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Understanding CO₂-brine-wellbore cement-rock interactions for CO₂ storage

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Abstract

There is a need to improve our understanding of wellbore integrity by conducting investigations into the flow, geomechanical and geochemical properties of cement and reservoir rocks under conditions representative of subsurface temperatures and pressures at the wellbore. A series of composite cement-host rock core samples were prepared and subjected to baseline flow and mechanical properties testing to determine porosity, permeability, strength and elastic properties. The hydrothermal experiments conducted have shown that variations in the solution profiles of Ca, Mg, and Fe were due to the dissolution of CO₂ for all sets of samples. The dissolution of muscovite and montmorillonite from the composite core samples resulted in increasing concentrations of Na, K and S.

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Keywords: Well integrity, cement degradation, caprock, CO₂-brine-cement-rock interaction

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1. Introduction

Poorly cemented casing/well annulus, casing failure and well abandonment failures have been recognised as some of the main reasons for well leakage when carbon dioxide is stored in geological formations [1]. The CO₂ injection in the reservoir, along with the occurrence of mineral reactions, could lead to the degradation of the wellbore cement under storage conditions [2]. CO₂-brine-rock reactions result in mineral dissolution/precipitation and adsorption/desorption of the mineral surfaces that could also alter the petrophysical properties such as porosity and permeability [2]. Extensive research on the integrity of well cements in contact with CO₂ and CO₂-brine (saturated formation water) reported in the literature have indicated that cement degradation in the well adjacent to the host rock or caprock can be important with respect to well integrity, as it may lead to potential CO₂ leakage pathways [3-6]. Therefore, the aim of this study is to improve our understanding of well integrity by conducting geochemical investigations of the CO₂-brine-wellbore cement-rock interactions. Research reported in this paper is carried out as part of the UK Research Councils Energy Programme funded consortium project investigating the long term effect of CO₂ storage on wellbore-cement-rock interaction with the ultimate goal of understanding well leakage risks.

2. Sample Preparation and Experimental Methods

A number of composite cement-rock core samples, with gas flow directions used during permeability experiments parallel (CB1P to CB5P) and perpendicular to bedding (C1 to C5), were prepared as shown in Fig. 1. The Doddington sandstone used in the experiments is representative of potential CO₂ storage formations considered. The cement used in the samples is Class G Portland cement (100 parts cement/44 parts water). The samples were first characterised for their baseline flow and mechanical properties to determine porosity, permeability and elastic properties. Bulk rock X-ray diffraction (XRD) analysis confirmed that the average major composition of the sandstone core is quartz. In the case of cement, the presence of quartz, nacrite, polythionite, mica, zimmerwaldite, olivine, muscovite and montmorillonite was confirmed. Table 1 presents the results of initial porosity/permeability characterisation experiments on the composite cement-sandstone samples. One of the composite samples (CB1P) was imaged by using micro-CT (Zeiss Xradia Versa 3D Microscope at University of Aberdeen). From visual inspection of the CT images (not shown here), the cement showed some micro-cracks, but not in the region in contact with the rock, which means that the composite samples prepared were suitable for the following hydrothermal experiments.

Table 1. Summary of porosity and permeability characterization tests for composite core samples.

Sample No.	Dimensions		Porosity -	Grain density (g/cm ³)	N ₂ permeability (×10 ⁻¹⁵ m ²)	CO ₂ permeability (×10 ⁻¹⁵ m ²)
	D (mm)	L(mm)				
CB1P – CB5P	38	76	0.1	2.3	2.3 - 6.7	2.4 - 6.4
C1-C5	38	61	0.1	2.4	0.7 - 1.2	0.5 - 0.7

Following baseline characterisation, the samples were aged using high-pressure and high-temperature hydrothermal vessels to mimic downhole environments ($P_{\max} = 25\text{MPa}$, $T_{\max} = 90^{\circ}\text{C}$) for periods of time varying between 3 to 11 months. The composite cement-host rock core samples placed in the vessels were submerged in synthetic low salinity brine to mimic downhole conditions. CO₂ was then injected to saturate the brine and curing conditions (temperature, pressure) were adjusted and maintained during the aging hydrothermal studies. The experiments were conducted in static batch vessels with corrosion resistant PTFE liners. These hydrothermal vessels have been designed to study CO₂-water-rock interactions and carbonation reactions, both for underground mineral trapping and above ground mineral carbonation [6-7].

