and not based on detailed data).

The 12 MPa (120 bar) data (Figure 7) are unusual in that they appear to give solubility values lower than expected when compared to the rest of the experimental data. The reasons for the apparently lower values are not totally clear at this time. However, if a small amount of localised depressurisation did occur, then any resulting degassing might be expected to be more apparent for solutions containing more dissolved CO₂ (i.e. those at highest pressure).

For the CO₂ solubility in pure water dataset produced in this study, the actual solubility values for a given temperature and pressure appear to be somewhat lower compared to previous studies. Indeed, at 37°C and 10 MPa (100 bar), CO₂ solubility appears to be approximately 10% lower. This is illustrated in Figure 8, where data from this study are compared with literature data (from: Kuk and Montagna, 1983; Wiebe, 1941; Wiebe and Gaddy, 1941). The data from this study plotted on Figure 8 are the *maximum* values obtained (i.e. the ones apparently suffering less degassing) at 10 MPa for a given temperature. The data at 35 and 70°C do appear to be unduly low, and are considered to be minimum values that help bracket the actual solubility value. However, the data at 37, 50 and 80°C do appear to show a consistent negative deviation from previous studies of 0.5 g of CO₂ per 100 g of water. The reasons for this unexpected deviation are not clear, especially as the same technique used at approximately 20 MPa (Czernichowski-Lauriol et al., 1996) produced a much better data fit with previous studies.

The reasons for the lower than expected CO₂ solubilities in pure water are not clear at this time. Although this study and previous studies involve extracting CO₂-saturated samples under pressure, the exact method of determining CO₂ content is quite different (e.g. analysis of preserved carbonate versus measurement of degassed CO₂). This may explain some of the differences in the results. It is also possible that the potential for aqueous volume changes described in Section 3.4 actually do have an important impact, and so cannot be assumed to be negligible – even though an initial assessment suggests that their effect is only minor.

A possible approach to investigate why lower solubility values were obtained would be to conduct analyses of CO₂-rich solutions under conditions of elevated temperature and pressure. This approach would not involve depressurisation of the solutions and hence any artefacts resulting from it would be removed from the final data. Infrared spectroscopic techniques are one way that such analyses might be achieved (e.g. Falk and Miller, 1992), however the necessary resources to investigate this were not available during the period of this short study.

4.2 SOLUBILITY OF CO₂ IN SYNTHETIC UTSIRA POREWATER

In a similar way to the experiments described above, these experiments were also conducted in two phases. The results of the experiments are presented in Table 3 and are also plotted on Figures 9-13.

Several observations can be made from the data:

- CO₂ solubility in synthetic Utsira porewater increases with decreasing temperature
- CO₂ solubility in synthetic Utsira porewater generally increases with increasing pressure
- there is less scatter in the data than for distilled de-ionised water, although there is still some scatter in the data

Extrapolation of the results to 20 MPa (200 bar) shows broad agreement with earlier data for similar salinity fluids (Czernichowski-Lauriol *et al.*, 1996).

For most of the data, the general solubility trends observed for pressure and temperature are in line with previous studies using pure water (as described above). Although there is some scatter in the data (also as described above), this appears to be somewhat less than for the distilled de-ionised water experiments. It is not clear at present whether this observation is just a chance artefact of 'operator error'. However, it can not be ruled out that saline solutions may have a slower rate of gas release should any slight depressurisation occur, and hence be less prone to degassing during sampling.

It is difficult to compare directly the CO₂-synthetic Utsira porewater dataset produced in this study with other data, as little previous experimental data could be found for the pressure, temperature and salinity of interest. For seawater salinity (approximately the same as the Utsira porewater), data are available at lower temperatures more applicable to oceanic disposal of liquid CO₂ (e.g. Teng and Yamasaki, 1998). Higher temperature data are limited to relatively simple solutions, with most of the data being above seawater salinity (e.g. Ellis and Golding, 1963; Takenouchi and Kennedy, 1965). However, indirect comparison is possible. Figure 14 shows a comparison between literature data for CO₂ solubility in pure water and several datasets having approximately the same salinity as the synthetic Utsira porewater. These datasets include; data produced for this study, data from experiments reacting synthetic Utsira porewater with Utsira sand and CO₂ (Rochelle *et al.*, 2002), and data from CO₂ solubility studies in 0.55 M NaCl solution at approximately 20 MPa (Czernichowski-Lauriol *et al.*, 1996). All these data show CO₂ solubility to be less than for pure water under similar conditions. However, as for the distilled de-ionised water system described above, the data at 35 and 70°C appear unduly low, and have therefore only been used to bracket CO₂ solubility.

Enick and Klara (1990) summarised various CO₂ solubility measurements for a range of fluids (seawater, brines, CaCl₂ solutions, and NaCl solutions), pressures (3-85 MPa), and temperatures (21-250°C). They found that there was a relatively simple relationship between the ratio of CO₂ solubility in saline fluids compared to that in pure water (the CO₂ solubility factor), and total dissolved solids (see Figure 15). A similar procedure was applied to the data shown in Figure 14, and the results are plotted on Figure 15. In general, *all* of the (more reliable) data produced in this study fall within the range of scatter of previous data. For all but one of the more saline fluids (synthetic Utsira porewaters, Utsira sand experiments, and 0.55 M NaCl solution) the match with literature data is relatively good. The one slightly spurious data point gives a slightly high CO₂ solubility factor, and comes from an experiment reported in Rochelle *et al.*, (2002). As other data from similar experiments do not show such

an elevated CO₂ solubility factor, it is possible that excess CO₂ (i.e. free supercritical CO₂) may have been captured during the sampling process. Also plotted on Figure 15 are solubility data for the distilled de-ionised water experiments (see previous section). Although these have a CO₂ solubility factor approximately 10% lower than expected, this is within the range of variability of data from other studies.

5 Conclusions

A range of experimental measurements have been undertaken to better constrain the solubility of CO₂ in synthetic Utsira porewater and in distilled de-ionised 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. A sample of the CO₂-rich aqueous phase was then removed (still at pressure) and reacted with 4M NaOH solution to preserve any dissolved carbon species. Once preserved, the sample could be depressurised without gas loss. This technique was practicable in the laboratory. However, during extraction of the CO₂-rich aqueous sample, great care had to be taken to prevent any pressure reduction, and consequent degassing. Partly degassed samples could be identified as they gave slightly lower than expected CO₂ solubility values. As a consequence, several samples were taken for each set of conditions, and the maximum solubility value obtained was taken as being most reliable.

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. 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.

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Figure 1 CO₂ phase diagram (based on Atkins, 1982).

