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Closing of micro-cavities in well cement upon exposure to CO_2 brine

E.A. Chavez Panduro[a], M. Torsæter[b*], K. Gawel[b], R. Bjørge[c], A. Gibaud[d], Y. Yang[e], H. O. Sørensen[e], P. Frykman[f], C. Kjøller[f], D. W. Breiby[a]

[a]*Department of Physics, Norwegian University of Science and Technology (NTNU), Høgskoleringen 5, 7491 Trondheim, Norway*
[b]*SINTEF Petroleum Research, Trondheim, Norway*
[c]*SINTEF Materials and Chemistry, Trondheim, Norway*
[d]*LUMAN, IMMM, UMR 6283 CNRS, Université du Maine, Le Mans Cedex 09, France*
[e]*University of Copenhagen, Department of Chemistry, Copenhagen, Denmark*
[f]*Geological Survey of Denmark and Greenland, Copenhagen, Denmark*

Abstract

Long-lasting cement plugging of wells is crucial for successful CO_2 storage in underground reservoirs. It requires a profoundly improved understanding of the behavior of fractured cement under realistic subsurface conditions including elevated temperature, high pressure and the presence of CO_2 saturated brine. Here we report computed X-ray tomography studies on the effects of CO_2 on cement. More specifically, we have exposed cured Portland G cement samples with pre-made microchannels mimicking fractures to CO_2 saturated brine at elevated pressure (100 bars) and room temperature. The microchannels were observed to get filled with calcite ($CaCO_3$) during the CO_2 exposure. The extent of this self-healing was dependent on the diameter of the leakage path, with narrower channels more readily getting clogged. Chemical simulations taking into account the cement composition, CO_2 availability, pH, pressure and temperature gave results consistent with our conceptual understanding of how the differences in dissolution/precipitation profiles in the cement may result from the availability of CO_2. In particular, the modelling provides an explanation why calcite precipitates preferentially in the channels rather than on the external cement sample surfaces. We conclude that the localized precipitation can be ascribed to higher pH inside the cavities compared to near the external surfaces, owing to long diffusion distances giving a locally limited CO_2 supply within the voids.

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Keywords: CO_2, cement, self-healing, microcomputed tomography

* Corresponding author. Tel: +47 4811-1159
E-mail address: malin.torsater@sintef.no

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1. Introduction

CO_2 Capture and Storage (CCS) using depleted oil and gas reservoirs is considered a promising solution for reducing global emissions of greenhouse gases but large-scale implementation is impeded by a fear of CO_2 leakage from the reservoirs[1]. The special report on CCS published by the Intergovernmental Panel of Climate Change (IPCC) outlines that wells are among the most probable leakage paths from CO_2 storage sites[1]. These wells are man-made structures of steel and cement that connect the storage reservoir with the atmosphere. If the steel or cement barriers break, leakage paths are likely to develop along the well. To estimate potential leakage rates over time, and to optimize well remediation protocols, the compatibility of Portland cement with CO_2 has been studied through several experimental campaigns[2–5].

When it comes to CO_2 exposure of cement, an important finding is that in addition to the critical fact that cement tends to get more brittle at the surface when carbonated, fractures in samples have been observed to heal - which is clearly promising[3,4]. Self-healing has been observed both at hydrostatic non-flow ("batch") conditions and CO_2 flow conditions. At non-flow conditions, where a sample is immersed in a CO_2-rich aqueous environment, a decrease of the porosity and permeability has been observed in artificially fractured cement bars[6]. Similar effects have been observed when CO_2 has been flowed through fractured samples, and the permeability decrease can in this case be ascribed to carbonation inside cracks[7,8]. It has been found that the chemical changes occurring in the samples are not the same in batch conditions and CO_2 flow conditions[9,10]. In the former case, the self-healing occurs by $CaCO_3$ precipitation but in the latter case the cement degrades into an amorphous layer on the fracture surfaces leading to a decrease of the permeability. In order to make use of this beneficial cement healing process in practice, a more detailed understanding is required of how it occurs and how it affects CO_2 leakage rates. To elucidate these issues, we have performed micro-computed tomography (μ-CT) experiments on artificially fractured cement to observe the healing process as well as the carbonation process at batch conditions. We have exposed cement samples with pre-made microchannels (mimicking defects) to CO_2 at high pressure. The experiments have been performed at 100 bars pressure and room temperature. The experiments were supplemented by modelling of compositional changes both within the cement sample as well as in the solution. The models have been set up in order to understand possible differences in dissolution profiles in the cement that may result from the availability of CO_2.

