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Cement Self-healing as a Result of CO₂ Leakage

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Abstract

Avoiding CO₂ leakages from storage reservoirs is crucial to ensure safe and cost-efficient Carbon Capture and Storage (CCS). This can only be done if effort is made to maintain well integrity throughout the entire life-cycle of a well. Cement integrity is especially important, since the interfaces between cement and rock or casing have been identified as weak links in today's well construction. The present paper focuses on the healing of fractures in well cement when the material is exposed to a CO₂-brine water-alternating-gas (WAG) flooding scheme. Specimen characterization using computed tomography combined with electron microscopy documents the self-healing procedure in detail for a composite cement-rock specimen subjected to a WAG flooding scheme. The study revealed volumetric data on self-healing of cement cracks and chemical changes in the specimen as well as in aqueous chemistry upon CO₂ exposure. The measured aqueous chemistry suggests CO₂-cement interaction to be less pronounced with time thereby together with the observed cement self-healing suggesting that the risk of compromising the safety of a storage site by cement-CO₂ chemical reactions is minimal.

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1. Introduction

The concept of geological CO₂ Capture and Storage (CCS) relies on the capability of a subsurface reservoir to contain sequestered gas for thousands of years. High leakage rates from storage to atmosphere can render the whole

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capture, transport and injection chain futile. Such CO₂ leakage can occur as a result of geological conditions (e.g. failed caprock integrity and/or faults) or it can be caused by loss of integrity of active and abandoned wells that penetrate the site. Typically, CO₂ flow in/along wells occurs through enhanced cement porosity, through fractures/channels in cement – or along the casing-cement or cement-rock interfaces.

It has been suspected that chemical reactivity of CO₂ with Portland cement, carbon steel and several rock types could increase the leakage probability from CCS reservoirs [1]. However, recent experimental studies have demonstrated that a simple view of the geochemical incompatibility of cement with CO₂ is not always consistent with the creation of leakage paths. Instead, a number of experimental studies have demonstrated that the permeability of fractured cement specimens or specimens with fractures along cement/rock interfaces decreases upon exposure to scCO₂ or CO₂ saturated brine [2-7]. This self-healing of cracks/microannuli in/along cement is often attributed to precipitation of reaction products such as CaCO₃ or amorphous silica in the microannuli [2-6], but is also suggested to be caused by mobilization of fines [7]. Thus, the details of this cement self-healing process have not yet been fully understood, and more information is required on how it affects CO₂ leakage rates and well remediation protocols.

In the present paper, the self-healing of fractures in/along well cement upon CO₂ flooding is investigated in detail. A cement-sandstone specimen allowing for CO₂ flow both at the cement-rock interface and through fractures in the cement matrix is used for water-alternating-gas (WAG) scCO₂-brine flooding and subsequent characterization using Scanning Electron Microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) and micro computed tomography (μ -CT). This reveals in detail how the specimen changes when exposed to CO₂, and specifically how fractures in cement gradually heal when CO₂ leaks through them. Chemical sampling of the effluent water from the flooded specimen provides data for qualitative assessment of the chemical reactions causing the self-healing of the fractured cement.

2. Experimental details

2.1. Specimen preparation

A hollow cylinder of Castlegate sandstone was prepared and the center cavity was filled with ordinary Portland G cement, as seen in Fig. 1. Castlegate is an outcrop sandstone that is measured by XRD to consist of 70.38% quartz, 10.71% K-feldspar, 1.11% Chlorite, 7.64% kaolinite, 8.33% mica/illite, 0.31% calcite, 0.05% siderite, 0.20% dolomite/ankerite, 0.13% pyrite and 1.14% sylvite. The mean grain size diameter is 0.19 mm, the sand size is fine and the sorting is moderate to well. The porosity (as a % of bulk volume) is *c.* 25. The pore network in this sandstone type is generally open and well connected.

The outer diameter of the hollow cylinder of Castlegate sandstone was 38 mm, the inner diameter was 30 mm, and the specimen length was 45 mm (Fig. 1). The cement was ordinary Portland G oil-well cement without additives, mixed with a water/cement mass ratio of 0.4. The cement paste was blended according to the American Petroleum Institute (API) 10A procedure, which is typically used for wells in the North Sea. After placement in the hollow Castlegate cylinder, the cement was left to harden in an oven at 66°C for 7 days.

