A novel technique for obtaining representative water samples during CO$_2$ core-flooding experiments on chalk at reservoir conditions

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There is a huge potential for using CO$_2$ gas to recover additional oil after water flooding in reservoir chalk. However, the injection of CO$_2$ into chalk reservoirs will disturb the chemical equilibrium between formation water, injection water and chalk. A proper understanding of these CO$_2$-induced interactions and the resulting changes in the physical properties at representative reservoir conditions is required. Unfortunately, reliable chemical data are rare because data cannot be acquired directly at reservoir conditions with present-day techniques. In published experiments, water samples are in many cases obtained at atmospheric conditions with the aid of a back-pressure regulator. Thus, water samples are not representative of *in situ* reservoir conditions and if proper care is not taken, the collected data cannot be used to judge the magnitude of the chemical reactions taking place at reservoir conditions. However, in some cases water obtained at laboratory conditions can give information on *in situ* reservoir conditions by using geochemical speciation models to account for dissolved gases that are lost from the effluents during sampling (Bachu & Adams 2003).

The objective of this study was to develop and test a new technique for obtaining water samples during CO$_2$-brine–rock interactions in reservoir chalk under representative reservoir conditions and gain a better understanding of the chemical interactions which occur during the injection of CO$_2$. The experiments were performed by injecting CO$_2$-saturated seawater at supercritical CO$_2$ conditions, at a pressure of 17.24 MPa (2500 psig; pounds per square inch of gauge pressure) and a temperature of 75°C. These values are typical of a region in a chalk field where the rock is exposed to long term reactions with flow of CO$_2$-bearing water. In addition, the numerical code PHREEQC-3 (Parkhurst & Appelo 2013) was used to reproduce the experiments by assuming equilibrium between calcite and injected fluids. In this way, we can validate the sampling procedure and investigate how the measured parameters (pH, CO$_2$ pressure, calcium (Ca) and bicarbonate (HCO$_3^-$) concentrations) compared with the calculated parameters.

Reservoir chalk samples

Chalk plugs for the experiment were sampled from the Maastrichtian Tor Formation in the central North Sea and were first cleaned of salt and oil with methanol and toluene. Following initial determination of porosity and permeability, the samples were saturated with synthetic formation water (FW). All plugs had a diameter of 3.81 cm and a length of approximately 7.5 cm; plugs with similar petrophysical properties (Table 1) were used to check the reproducibility of the studied sampling procedure. The compositions of synthetic formation water, synthetic seawater and CO$_2$ synthetic saturated seawater are listed in Table 2.

Experimental setup

The setup/rig for the experiments is shown in Fig. 1. It includes three cylinders with pistons placed in an oven to maintain constant temperature. Two of the cylinders were used
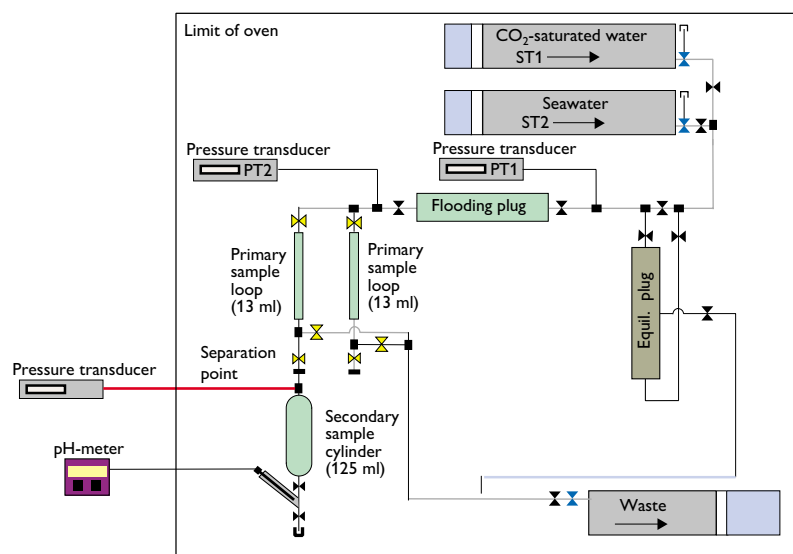

Fig. 1. Experimental setup/rig within the oven. The rig has two primary sample loops.