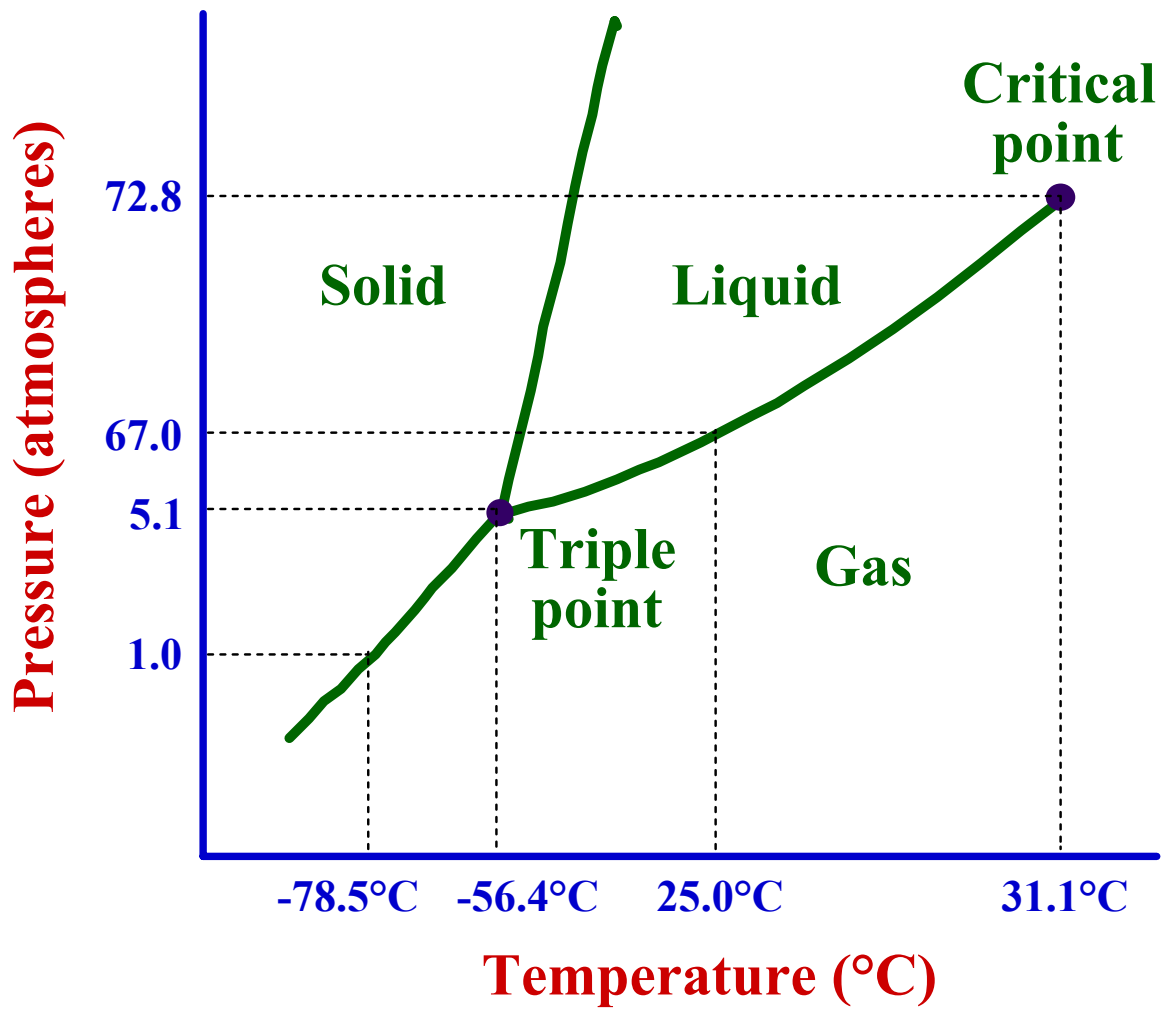


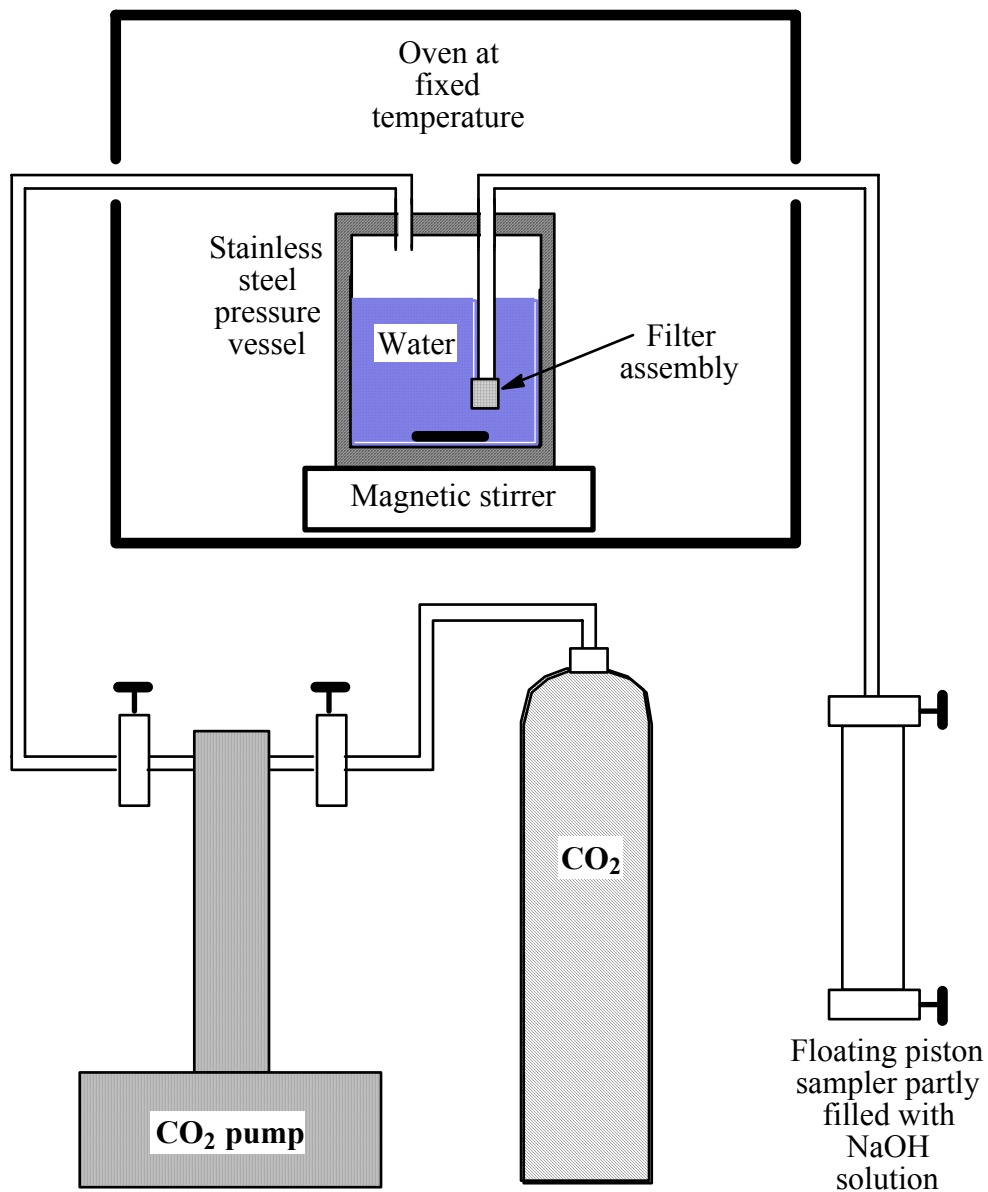
Figure 2 Schematic representation of equipment used for CO₂ solubility studies.