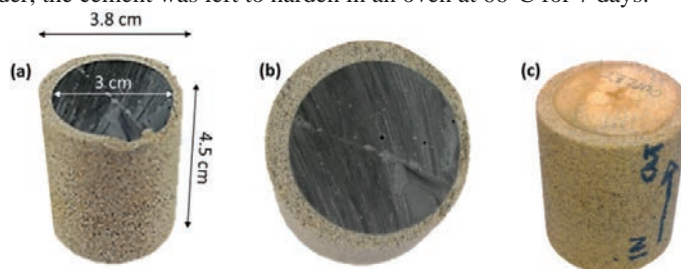


Fig. 1. (a) The geometry of the specimen consisting of a hollow Castlegate sandstone cylinder filled with Portland G cement. (b) A close look at the top of the specimen before CO₂ flooding. (c) The specimen after CO₂ exposure.

2.2. WAG flooding procedure

A water-alternating-gas (WAG) flooding with sc-CO₂ and 10% (w/w) KCl brine was performed with the specimen in a vertical position and a top-down flooding direction. This flooding scheme was chosen in order to create the best possible conditions for chemical reactions to take place in the specimen. The specimen was first mounted in a hydrostatic core holder and the core holder was subsequently placed in an experimental rig at 40°C and 100 barg pore pressure in order to simulate conditions in a reservoir with sc-CO₂. During the entire experiment, data logging of flow-rates and differential pressure across the specimen was carried out. Initially, the specimen was saturated with brine, and flooding with brine was performed for 2 pore volumes (PV). Subsequently, a total number of five WAG-cycles were carried out, each cycle comprising flooding with *c.* 1-2 PV of CO₂ followed by *c.* 6-7 PV of KCl brine until the differential pressure was stable, reflecting steady state brine flow. Water samples were collected continuously from the downstream end of the core holder during the entire flooding. The sampling was performed downstream a back pressure regulator (BPR) where the fluid pressure was decreased from 100 barg to atmospheric pressure in one step, and as a consequence of this sampling technique some CO₂ was allowed to degas from the water before samples for chemical analyses were collected. The result is a semi-quantitative chemical dataset allowing for qualitative assessment of chemical trends during flooding while quantitative calculation of mineral saturation indices, etc. based on the dataset would be somewhat doubtful. The semi-quantitative character of the dataset is specifically the case for chemical components associated with the aqueous carbonate system such as Ca, Mg, HCO₃⁻ and pH. Quantification of the uncertainty associated with this sampling technique is not possible as the amount of CO₂ degassing from the sample varies. The collected water samples were filtered through 0.2 µm cellulose acetate (CA) filters and subsequently analyzed for content of major elements (except K) and several trace elements by inductive coupled plasma mass spectrometry (ICP-MS), while Cl⁻ and SO₄²⁻ contents were analyzed spectrophotometrically. Samples for ICP-MS analysis were preserved by adding 1% 7M suprapur HNO₃ to the samples immediately after filtration. The exception was samples for Si analyses which were preserved with 10% 5M NaOH according to the procedure suggested by Rimstid and Barnes [8]. The pH of the produced fluids was measured using a pH meter at the downstream end of the core holder and Gran-titration with 0.1 M HCl was used to determine the alkalinity (HCO₃⁻-concentration). The latter two analyses were performed as fast as possible after sample collection.

2.3. Specimen characterization

The specimen was investigated visually, by micro computed tomography (µ-CT), and Scanning Electron Microscopy (SEM) before and after CO₂ flooding. Two different scanners were used for µ-CT studies, namely a Nanotom 180 (before flooding) and a Nikon XT H225 (after flooding). The specimen was exposed to 130 keV X-rays and a beam current of 130 µA for 750 ms per projection image, and the rotation angle was 360° in steps of 0.25° per projection image. The two dimensional (2D) projection images resulting from µ-CT scanning were reconstructed into three dimensional (3D) volumes using the Avizo software. This program enables visualization and segmentation of volumes. Segmentation was done based on pixel intensities (threshold values) that enabled large pores, cement and rock to be clearly distinguished by visual inspection. However, the resolution of the µ-CT images did not allow for detailed studies of the pore network in the cement [13]. SEM analyses were performed using a Hitachi S-3400N low-vacuum SEM equipped with a tungsten filament. The specimens were not polished prior to SEM studies.