Table 1. Petrophyscial properties of plugs prior to the injection of CO_2-saturated water at 17.24 MPa (2500 psig) and 75°C

Plug ID	Porosity (%)	Pore volume (ml)	Permeability (mD)
17A	32.60	26.94	1.36
19A	30.60	25.59	1.49

Table 3. Composition of resulting solutions at the two different equilibrium steps followed by the de-pressurisation step based on calculations with phreeqc.dat database in PHREEQC-3

Chemical parameter	Step 1	Step 2	Step 3
pH	3.2	4.8	6.3
Ca (mg/l)	438	1970	1970
Alkalinity, HCO_3^- (mg/l)	82	3274	3308
Saturation index (calcite)	−3.78	0	1.43

for the delivery of CO_2-saturated seawater and seawater. The third cylinder was used as a waste tank and for maintaining fluid pressure. All the fluids were injected at a constant rate of 6.5 ml/h with the plug in a horizontal position. The injection of CO_2-saturated seawater was preceded by injecting close to 3.5 pore volume (PV) of seawater to mimic the present-day water flooding. At the end of the injection of CO_2-saturated seawater, seawater was again injected through the plug. At this point, equilibrium with calcium carbonate was obtained in the injection fluid by first passing the seawater through the equilibrium plug (Fig. 1). This was done in order to avoid any further dissolution of chalk in the plug under study. The final seawater flooding was performed to displace any residual CO_2 gas and bring the concentrations back to initial levels.

Water sampling technique

The system for obtaining water samples was located at the downstream end of the rig (Fig. 1). It consists of two primary sample loops each with a volume of *c.* 13 ml. This enabled continuous collection of water samples for every 13 ml (*c.* 0.5 pore volume) of plug flooded. The sampling was done by alternating the flow process between the two primary loops with the aid of computer-controlled valves (CV-210 valves) without disrupting the injection process. The primary sample loops were connected to a secondary sample cylinder with a volume of 125 ml by a separation point. Water samples were transferred from the primary sample loop to the secondary sample cylinder by a de-pressurisation step. This made it possible to collect water samples for a set of chemical parameters (Ca and HCO_3^- concentrations) at predefined sampling intervals. The pH and CO_2 pressures of the de-pressurised

effluents were measured on-line in the secondary sample cylinder after the de-pressurisation step. The sampling from the secondary sample cylinder was subsequently done as fast as possible, in less than 5 min., thereby providing a consistent chemical dataset for the conditions prevailing in the secondary sample cylinder. In this way it was possible to validate the subsequent numerical calculations used to estimate the *in situ* chemical conditions. A detailed description of the sampling procedure as well as documentation for the consistency of the collected dataset was published by Kjøller & Zuta (2012).

Batch modelling with PHREEQC-3

The modelling was performed at the same conditions – pressure and temperature of 17.24 MPa (2500 psig) and 75°C as the experiments, in order to estimate the true *in situ* reservoir condition chemistry. Three equilibrium steps in a closed system were investigated: (1) equilibrium between CO_2 and seawater corresponding to the injected solution, (2) equilibrium between CO_2-saturated seawater and calcite, representing reservoir conditions, and (3) composition of the solution after de-pressurisation in the secondary sample cylinder. A good fit between experimental and numerical data after step
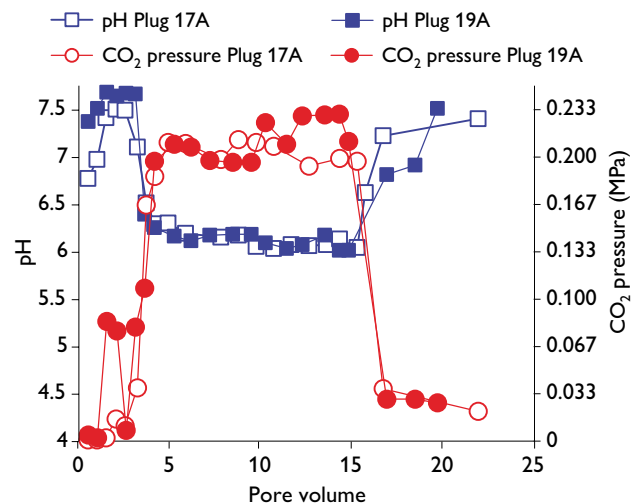
Table 2. Composition (in mg/l) of synthetic formation water (FW), seawater (SW), and CO_2-saturated seawater (CSW)

Ions	(FW)	(SW)	(CSW)
Na	22866	11090	11090
K	175	408	408
Mg	226	1370	1370
Ca	1244	434	434
Sr	142	6.8	6.8
Cl^-	38383	20173	20173
HCO_3^-	22	30	70
SO_4^{2-}	–	2780	2780

Fig. 2. Measured pH and CO_2 pressure for plug 17A and parallel plug 19A versus cumulative, injected pore volume.