Figure 3 Measured solubility of CO₂ in distilled de-ionised water at 8 MPa.

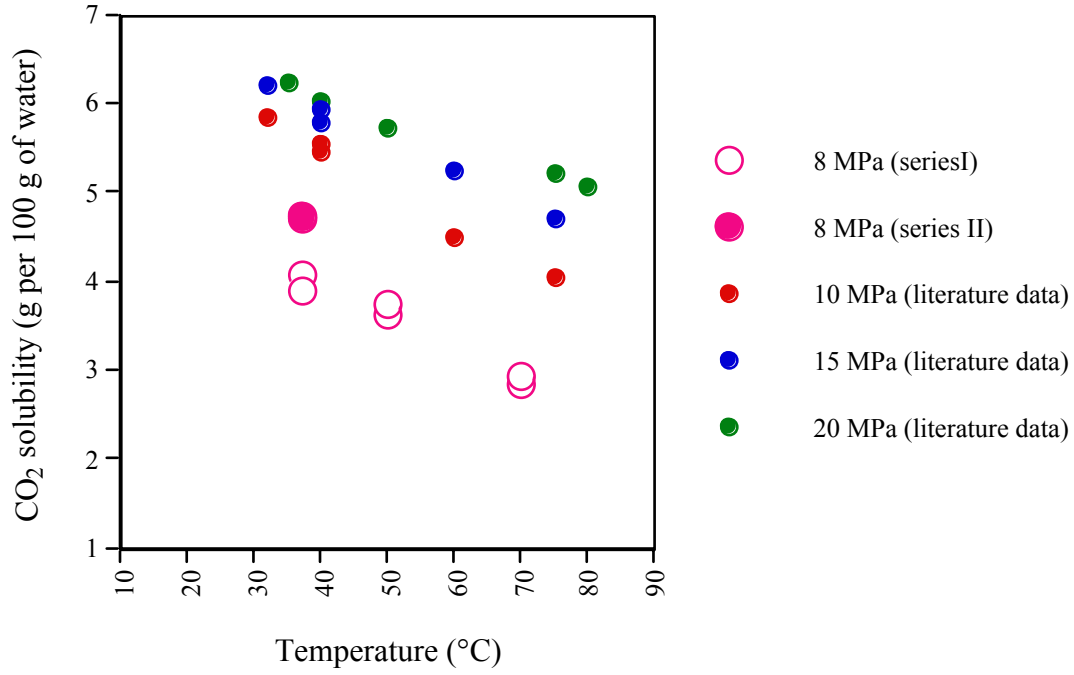


Figure 4 Measured solubility of CO₂ in distilled de-ionised water at 9 MPa.

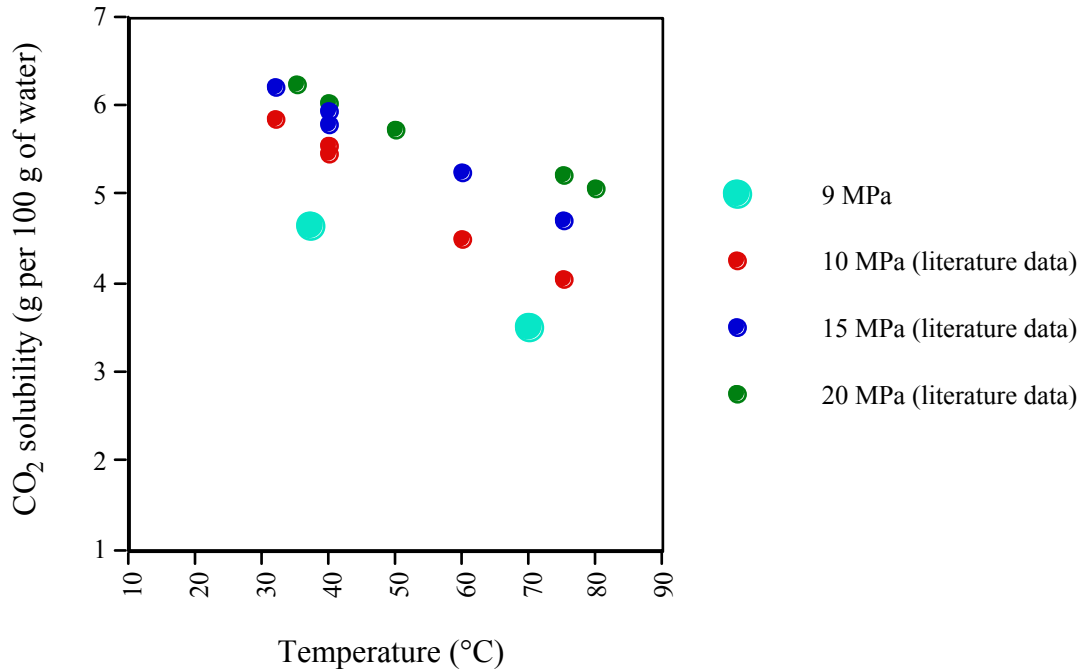


Figure 5 Measured solubility of CO₂ in distilled de-ionised water at 10 MPa.