3. Results

3.1. WAG flooding

Figure 2 shows the flow rates used and differential pressure across the composite sandstone-cement specimen during the experiment. As shown, five water alternating gas (WAG) cycles were performed. Pore volume is here the average pore volume of the composite specimen prior to the experiment of 13.6 mL as measured by He-porosity. The initial 2 PV water flooding of the specimen shows good correlation between flow rate and differential pressure, reflecting saturated flow in the specimen prior to WAG flooding. In the part of the experiment where the WAG

flooding scheme is followed, the introduction of a second fluid (scCO₂ or brine) initially causes an increase in differential pressure which levels off to a constant level towards the end of each WAG cycle (Fig. 2). This pattern is especially pronounced during the part of the WAG where brine flooding is taking place and reflects that two phase flow in the specimen takes place in the specimen. The constant differential pressure towards the end of each WAG cycle corresponds to steady state flow of brine and in this phase the specimen is probably close to 100% saturated with respect to brine. It should be noted that the entry pressure for brine, corresponding to the peak in differential pressure occurring when the influent is shifted to brine, seems to increase as the experiment proceeds. This is especially the case between the first and second WAG cycle (Fig. 2). Initially, before WAG flooding was performed, the liquid permeability of the composite specimen was measured to *c.* 200 mD. If we assume that the specimen is 100% saturated with brine during steady state conditions, the permeability of the specimen has decreased to *c.* 100 mD as a result of the WAG treatment (Fig. 2).

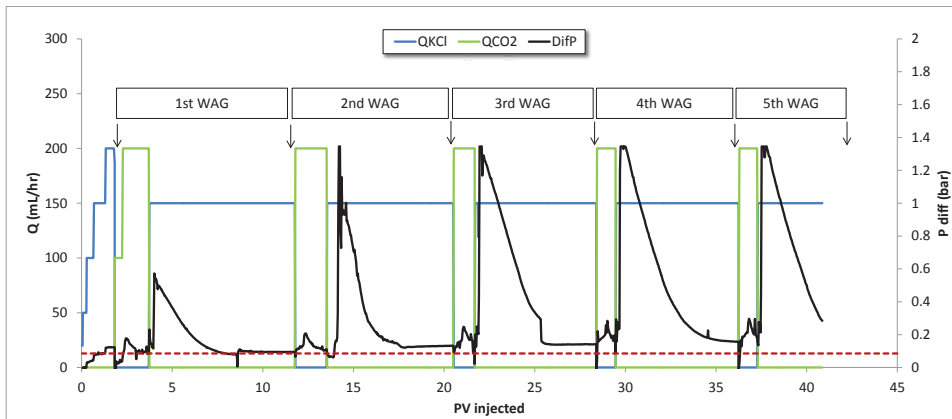


Fig. 2. Procedure for CO₂ flooding through the composite sandstone-cement specimen. As seen in the figure the flooding procedure involved five water alternating gas (WAG) cycles. Pore volume is here the average pore volume from He-porosity measurement. The dotted line corresponds to the calculated differential pressures of a 100% brine saturated specimen using a flow rate of 150 mL/hr and a permeability of 200 mD.

3.2. Aqueous chemistry

In the initial phase of the experiment where flooding with KCl brine is performed, only limited chemical reactions take place in the composite specimen, which is reflected by low concentrations of aqueous chemical components in the effluent (Figs 3 and 4).

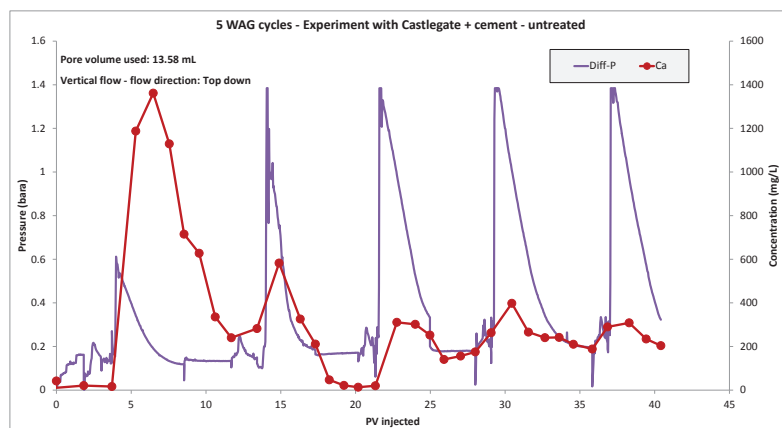


Fig. 3. Ca-concentration of effluent water during the WAG treatment of the cement-sandstone composite specimen. For comparison, also shown is the differential pressure across the specimen during the experiment.