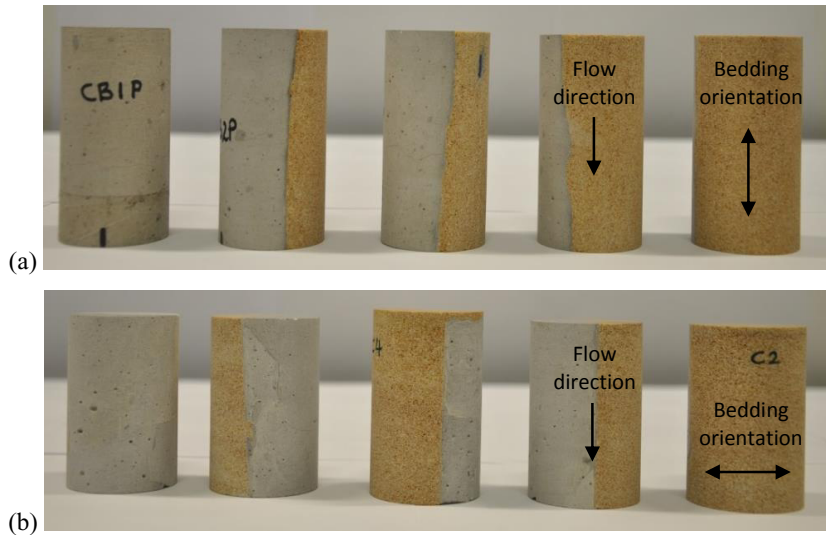


Fig. 1. Composite cement-sandstone core samples: (a) those prepared with flow direction parallel to bedding; (b) those prepared with flow direction perpendicular to bedding.

Synthetic low salinity brine composition of a typical oil field in North Sea was selected as the target concentration of the main ions (Table 1), including Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} . The synthetic brine was prepared by dissolving the following salts associated with the ions, including NaCl , KCl , $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, and $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ in 1 litre of Millipore water. The total salinity of the target synthetic brine is 10,285 mg/l. These salts were selected in this study because they did not involve any other ions except the major ions expected. The chemical composition of the aqueous samples and the stock solutions were analysed using inductive coupled plasma mass spectroscopy (ICP-MS). Samples were prepared volumetrically by using an internal standard solution in 2% nitric acid. A fully quantitative analysis was performed by using a linear calibration curve based on known standards.

Upon completion of the hydrothermal tests, the reacted samples will be analysed by a series of analytical techniques, including XRD and SEM, to achieve a comparison between the initial properties of the composite samples and determine time dependent changes. In addition, some of the aged samples will also be analysed using a micro-CT scanner to image changes in flow paths as a result of reaction between CO_2 -rich brines and the rock/cement composite samples. Finally, porosity, permeability, strength and elastic properties of the aged samples will be determined for comparison with the baseline data. This paper describes the preliminary findings of the experimental work carried out so far.

3. Results and Discussion

Table 1 shows the target and current concentration of the prepared synthetic low salinity brine. It can be seen that with the exception of Na, the prepared concentrations are close to the target values.

Table 2. Target and current composition of the synthetic low salinity brine.

	Na (mg/l)	K (mg/l)	Ca (mg/l)	Mg (mg/l)	Sr (mg/l)	Ba (mg/l)
Target concentration	8,963	227	639	69	59	328
Current concentration	5,433	303	612	63	54	281

The experimental results from the reaction of supercritical CO_2 with some of the composite sandstone and wellbore cement samples in low salinity brine at 90°C and 25 MPa are described here.

Fig. 2 shows the change in the brine composition with respect to time for the some of the composite cores prepared with the flow direction perpendicular to bedding, including sodium and potassium (Fig. 2a), calcium, barium and sulphur (Fig. 2b) and magnesium, strontium, and iron (Fig. 2c) for 3 months (sample C3) and 11 months (duplicate samples C1 and C2). It can be seen that Na, Ca and Sr were consumed in the early stages (3 months, sample C3) and later re-dissolved back in the solution for the 11 months samples. Solution profiles show decreasing Mg and Ba concentrations with time, whilst K is increasing initially (3 months) followed by a decrease over time (11 months). There is also a marked increase in the concentration of dissolved Fe and S, possibly due to the carbonation reaction of the cement-host rock samples [8]. However, no precipitates were observed during the filtration of the solution brine at the end of the experiment. This indicates that the consumption of elements from the brine solution is due to precipitation either on the mineral surface of the composite samples or on the interface between the cement and the sandstone.