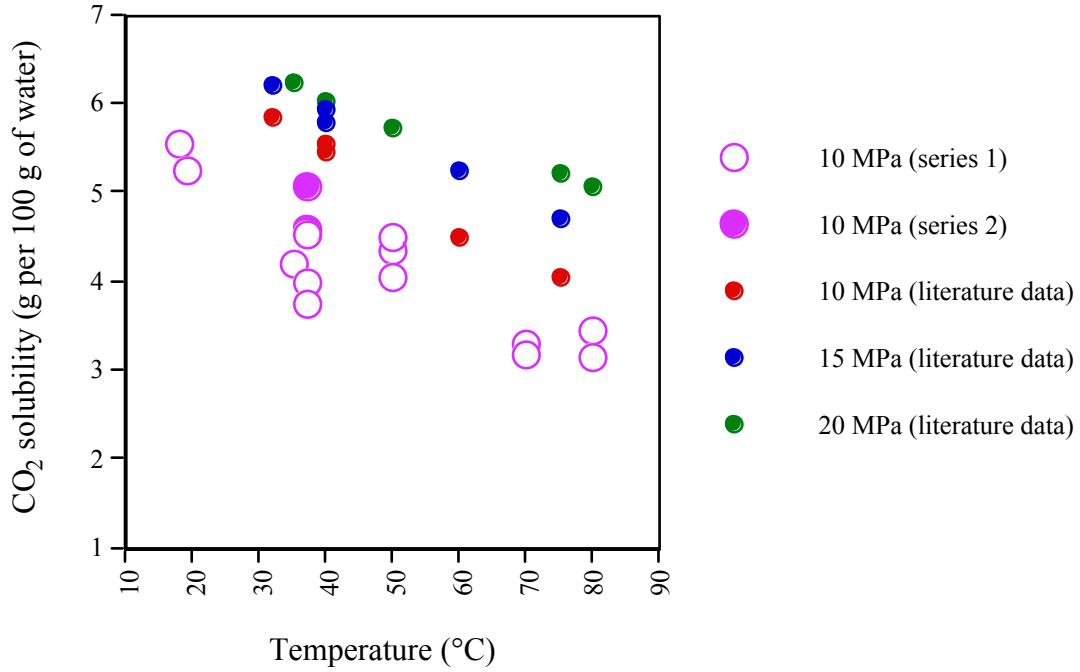


Figure 6 Measured solubility of CO₂ in distilled de-ionised water at 11 MPa.

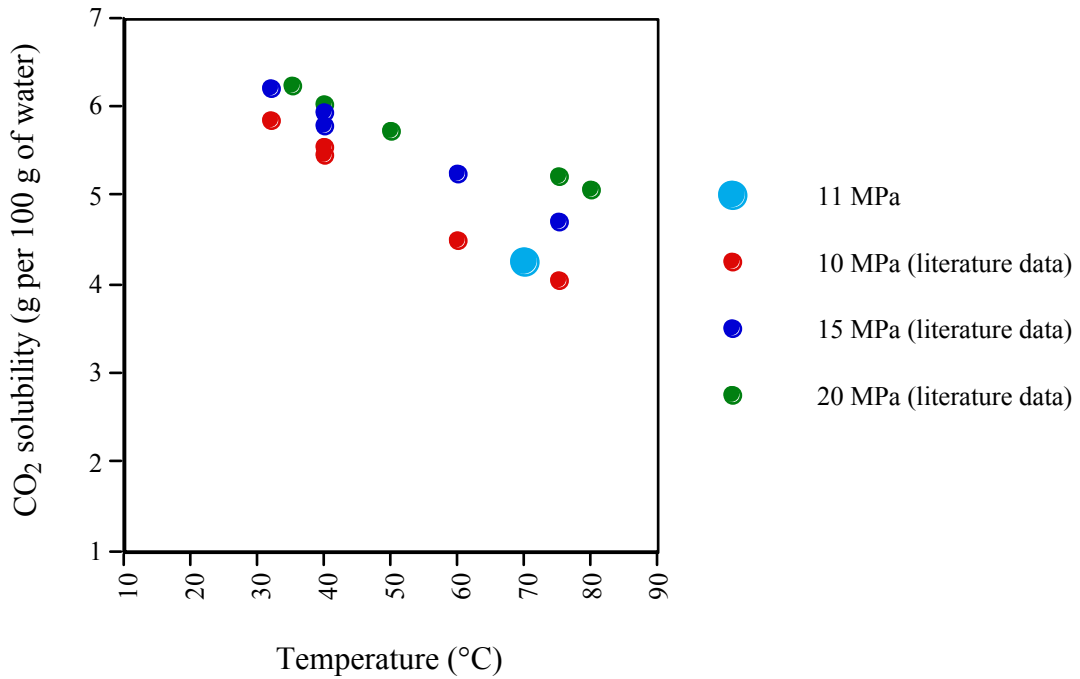


Figure 7 Measured solubility of CO₂ in distilled de-ionised water at 12 MPa.

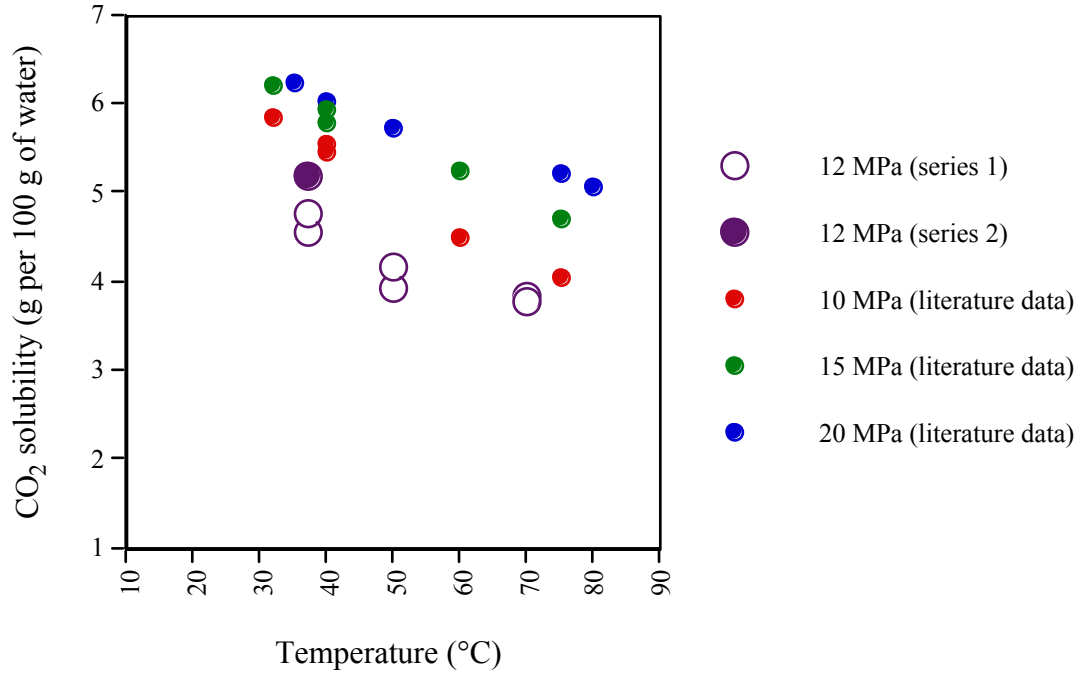


Figure 8 Comparison of CO₂ solubility in pure water at 10 and 20 MPa.