However, after WAG flooding is initiated, the effluent concentrations change dramatically, reflecting that chemical reactions take place in the specimen. During the first WAG cycle, the measured Ca concentration reaches a level of 1,400 mg/L which is probably even higher at the reservoir condition prevailing in the specimen as some CaCO_3 precipitates during depressurization of the water in the back pressure regulator (BPR) (cf. Section 2.2). Precipitation of CaCO_3 in the BPR was verified by XRD analyses of fines collected from the BPR (data not shown). As the water saturation in the specimen increases during the first WAG cycle, the Ca concentration decreases to a lower level around 200 mg/L (Fig 3).

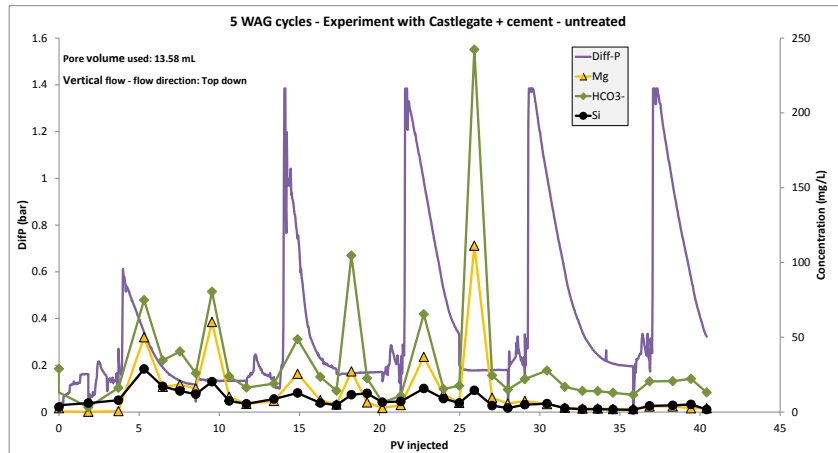


Fig. 4. Mg and HCO_3^- concentrations of effluent water during the WAG treatment of the cement-sandstone composite specimen. For comparison, also shown is the differential pressure across the specimen during the experiment.

The pattern with occurrence of peaks in the Ca concentration initially during each waterflood followed by a decrease in Ca concentration to a lower level is repeated for the following four WAG cycles. However, the peak in Ca concentration becomes smaller with time to *c.* 3-400 mg/L during the fourth and fifth WAG cycle.

In contrast to the Ca concentration, several other components, including Mg, Si, Fe, Mn, and HCO_3^- , show the occurrence of two peaks in concentration during each WAG cycle (Fig 4; Fe and Mn not shown). The first peak is occurring together with the peak in Ca concentration just after brine flooding is initiated while the second peak appears as the differential pressure becomes constant, reflecting steady state brine flow in the specimen. The exception is the measured effluent Na concentration, in general suggesting that only a peak corresponding to steady state flow in the sandstone occurs (Fig 5). As will be discussed below, the observed pattern of the effluent aqueous chemistry suggests that flow of liquid in the specimen generally takes place through two distinct flow systems.

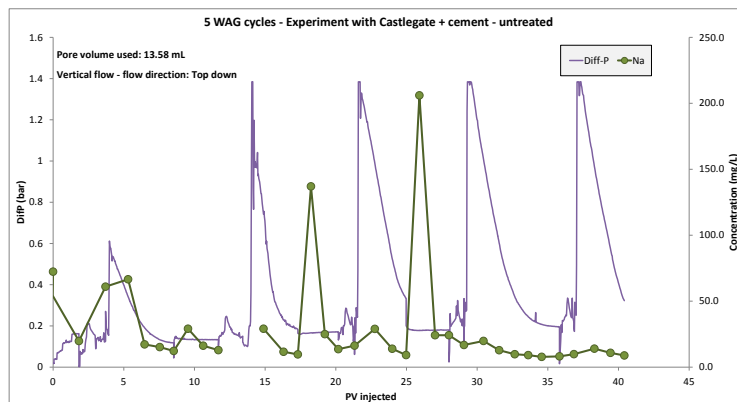


Fig. 5. Na-concentration of effluent water during the WAG treatment of the cement-sandstone composite specimen. For comparison, also shown is the differential pressure across the specimen during the experiment.