2. Experimental

2.1. Sample preparation

Portland G cement (High Sulfate Resistant Well Cement, Norcem AS) was mixed according to API recommended practice[11] with a water/cement ratio mass of 0.44. The slurry was poured into cylindrical plastic moulds of diameter 3 mm. Nylon fishing lines (ø = 0.2 and 0.5 mm) were inserted into the cement slurry in order to form channels in the samples. The samples were cured for 3 days at ambient temperature and pressure. Then both moulds and fishing lines were carefully removed, thereby leaving a cylindrical cavity running through the free-standing sample. The samples were left for further curing in plastic bags to avoid water evaporation and drying. The curing lasted for two weeks before CO_2 exposure.

2.2. CO_2 exposure and X-ray microtomography

The experiments were performed at 100 bars and room temperature at batch conditions in a small pressure cell dedicated for in-situ CT studies. The pressure cell was equipped with a sample holder with an inner diameter of 4 mm and ~1 cm^3 in volume. The batch aqueous solution contained 1 wt% of NaCl. The hydrostatic pressure was increased up to 100 bars within 2 hours and maintained for 2 hours at room temperature. The pressure was lowered from 100 bars back to ambient over 30 minutes.

The μ-CTs images of cement sample during the CO_2 exposure were collected using a Nikon XT H225 μ-CT at 145 keV and 87 μA at the Department of Physics, NTNU. Each tomogram was reconstructed from 3142 projections collected over 360 degree rotation and with an exposure time of 2 s for each projection. The reconstructed 3D tomogram had a resolution of about 10 μm (voxel size of 3.8 μm) using the CTAgent software.

Image visualization and segmentation were carried out using VGstudio and Fiji[12] software. Segmentation of the carbonated zones and the precipitated calcium carbonate from the μ-CT image was done under the assumption that the calcium carbonate containing layer is denser, and therefore brighter and more homogeneous in the (inverted) μ-CT images. The mineral precipitation was segmented by using a threshold of the gray-scale histogram in the microcavity section.

2.3. Modelling

Reactive geochemical modelling was carried out using the numerical code PHREEQC[13] with the Thermoddem database[14] in order to be able to represent the cement in the model. In order to simulate chemical reactions taking place at the water/cement interface, two 1D transport models where set up. In both cases, the numerical grid represented a cross-section across the interface, i.e. the water/cement interface was present at one end of the model while the other end represented the interior of the cement. At the cement end of the model grid, the boundary was simulated as a closed boundary (Neumann boundary condition) while at the interface end of the model grid, the boundary condition varied in the two conceptual models. In one model, the boundary condition was of Dirichlet type (open boundary) obtained by keeping the water in equilibrium with a constant CO_2 pressure of 50 bars in order to model a situation with unlimited supply of CO_2 to the water phase. In the second model, the boundary condition was of Neumann type (closed boundary) but with an initial concentration of CO_2 in the water corresponding to equilibrium with a CO_2 pressure of 50 bars to model the limited supply of CO_2. Except for the different boundary conditions at the water/cement interface, the two conceptual models were similar.

The numerical grid was represented by a 1D column with 25 cells, each 0.1 mm long, of which five cells at one end represented the water phase. Transport was simulated as diffusion only since the permeability of the cement is assumed to be very low. The diffusion coefficient for CO_2 was set to 1.6×10^{-9} m^2/s which is line with Cadogan et al.[15].