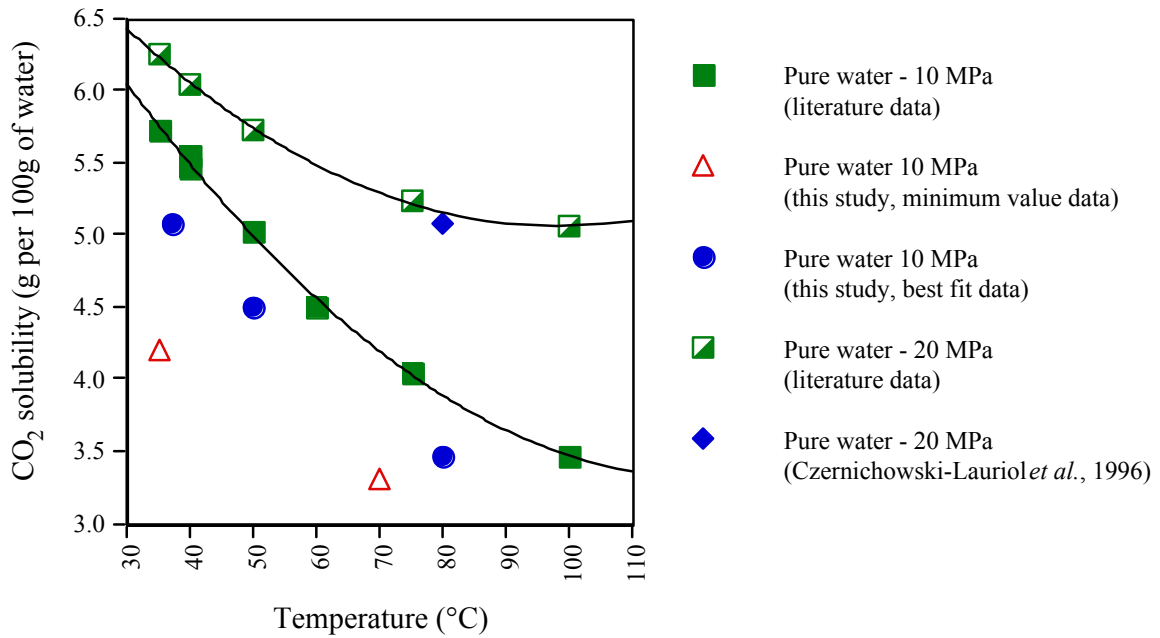


Figure 9 Measured solubility of CO₂ in synthetic Utsira porewater at 8 MPa.

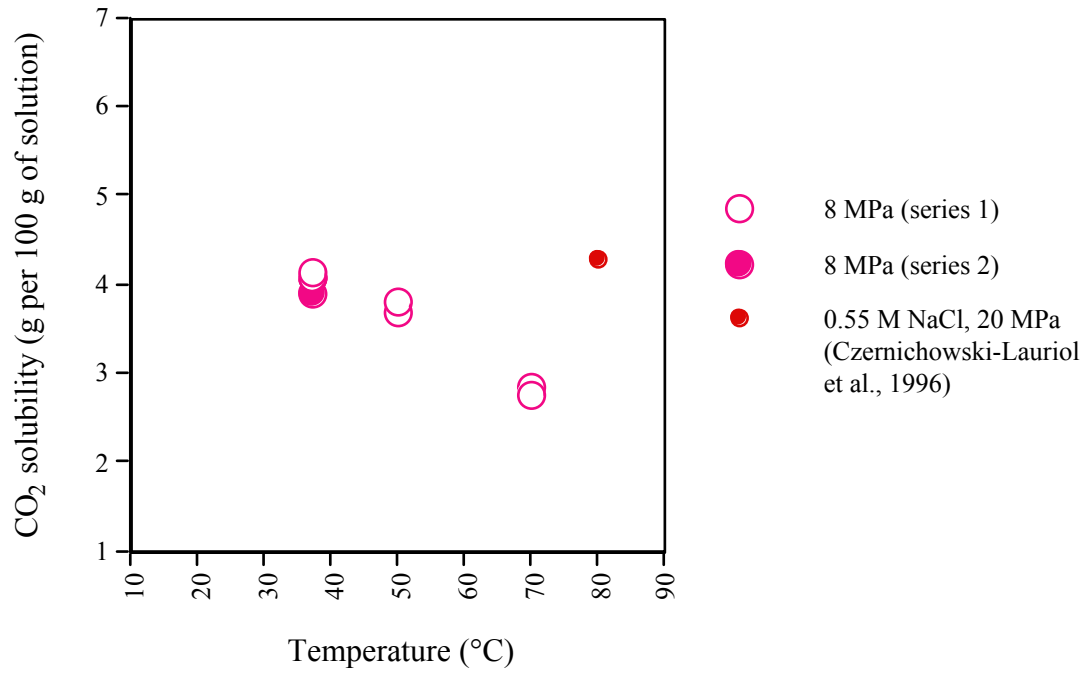


Figure 10 Measured solubility of CO₂ in synthetic Utsira porewater at 9 MPa.

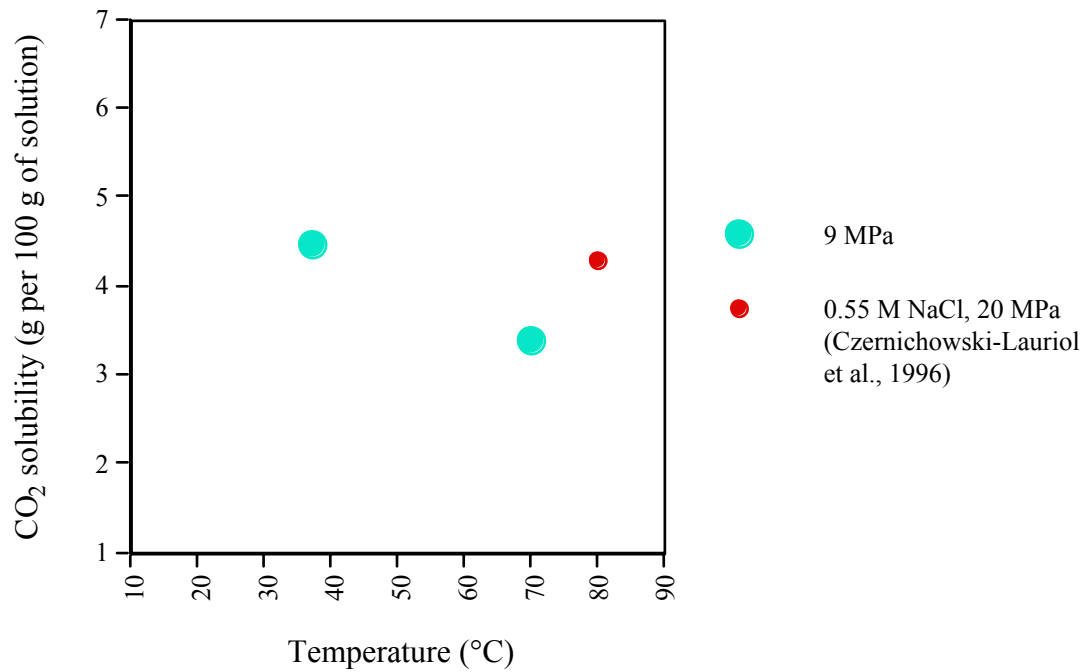


Figure 11 Measured solubility of CO₂ in synthetic Utsira porewater at 10 MPa.