3.3. Comparison of μ -CT data before/after flooding

By inspecting the raw μ -CT data (Fig. 6) from before and after the experiment, it is evident that a set of fractures that were traversing the bulk cement were closed up as a result of the CO_2 -brine WAG flow. The cement-rock bonding was good, and it was not significantly aggravated by the applied flooding scheme. A three dimensional (3D) reconstruction of pores/fractures in and along the cemented cylinder of the composite core is given in Fig. 7. The figure is based on segmented μ -CT data and shows the reconstruction of the porous space before (Fig 7a) and after (Fig 7b) the experiment. The figure also gives the volume fraction of pores in the specimen before/after the experiment. As shown, the closing of the three-bladed fracture structure in the central part of the cement plug as a result of the CO_2 -brine WAG treatment is verified by the 3D reconstruction as the observed pore system in the central part of the cement plug before experiments (Figs 7a and 7b) seems to disappear as a result of the experiment (Figs 7c and 7d). The result is further a decrease in porosity of the cement plug from 0.8% to 0.5%.

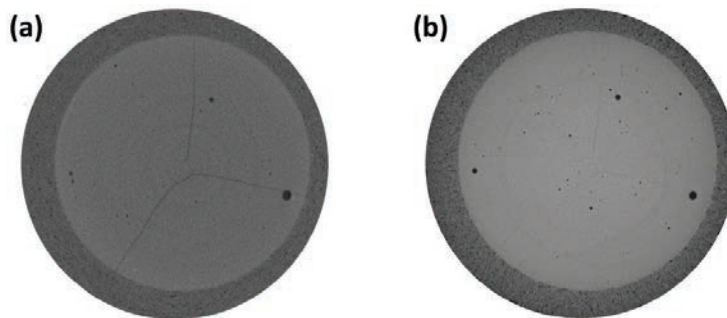


Fig. 6. Micro computed tomography (μ -CT) data from (a) before CO_2 -brine WAG flooding, and (b) after CO_2 -brine WAG flooding. It is clear that the permeable fractures in the center of the cement plug have healed as a result of the experiment (even if resolution is higher in (b) the fractures are more visible in (a)).

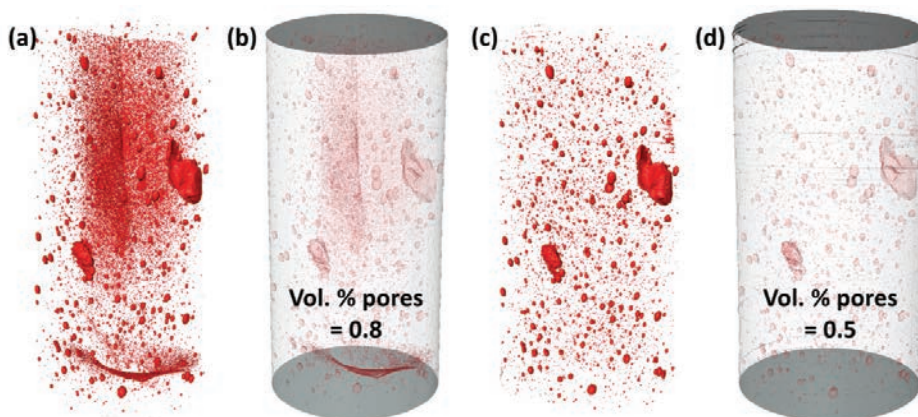


Fig. 7. Micro computed tomography (μ -CT) data for the cement part of the composite cement-sandstone specimen before and after the experiment. (a) Pore volume in the cement plug before flooding, (b) Pore volume in the cement plug before flooding together with the cement cylinder. The volume percentage of pores is 0.8% relative to the bulk volume of the cement plug. (c) Pore volume in the cement plug after flooding, (d) Pore volume in the cement plug after flooding together with the cement cylinder. The volume percentage of pores is 0.5% relative to the bulk volume of the cement plug.

3.4. Comparison of SEM and EDX data before/after flooding

As seen in Fig. 1, the cement in the WAG flooded cement/sandstone specimen has an orange/light-brown ring near the cement/sandstone interface, which was studied by combined SEM and EDX analyses (Fig 8). This analysis was somewhat hampered by the fact that the specimen was allowed to dry without prior removal of the residual KCl brine. Therefore, the majority of our SEM images show the occurrence of a massive layer of rod-shaped and curved KCl crystals making specific conclusions about precipitates at the interface difficult. However, the SEM/EDX analysis of the interface clearly shows that the cement seems to disintegrate at the interface as a result of the experiment (Fig 8). Away from the interface in the cemented part of the specimen, the density of KCl particles decreased and calcium carbonate (CaCO_3) as well as cement phases containing Ca and Si and traces of Al, Mg, Fe, and Mn were found.