The cement was represented as a simple cement consisting of calcium-silica-hydrate (C-S-H(1.6)) and portlandite ($Ca(OH)_2$), and the relative amounts of these minerals initially present in the cement were taken from Soive et al.[16]. As a consequence of the reactions between CO_2 and cement, calcite ($CaCO_3$) was allowed to precipitate in the model, but was not considered to be present in the sample initially. The models simulated a total of 275 min of reactive transport by 400 time steps, each 126 sec long.

3. Results and discussion

CO_2 exposure of Portland G cement cylinders (ø~3 mm) containing one through-going microcavity (ø~0.2 and 0.5 mm) were studied using μ-CT. The samples were immersed in brine solution and then exposed to CO_2 at 100 bars for 20 hours. After the CO_2 exposure at batch conditions, mineral precipitation in the micro-cavities was observed. Figure 1 shows the cross-sections through cement samples before and after exposure. Micro-cavities of both cement samples were partially filled with precipitate after exposure to CO_2 saturated brine. The precipitate was calcium carbonate ($CaCO_3$), and X–ray diffraction on the exposed samples indicated that the polymorph was calcite. The $CaCO_3$ crystals were randomly located along the cavity surface. After 20 h the mineral occupied about 40 % and 22 % of the 0.2 mm and 0.5 mm diameter microcavities, respectively. Notably, no precipitate was observed at the external sample surfaces being in contact with large solvent volumes.

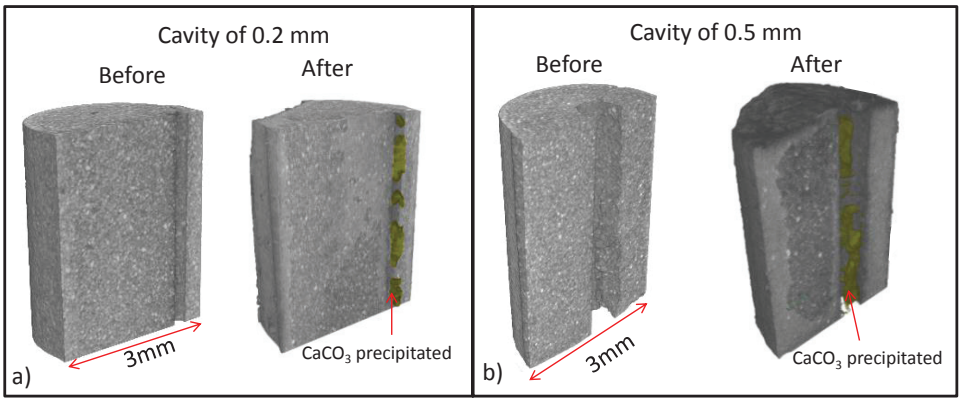

Fig. 1. Vertical cross-sections through micro computed tomography (μ-CT) reconstructed volumes for samples with a) 0.2 mm and b) 0.5 mm void diameters before and after CO_2 exposure. $CaCO_3$ was found to precipitate inside, and thereby nearly close, the voids, while no precipitates was found on the external sample surfaces.

Figure 2 shows representative cross-sections of the samples with 0.5 and 0.2 mm diameter cavities after 20 hours of CO_2 exposure. In addition to the carbonation of the bulk cement, calcium carbonate was found to precipitate in the microcavities. Calcium carbonate formed also in the cement matrix giving rise to increased material density and thus enhanced X-ray absorption manifested in the μ-CT images as increased brightness. The brighter zones in the μ-CT images were identified as the carbonation zone. Within the carbonation zone the dissolved portlandite is being precipitated as calcium carbonate in the cement micrometer size pores (being below the resolution of the experiment). In the case of the sample with a 0.5 mm cavity the carbonated zone progressing from the external sample surface was on average thicker than the zone progressing from the void surface. This observation suggests that the carbonation processes are faster nearby the external sample surface. Similar observations were made for the sample with 0.2 mm cavity although the carbonation of this sample was less than for the 0.5 mm cavity sample, possibly suggesting that the cement in this sample had a different porosity.