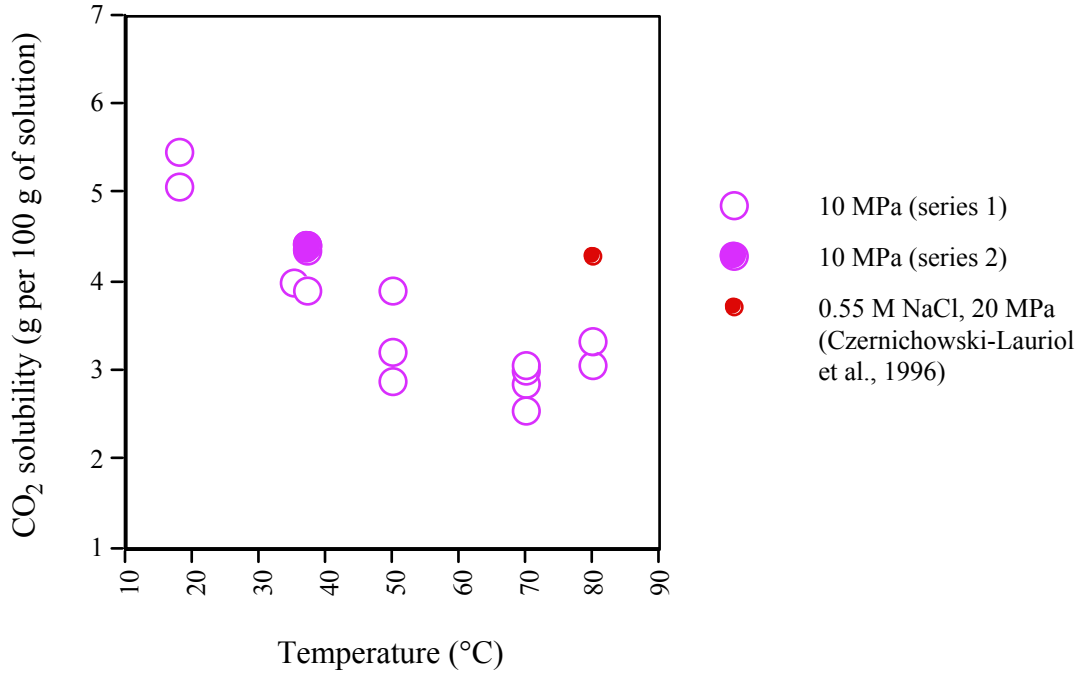


Figure 12 Measured solubility of CO₂ in synthetic Utsira porewater at 11 MPa.

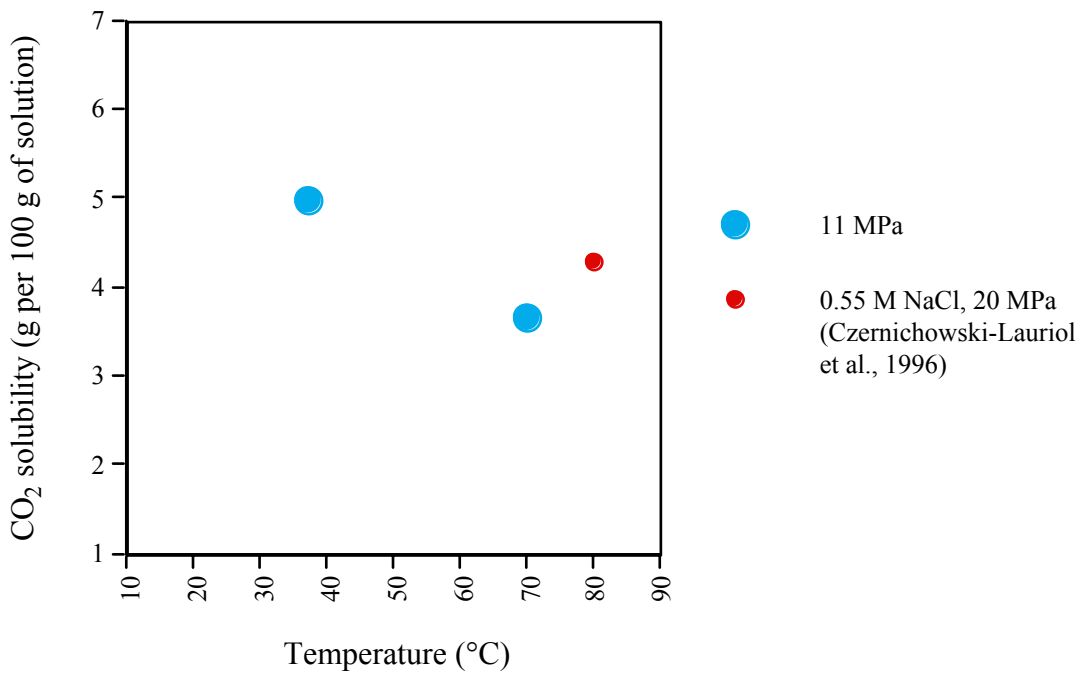


Figure 13 Measured solubility of CO₂ in synthetic Utsira porewater at 12 MPa.

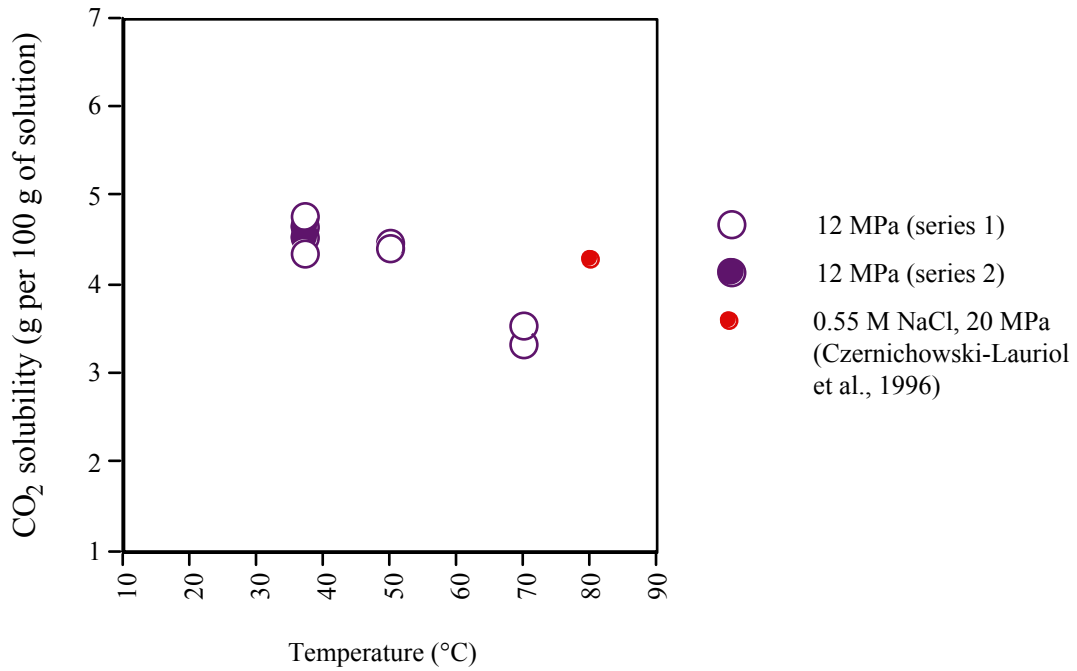


Figure 14 Comparison of CO₂ solubility data for saline waters equivalent to Utsira porewater composition at 10 and 20 MPa.