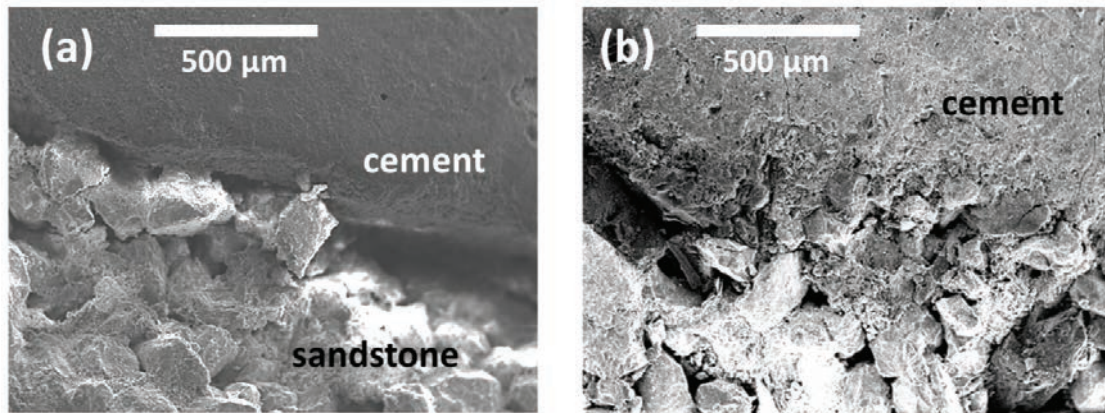


Fig. 8. SEM images from the cement-sandstone interface (a) before and (b) after WAG flooding. The cement is apparently changing its structure at the interface upon reaction with the CO_2 .

Additional SEM/EDX analysis of the three-bladed fracture in the central part of the of the cement plug clearly showed that the fractures were filled with fresh precipitates of CaCO_3 (Fig 9).

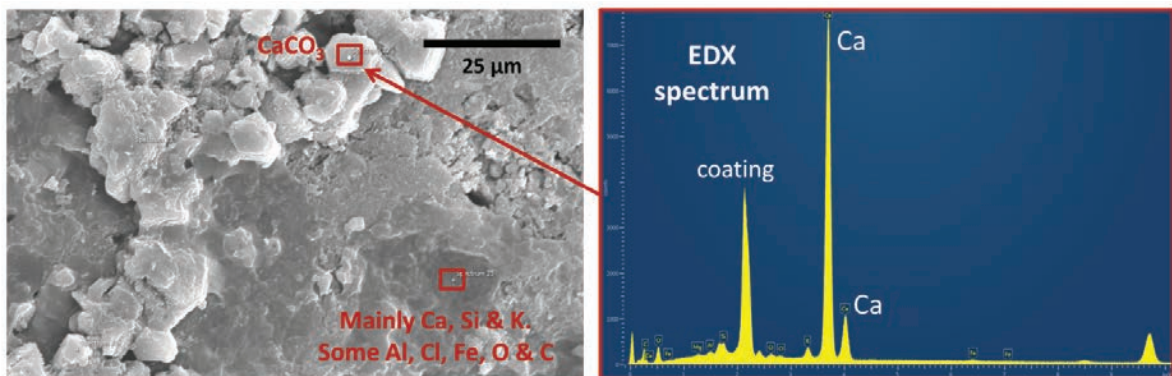
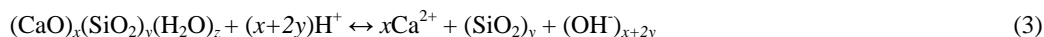


Fig. 9. SEM image (left) from the fracture in the center of the cement cylinder which was seen to close in μ -CT images. Energy Dispersive X-ray spectroscopy (EDX) maps were collected from various regions. The figure to the right shows the EDX map from the precipitated phase inside the fracture. Judging from the Ca content and the crystal shape it is likely that this fracture-closing phase is CaCO_3 .

4. Discussion

The observed pattern for the Ca concentration of the effluent (Fig 3) is consistent with findings from previous experimental studies of CO₂ flooding of fractured cement or cement/rock composite specimens [e.g. 3,7]. Thus, the high Ca concentrations occurring immediately when brine is introduced in the specimen after scCO₂ flooding, reflect the dissolution of portlandite (Ca(OH)₂) and C-S-H (calcium-silica-hydrate), in the cement, and the release of Ca to the porewater according to the following reactions:



Following dissolution of the cement with CO₂, the specimen, and therefore also the fractures in the central part of the cement plug and the cement/rock interface, are re-saturated with brine which towards the end of each WAG cycle becomes practically free of CO₂. As the brine contains less CO₂ in this part of the experiment, the Ca concentration accordingly decreases to lower levels towards the end of the brine flooding period.