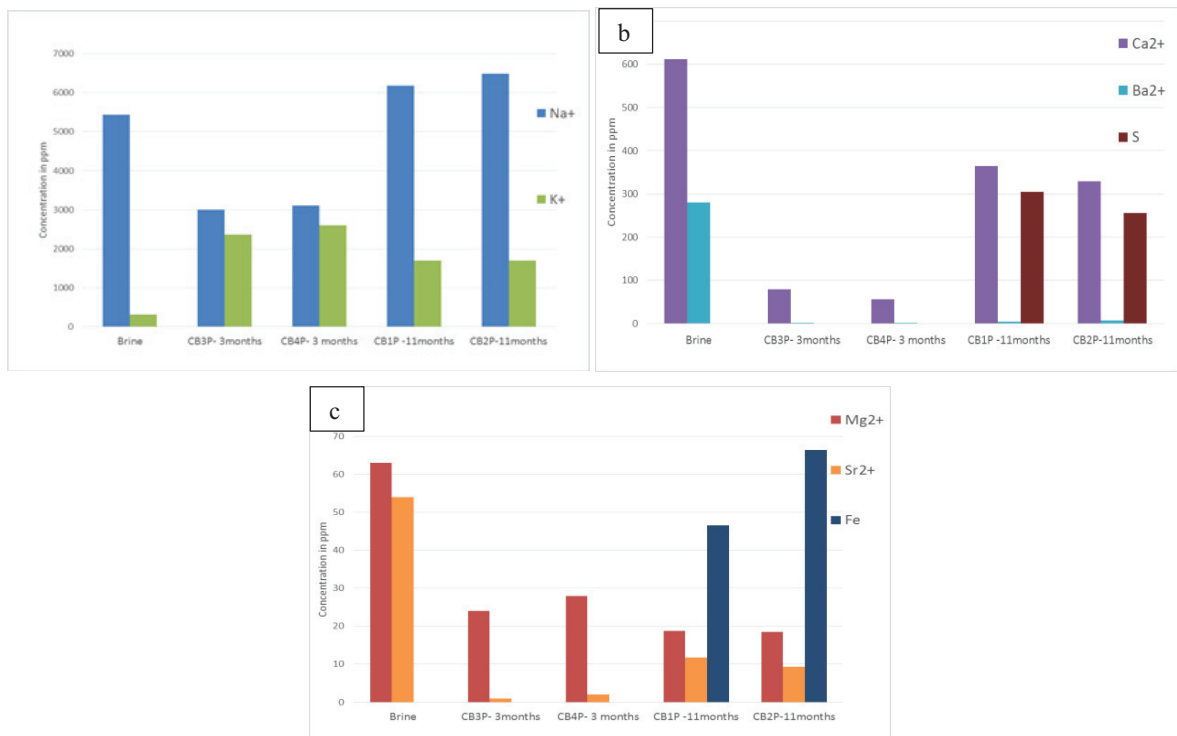


Fig. 2. Concentration of ions present in the brine: (a) sodium and potassium; (b) calcium, barium, sulphur; and (c) magnesium, strontium and iron after CO₂ injection for 3 months (for sample C3) and 11 months (duplicate samples C1 and C2) for the cores prepared with the flow direction perpendicular to bedding.

Solution profiles for the cores prepared with the flow direction parallel to bedding are presented in Fig. 3, including sodium and potassium (Fig. 3a), calcium, barium and sulphur (Fig. 3b) and magnesium, strontium, and iron (Fig. 3c) for 3 months (duplicate samples CB3P and CB4P) and 11 months (duplicate samples CB1P and CB2P). As expected, similar variations of the concentrations of ions to those reported for the cores prepared perpendicular to bedding were observed, with Na, Ca and Sr concentrations decreasing initially, decreasing Mg and Ba concentrations with time, and K increasing initially (3 months) followed by a decrease over time. As described for the cores prepared perpendicular to bedding (Fig. 2), iron and sulphur were dissolved from the cores, as they were not present in the prepared brine.

Variations in the solution profiles of Ca, Mg, and Fe in response to initial acidity due to the dissolution of CO₂, indicate that the brine solution is supersaturated with respect to calcite, magnesite and siderite corresponding to the

respective three possible phases of these elements [9]. The dissolution of Fe in the CO₂ rich brine may be a source of long term mineral trapping of CO₂ and the precipitation of secondary Fe carbonates could alter reservoir and seal permeability by clogging pores and network fractures [10]. At the initial stage of the experiment, the decrease in Mg during the cement hydration phase and further recovering back in solution indicates that some of the cement was carbonated [10].