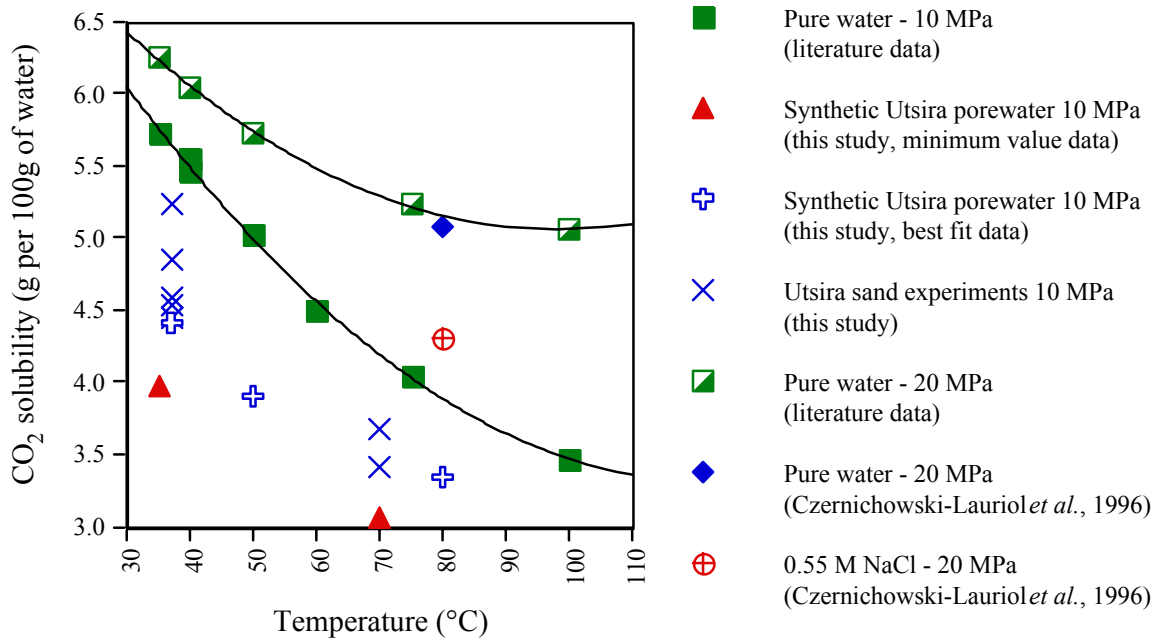


Figure 15 Comparison of CO₂ solubility data for a range of salinities.

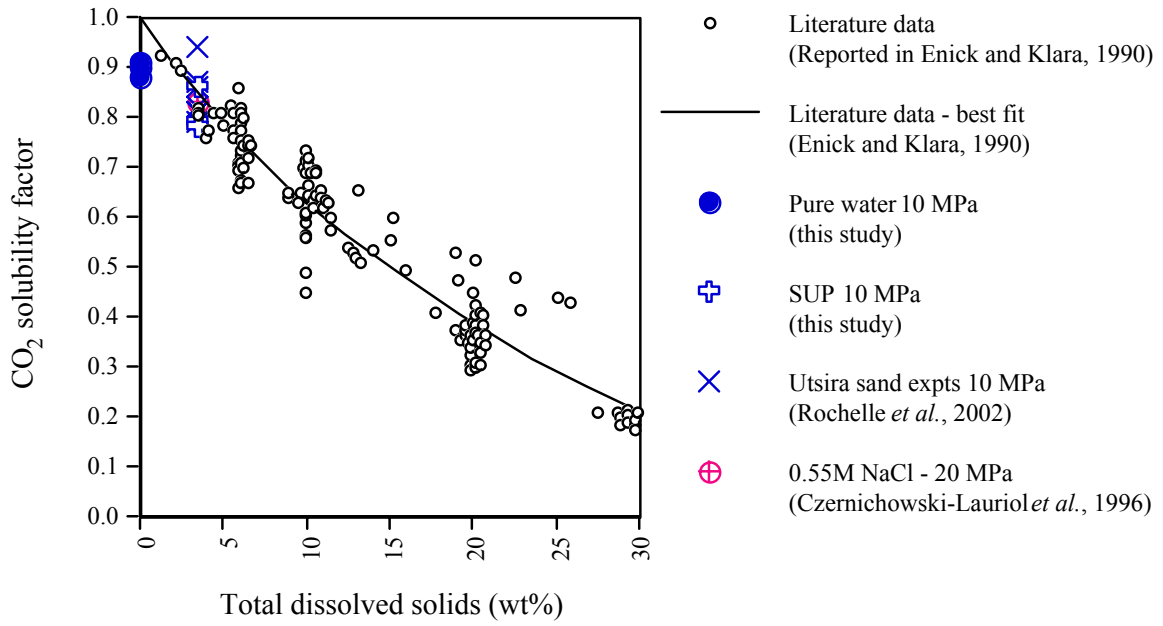


Table 1 Composition of Oseberg, Brage and SUP porewaters (units are mg l⁻¹ except for TIC and TOC which are mol l⁻¹).

Analyte	Oseberg porewater from Gregersen <i>et al.</i> (1998)	Average Brage analyses conducted at BGS	Average synthetic Utsira porewater starting solution
pH ($\approx 20^{\circ}\text{C}$)	7.1	7.65	7.77
Li	-	1.77	-
Na	10392	9934	10306
K	208	317	225
Mg	630	664	633
Ca	426	412	432
Sr	10	9.65	10
Ba	0.5	6.17	0.31
Mn	-	<0.02	-
Total Fe	2	0.28	1.21
Al	-	<0.1	0.35
Total P	-	<0.1	-
Total S	-	<2.5	1.05
Si	-	23.7	0.58
SiO ₂	-	50.7	1.23
Cl	18482	18921	18659
Br	-	71.5	<2.00
NO ₃	-	8.4	-
SO ₄	ND	<60	<2.00
HCO ₃	707	842	386
TIC (CO ₃ ²⁻)	-	0.003	-
TOC		<0.0003	

Table 2 Summary of CO₂ solubility experiments in distilled de-ionised water.