Previous studies have shown that as a result of cement-CO₂ interaction at the interface between fluid and cement, a distinct zonation of the cement takes place, resulting in precipitation of amorphous silica closest to the fracture and carbonation of the cement occurring further away from the interface but immediately adjacent to the zone containing amorphous silica [e.g. 4, 10]. In this context, we can explain the general decrease in peak Ca concentration that we observe as the experiment progresses (compare first WAG cycle with following WAG cycles in Fig 3) by the formation of the silica and carbonate zones making direct/immediate contact between Ca(OH)₂ and C-S-H of the cement with scCO₂ and/or carbonated water in the fracture less pronounced; i.e., as the experiment progresses, the dissolution of cement becomes controlled by the diffusion of CO₂ through the silica and carbonate zones. This eventually results in generally lower Ca-concentrations in the effluent water. Newell and Carey [7] showed similar aqueous chemical results in experiments where a cement/shale composite specimen was flooded by co-injection of brine and scCO₂, and Abdoulghafour et al. [3] also observed decreasing effluent Ca concentrations while flooding a fractured cement specimen with CO₂ rich brine. In both cases, the decrease in Ca concentration was explained by the formation of the silica and carbonate layers in the cement and diffusion control of the aqueous Ca concentration. In our case, the formation of these distinct zones was not investigated in further detail but will be subject to future studies.

Abdoulghafour et al. [3] further argued that dissolution of CaCO₃ could potentially control the aqueous Ca concentration towards the later stage of their experiment, while the Si concentration was controlled by the precipitation of the Si-rich amorphous layer. Equilibrium control of the aqueous Ca concentration by dissolution of CaCO₃ could very well also be the case in our experiments for the part of the WAG flood where steady state brine flow occurs in the specimen. Thus, the SEM/EDX analysis showed clear evidence of CaCO₃ precipitates in the fracture system in the central part of the cement plug as well as in the vicinity of the cement/rock interface. In the central part of the cement plug, the CaCO₃ precipitate is apparently filling up the entire fracture (Fig 9), and as a consequence, the bulk brine permeability of the composite specimen decreases by a factor of two from c. 200 mD to c. 100 mD due to the CO₂-brine WAG treatment (Fig 2). In fact, the observed massive CaCO₃ precipitate in this fracture system, together with the decrease in permeability, suggests that brine flow is close to zero in the fracture system towards the end of the experiment, and that the CO₂-brine WAG treatment has caused a self-healing of the fracture. Similar self-healing has been observed by several other authors [2,3,4,7] though, e.g., Newell and Carey [7] suggested that their observed decrease in permeability was more likely to be caused by fines mobilization than actual precipitates filling up the cement/rock interface.

In a different study (unpublished data), the permeability was measured to be 375 mD of a Castlegate sandstone specimen similar to the sandstone used in the present study, and we have found no reason to believe that the permeability of the sandstone part of our composite specimen decreases much below this value as a result of the treatment with CO₂ and brine. Furthermore, the cement/rock bonding in our composite specimen was good. Together

with the observed self-healing of the fractured cement, the Ca-concentration in the final stage of the experiment is therefore most likely controlled by CaCO_3 equilibrium near the cement/rock interface.

Chemical speciation calculations using PHREEQC and the *lnl.dat* database [12] show that the effluent water in our experiment is likely to be saturated with respect to a quartz- or chalcedony-like phase (data not shown) which is in good agreement with the suggestion that Si concentrations are controlled by the precipitation of an amorphous silica rich phase. The latter conclusion is, however, somewhat uncertain taking the semi-quantitative nature of our dataset into consideration.