The pre experimental XRD results confirmed the presence quartz, nacrite, polythionite, muscovite and montmorillonite which combined with the hydrothermal lab experiments shows the significant increase in the concentration of cations compared with the brine initially. The release of Na, K and S in the solution brine may indicate the dissolution of muscovite and montmorillonite from the composite sandstone cement reservoir samples. However, the amount of Fe and S released seem to be dependent on bedding type of the rock, with higher concentrations in the parallel bedding type cores.

The results of this research are in agreement with the findings of other authors [10-12], which indicate CO₂ dissolution promotes acidification, and creates more H₂CO₃, which can precipitate carbonates. This leads to the increase in porosity, and potentially damage wellbore integrity. Thus not only pH, but also concentration of carbonic species should be considered in order to limit the precipitation of carbonates.

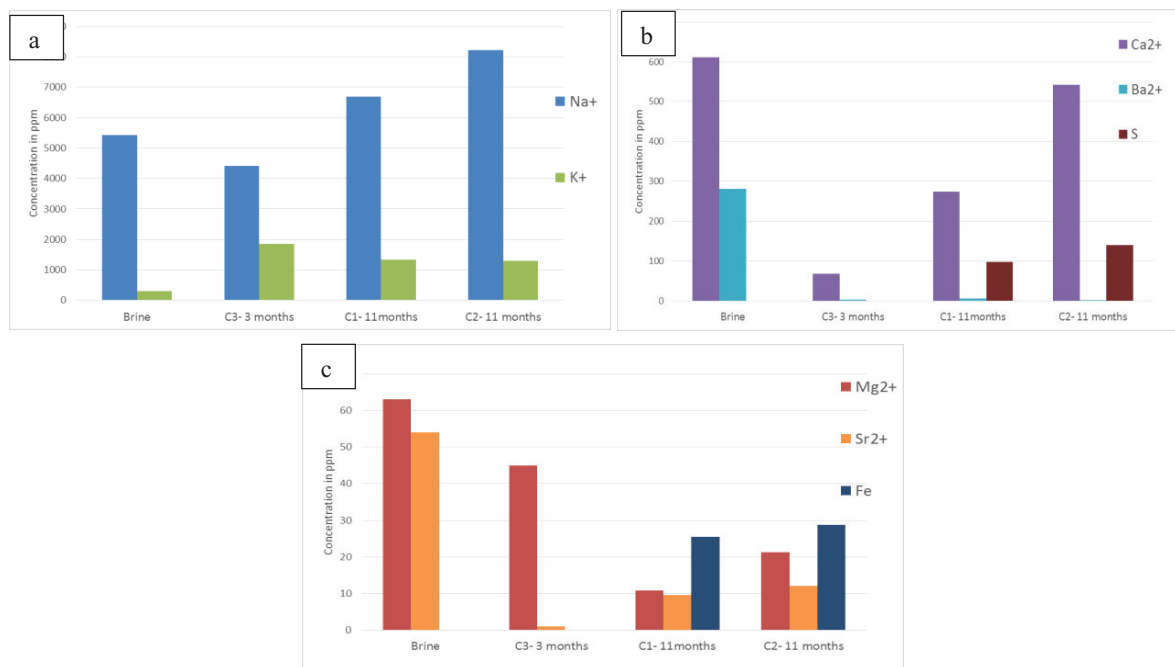


Fig. 3. Concentration of ions present in the brine: (a) sodium and potassium; (b) calcium, barium, sulphur; and (c) magnesium, strontium and iron after CO₂ injection for 3 months (duplicate samples CB3P and CB4P) and 11 months (duplicate samples CB1P and CB2P) for the parallel bedding type cores.

4. Conclusions

In order to improve our understanding of well integrity, hydrothermal studies were conducted in a series of cement-rock cores at 90°C and 25 MPa. Solution profiles for a number of composite cement and sandstone cores were determined for Na, K, Ca, Ba, Mg, Sr, Fe and S. As expected, similar trends in the ions concentrations are observed for the composites prepared perpendicular and parallel to bedding. Variations in the solution profiles of Ca, Mg, and Fe were observed in response to initial acidity due to the dissolution of CO₂. The increase in the concentrations of Na, K and S is related to the dissolution of muscovite and montmorillonite from the composite cement sandstone

samples. Experimental results also confirmed the presence of dissolved S and Fe.

Further analytical studies (SEM, XRD, CT) of the composite cement-sandstone samples are underway to fully understand the element trends reported here as well as their impact on wellbore integrity. The results of these experiments will then be utilised as data input for numerical modelling of the behaviour at the cement-rock interface.

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