Run Number / sample	Temperature (°C)	Pressure (MPa)	g CO ₂ per 100g of solution
904/1	70	10	3.31
904/2	70	10	3.19
904/3	70	10	Failed sample
906/1	37	10	3.99
906/2	35	10	4.20
908/1	70	8	2.84
908/2	70	8	2.94
925/1	50	10	4.36
925/2	50	10	4.49
925/3	50	10	4.05
926/1	37	10	3.75
926/2	37	10	4.52
929/1	37	8	4.09
929/2	37	8	3.91
936/1	37	12	4.57
936/2	37	12	4.78
937/1	18	10	5.54
939/1	50	8	3.62
939/2	50	8	3.74
939/3	70	12	3.83
942/1	19	10	5.26
942/2	80	10	3.46
942/3	80	10	3.15
944/1	37	9	4.66
944/2	37	11	Failed sample
948/1	50	12	3.93
948/2	50	12	4.17
949/1	70	12	3.77
949/2	70	11	4.25
949/3	70	9	3.51
1008/1	37	8	4.71
1008/2	37	8	4.75
1008/3	37	10	5.07
1008/4	37	10	4.59
1008/5	37	12	5.18

Table 3 Summary of CO₂ solubility experiments in synthetic Utsira porewater (SUP).

Run Number/sample	Temperature (°C)	Pressure (MPa)	g CO₂ per 100g of solution
901/1	50	10	3.90
901/2	50	10	2.89
902/1	50	10.141	3.21
903/1	70	10	2.55
903/2	70	10	2.84
903/3	70	10	3.01
903/4	70	10	3.06
907/1	37	10	3.91
907/2	35	10	3.98
909/1	70	8	2.85
909/2	70	8	2.77
928/1	37	8	4.09
928/2	37	8	4.15
928/3	37	12	4.78
938/1	18	10	5.47
940/1	50	8	3.69
940/2	50	8	3.82
940/3	70	12	3.34
940/4	70	12	3.54
943/1	80	10	3.06
943/2	80	10	3.34
943/3	18	10	5.07
945/1	37	9	4.47
945/2	37	11	4.98
945/3	50	12	4.48
947/1	50	12	4.40
947/2	37	12	4.35
947/3	70	11	3.65
947/4	70	9	3.38
999/1	37	8	4.07
999/2	37	8	4.07
999/3	37	8	3.89
999/4	37	12	4.54
1003/1	37	10	4.35
1003/2	37	10	4.41
1003/3	37	10	4.40
1003/4	37	12	4.66

Table 4 Recipe for synthetic Utsira porewater (SUP). Weights given for a 25 l volume of SUP. Chemicals sourced from Fisher Chemicals.

Component	Grade	Manufacturers quoted purity	Weight (g)
NaCl	Aristar	99.5% min. assay	646.6897
KCl	Aristar	99.5% min. assay	9.9146
CaCl ₂ .2H ₂ O	AnalaR	99.5% min. assay	39.0669
MgCl ₂ .6H ₂ O	AnalaR	99.08% assay	131.732
SrCl ₂ .6H ₂ O	AnalaR	98.5% min. assay	0.7608
BaCl ₂ .2H ₂ O	AnalaR	99% assay	0.0227
FeCl ₃ .6H ₂ O	AnalaR	100.89% assay	0.2420
NaHCO ₃	AnalaR	99.5% min. assay	19.7003

Appendix I

FLUID CHEMICAL ANALYTICAL DATA FOR THE SYNTHETIC UTSIRA POREWATER

BGS EXPERIMENTS - STARTING SOLUTIONS

	OSEBERG		BRAGE		SUP			SUP					
	Oseberg composition from Task 0 report		Average of analyses conducted at BGS		Synthetic Utsira Porewater - starting solution Initial composition at make up (29/7/99) SUP for expts § E641A / SUP § E642 / SUP §			Synthetic Utsira Porewater starting solution (Average of 'E641A / SUP' E642 / SUP' and 'SUP for expts')	Synthetic Utsira Porewater - stock solution held in lab (at about 20°C). Batch made on 29/7/99 Compositional variation over time				
Sampling date					0 days			0 days	14/10/99 § 77 days	11/11/99 105 days	18/12/00 508 days	4/5/01 645 days	5/9/01 769 days
Age of SUP					0 days			0 days	14/10/99 § 77 days	11/11/99 105 days	18/12/00 508 days	4/5/01 645 days	5/9/01 769 days
Main LIMS number			06678-00001		06423-00017	06423-00007	06423-00014	-	06423-00018	06448-00005	06859-00001	10001-00001	10104-00001
pH (≈ 20 °C)	7.1		7.65		7.72	7.77	7.83	7.77	7.72	7.92	7.98	7.90	8.17
Li mg/l	-		1.77		-	-	-	-	-	-	-	-	-
Na mg/l	10392		9934		10502	9829	10588	10306	9179	10682	11119	11388	11389
K mg/l	208		317		226	228	220	225	241	220	232	241	255
Mg mg/l	630		664		646	614	639	633	586	640	611	607	625
Ca mg/l	426		412		440	429	428	432	334	347	307	281	269
Sr mg/l	10		9.65		10.2	9.62	10.3	10.0	7.52	8.10	6.05	5.61	5.48
Ba mg/l	0.5		6.17		0.32	0.42	0.20	0.31	1.10	1.82	0.38	0.38	0.395
Mn mg/l	-		<0.02		-	-	-	-	-	-	-	0.05	<0.040
Total Fe mg/l	2		0.28		1.50	<0.2	2.12	1.21	1.98	11.5	0.53	0.27	<0.20
Cr mg/l	-		-		-	-	-	-	-	-	-	<0.04	<0.040
Al mg/l	-		<0.1		0.06	0.54	0.44	0.35	0.05	7.00	0.10	0.38	0.04
Total P mg/l	-		<0.1		-	-	-	-	-	-	-	-	-
Total S mg/l	-		<2.5		1.18	1.34	0.62	1.05	<1.0	1.55	<5.00	<5.00	<7.00
Si mg/l	-		23.7		<1.50	0.58	0.58	0.58	<1.50	<0.30	<1.5	<1.50	<1.5
SiO ₂ mg/l	-		50.7		<3.21	1.23	1.23	1.23	<3.21	<0.64	<3.2	<3.21	<3.21
Cl mg/l	18482		18921		18589	18679	18709	18659	18575	18650	18811	18388	18772
Br mg/l	-		71.5		<6	<6	<6	<2.00	<6.0	<6.0	<7.5	<6.00	<6.00
NO ₃ mg/l	-		8.40		-	-	-	-	-	-	-	-	-
SO ₄ mg/l	ND		<60		<60	<3	<60	<2.00	<60	<60	<75	<60.0	<60.0
HCO ₃ * mg/l	707		842		395	388	374	386	334	285	203	115	86.0
Ionic balance %	-		-3.07		0.67	-2.67	0.62	-	-5.78	1.03	1.97	4.15	3.28
TIC (CO ₃ ²⁻) mol/l	-		0.0030		-	-	-	-	-	-	-	-	-
TOC mol/l	-		<0.0003		-	-	-	-	-	-	-	-	-

LIMS = Laboratory Information Management System

ND = Not detected

* = Analyses done several days after sampling so be aware of possible decreases over time due to loss of CO₂ to the atmosphere. Alkalinity measurements by potentiometric titration.

§ = Si and Al specially re-analysed on 1/10/01 with improved background corrections. This was done after the preserved samples had been in store for over a year.