In contrast to the observed pattern in effluent Ca-concentration, several other chemical components showed the occurrence of two peaks in effluent concentration during the part of the WAG cycles where brine flooding takes place (Fig 4). The first peak most likely reflects that other reaction products than Ca are resulting from the cement- CO_2 interaction, while the second peak reflect chemical reactions taking place in the sandstone or at the cement/rock interface. The presence of other reaction products than Ca and Si from the CO_2 -cement interactions is supported by the EDX data that suggests the presence of traces of Mg, Al and Fe in the cement (Fig 9) and is also in line with previous studies [4,5,7]. The source of these chemical components is probably because the C-S-H of the cement contains traces of these components. The concomitant occurrence of increased HCO_3^- concentrations in the first peak during each WAG cycle further supports this interpretation as the increase in HCO_3^- concentration indicates concomitant pH-buffering due to CO_2 -cement interaction. The occurrence of the second peak in the effluent concentration, corresponding to the steady state brine flow period (Fig 4), is somewhat less straight forward to interpret. Thus, a corresponding increase in HCO_3^- concentration is also observed during this part of the WAG cycles (Fig 4), which indicates pH-buffering and CO_2 -cement interaction. However, the general trend of the effluent Na concentration with only one peak occurring at steady state brine flow (Fig 5) suggests that other chemical reactions, such as dissolution of feldspar or mica may be related to this peak. In this case, the pH buffering could be a result of dolomite/ankerite dissolution in the sandstone as preferential dissolution of carbonates in sandstone due to CO_2 exposure has been shown previously [10]. However, while the occurrence of the peak in chemical concentrations at steady state brine flow is probably a combination of these two explanations, the chemical data strongly indicate that two parallel flow systems occur in the specimen during the experiment: i) one flow system reflecting the flow in the fractured system in the central part of the cement plug, and ii) one flow system reflecting the flow and chemical reactions taking place in the porous sandstone and at the cement/rock interface. In both of these flow systems, CO_2 -mineral/cement interaction seems to become less pronounced as the number of WAG cycles increase; in the fracture system due to cement self-healing by CaCO_3 precipitation and in the interface system most likely due to formation of the silica and carbonate interlayers at the cement/rock interface. For the pure sandstone the decrease in reactivity may be due to depletion of minerals that are dissolved [10]. It should be noted that in the initial phase of the experiment where CO_2 is not introduced in the specimen, the dual flow system is not possible to discern in the collected data because chemical reactions between brine and specimen are minimal in this phase of the experiment.

In summary, our study shows that cement-sandstone specimens exposed to alternating conditions with scCO_2 and brine are chemically altered. As the cement to a large extent consists of portlandite ($\text{Ca}(\text{OH})_2$) and C-S-H (calcium-silica-hydrate), the measured effluent chemistry suggests that cement is indeed dissolved as part of the WAG treatment. However, as the aqueous concentrations of Ca and alkalinity become very high due to the WAG treatment, the result is apparently the precipitation of calcium carbonate (CaCO_3) in fractures in the central part of the cement plug which eventually causes closure/healing of the fractures and a decrease in bulk specimen permeability. Apparently, a second set of chemical processes seem to occur parallel to the self-healing of fractures in the cemented part of the tested specimen where carbonate precipitation prevails.

The observed self-healing of cement which can be observed even in this case where a substantial flow of CO_2 and brine takes place in the sandstone is important for CCS, as it means that the risk of compromising the safety of a storage site by cement- CO_2 chemical reactions is minimal. Furthermore, the results to some extent suggest that leakage of CO_2 is possibly self-limiting, and that CO_2 might even be a useful remediation fluid for ordinary petroleum wells.

However, in order to fully understand the cement self-healing process and understand the possible implication of this process, more studies are needed. These may include:

- Detailed studies of self-healed fractures as well as the cement/sandstone interface in a cleaned specimen.
- Dynamic geochemical modelling supporting the interpretation of a double porous flow system.

- Similar studies to the present study with cement/caprock composite specimens to study the possible self-healing along cement/cap-rock interfaces.

5. Conclusions

The present study has investigated how a composite cement-sandstone specimen is altered by CO₂-brine WAG flooding. The following main conclusions can be drawn from the study:

- During CO₂-brine WAG flooding, the liquid permeability of the specimen decreased from c. 200 mD to 100 mD.
- The decrease in permeability is explained by closure of a fracture system in the cemented part of the specimen due to precipitation of CaCO₃ in the fractures.
- The suggested self-healing of the fractured cement is supported by both visual comparison of the specimen before and after experiments, μ -CT scanning data, SEM/EDX data, and aqueous chemical data obtained from the effluent during the CO₂-brine WAG flooding.
- Effluent chemical data together with the trend in differential pressure during the CO₂-brine WAG flooding further indicate the occurrence of two parallel flow systems with different chemistry in the specimen during the CO₂-brine WAG flooding.
- With increasing number of WAG cycles, the CO₂-cement-rock interaction decrease.

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