Total pressure	2.00 MPa (28.9 psig)
Gas volume	1.25e-001 litres
Molar volume	1.38e+001 litres/mole
P×Vm/RT	0.99228 (compressibility factor Z)

3 is considered as a validation of the numerical estimate of reservoir conditions in step 2 (Kjøller & Zuta 2012).

Results

Figures 2–4 show pH, CO_2 pressure, Ca, and HCO_3^- concentrations measured as a function of injected cumulative pore volumes. The compositions of the resulting solutions calculated at the three steps with PHREEQC-3 are shown in Table 3. Equilibrium of CO_2 and seawater results in an initial CO_2-saturated seawater solution with a pH of 3.2 and a saturation index of calcite of –3.78 (Table 3, step 1), an indication of a strong dissolution potential for chalk. Thus, CO_2 is dissolved and reacts with water to form carbonic acid (H_2CO_3). It is part of this acidity that is removed as the dissolution process advances into the plugs. The dissolution of calcium carbonate in the plugs takes place according to the overall chemical reaction:

$$H_2CO_3 + CaCO_3 \rightarrow Ca^{2+} + 2HCO_3^-$$
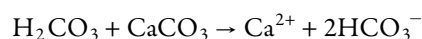
During the injection of seawater within the first 3.5 pore volume, the pH increases to between 7.5 and 7.7 and subsequently decreases to an average of 6.1 during the injection of CO_2-saturated seawater (Fig. 2). At the final stage of the ex-

periment, the pH increases again to the initial seawater pH level, an indication that all the residual CO_2 was removed from the plugs during the injection of seawater in equilibrium with chalk. The calculated decrease in pH at reservoir conditions (Table 3, step 2) corresponds with the measured decrease in pH after 3.5 pore volume, where breakthrough of the CO_2-saturated seawater is observed. However, the calculated reservoir condition pH of 4.8 is much lower than the average measured pH during the injection of CO_2-saturated seawater. This was expected since the pH was measured after the de-pressurisation step where CO_2 gas had already degassed from the solution. Thus, taking the pH (6.3) of the degassed solution into account in the numerical simulation provides an excellent fit to the average measured pH of 6.1 (Table 3, step 3). The CO_2 pressure in the secondary sample cylinder varied between 0.17 MPa (25 psig) and 0.24 MPa (35 psig) at the de-pressurisation stage during the injection of CO_2-saturated seawater (Fig. 2). This matches with the calculated CO_2 pressure of 0.20 MPa (28.9 psig) in the gas phase of the secondary sample cylinder (Table 4), and further validates the numerical calculations.

According to the equation, degassing of CO_2 from the water samples, caused by the transfer of water samples from the primary sample loop to the secondary sample cylinder, was expected to result in precipitation of $CaCO_3$. Comparison of Ca and HCO_3^- concentrations measured in both filtered and unfiltered water samples showed no evidence of mobilisation or precipitation of fine particles during the de-pressurisation stage, neither in plug 17A nor in plug 19A (Fig. 3A, B). The Ca concentration decreases during the first 3.5 pore volume to the Ca-concentration level in seawater
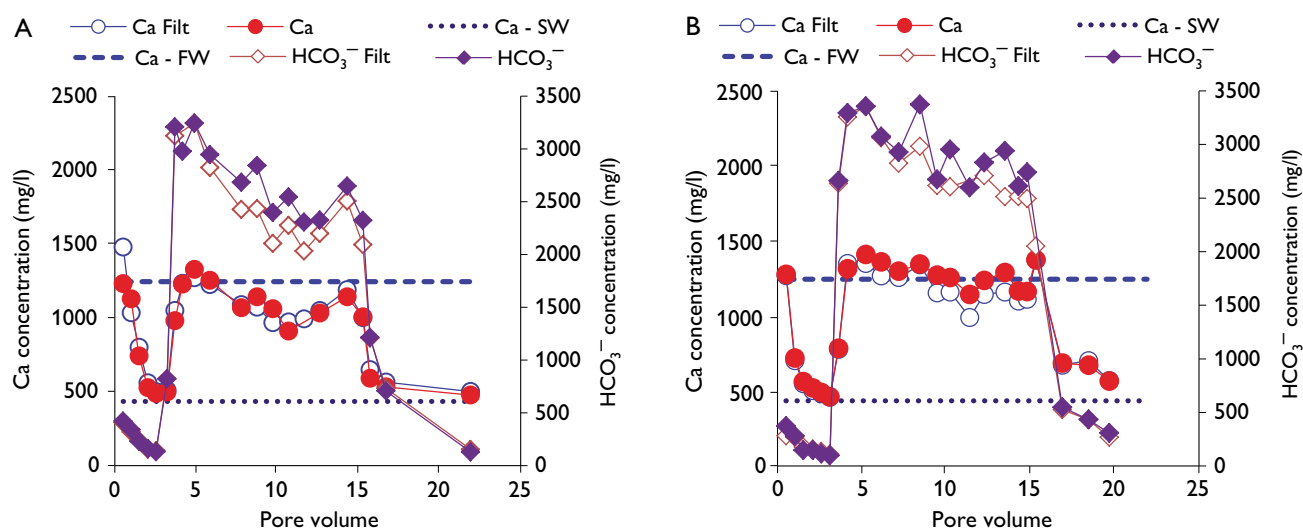

Fig. 3. Measured Ca and HCO_3^- concentrations for filtered and unfiltered water samples in plugs 17A (**A**) and 19A (**B**) versus cumulative, injected pore volume. **Filt**: filtered. **SW**: synthetic seawater. **FW**: synthetic formation water.

of *c.* 450 mg/l. Subsequently, the measured Ca concentration increases to an average of 1200–1300 mg/l during the injection of CO_2-saturated seawater, which is due to dissolution of calcium carbonate in the plugs. At the final steps of the experiment, the Ca concentration again decreases to the seawater level during injection of seawater to remove residual CO_2 from the plugs. In the geochemical model, the calculated Ca concentration of 1970 mg/l at reservoir conditions (Table 3, step 2) is simulated by dissolution of calcite at reservoir conditions, and does not take into account the possible precipitation of calcium carbonate during sampling. Therefore, the calculated reservoir-condition Ca concentration is higher than the concentrations measured in the experiments during the period with CO_2-saturated seawater flooding. Since no mobilisation or deposition of suspended fine particles in the water samples were observed, the difference in Ca concentration must be attributed to deposition of fine calcium carbonate particles on the inner surface walls of the secondary sample cylinder during the pressure-reduction stages. In line with this, the simulated saturation index (SI) with respect to calcite of 1.43 after de-pressurisation (Table 3, step 3) is higher than the saturation indices between 0.6 and 1.2 that can be calculated based on the measured water chemistry.

If the saturation index with respect to calcite is constrained to be between 0.6 and 1.2 in the numerical calculations in step 3, the calculated Ca concentration at the sampling conditions varies between *c.*1150–1650 mg/l, which is in much better agreement with the actually measured Ca concentrations (Fig. 3). Similar considerations and conclusions can be made for the HCO_3^--concentration trend during the experiment. Thus, the measured HCO_3^- concentration averages 2350–2550 mg/l during the injection of CO_2 saturated seawater, while the calculated HCO_3^- concentration after de-pressurisation is 3308 mg/l when no constraints on the saturation index with respect to calcite are applied (Table 3, step 3). However, accounting for some calcium carbonate precipitation during de-pressurisation will diminish the difference between calculated and measured concentrations, and overall it is suggested that the calculated reservoir condition concentrations shown in Table 3, step 2 represent the true *in situ* reservoir conditions prevailing in the plugs during experiments.

The general decrease in measured Ca and HCO_3^- concentrations during the injection of CO_2-saturated seawater from 3.5 to 15 pore volume (Fig. 3), suggests that, with time, there is an increasing amount of calcium carbonate precipitating in

the secondary sample cylinder during sampling. For future studies, this gradual change in calcium carbonate precipitation should be avoided in order to minimise the uncertainty in the measured data, and thereby also the uncertainty of the numerical estimate of the reservoir condition chemistry (Table 3, step 2).

Conclusions

- A new sampling technique was developed and used to study CO_2-brine–rock interactions in reservoir chalk at reservoir conditions.
- The similar results obtained in the parallel plugs validate the sampling procedure and show a high degree of reproducibility.
- The results from the experiment and the modeling show increased levels of calcium and alkalinity (HCO_3^-) with decreasing pH during the injection of CO_2-saturated water at reservoir conditions. There were, however, differences between the measured and calculated calcium concentration and HCO_3^- concentration which is probably due to accumulation of fine calcium carbonate particles on the inner walls of the secondary sample cylinder during the de-pressurisation stage.
- Further refinement of the method may include modification of the secondary sample cylinder, in order to minimise the accumulation of fine calcium carbonate particles on its inner surface walls.

References

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