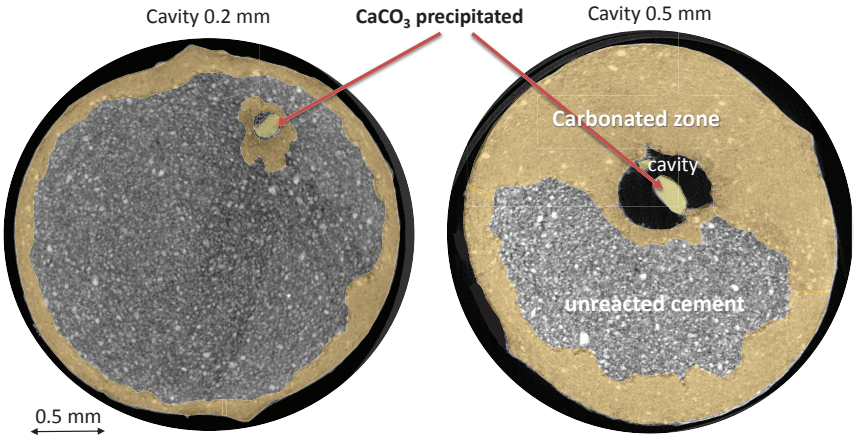

Fig. 2. Horizontal cross sections (μ–CT) of the cement samples with 0.2 and 0.5 mm void after 20 hours of exposure to CO_2 saturated brine.

The CO_2 exposed samples were further imaged by using a scanning electron microscope (SEM) equipped with a backscattered electron (BSE) detector. The SEM-BSE image obtained for the sample with 0.5 mm void is presented in Figure 3. The four regions characteristic for carbonated cement have been distinguished according to Kutchko et al.[2]: I) unreacted cement, II) $Ca(OH)_2$ depleted zone, III) fully carbonated zone and IV) calcium carbonate depleted zone.

The unhydrated cement grains in zone I appeared as the brightest spots with well-defined boundaries. Pores and silica gel appeared as the darkest spots and could be well distinguished within zone IV. The portlandite ($Ca(OH)_2$) and calcium-silicate-hydrate (C-S-H) phases having an intermediate brightness were seen as regions with diffuse outlines rather than well-defined grains and can be observed in regions I and II. Calcium carbonate appeared in zone III as the regions filling up the space between the darkest and the brightest spots, which are pores/silica gel and unhydrated grains, respectively.

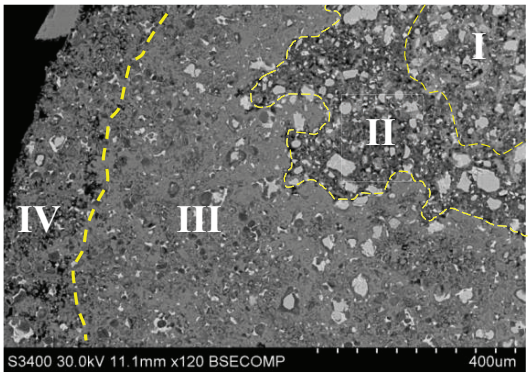

Fig 3. a) SEM-BSE image of cement with 0.5 mm cavity exposed for 20 hours to CO_2 showing the different carbonation zones: I- unreacted cement; II - C-H depleted zone; III- carbonated zone; IV- $CaCO_3$ dissolution zone.

Chemical numerical simulations were performed in order to conceptually understand the observed differences in the dissolution and precipitation profiles within the cement surrounding the cavity compared to the regions nearby the external surfaces of the cement sample. The differences might have resulted from different availability of CO_2 in the system. To test this hypothesis, two types of models were established: the *open* and *closed* system with respect to CO_2 supply to the cement. Fig. 4 shows a schematic representation of the two models used. In the closed system, all cells are initially in the equilibrium with the CO_2 at 50 bars but a limited amount of CO_2 is available. In the open system, the amount of available CO_2 was unlimited and all cells in water were in equilibrium with CO_2 at 50 bar. Changes in the composition within both aqueous and cement phases after 275 min of reaction were calculated. The data are presented in Figure 5.

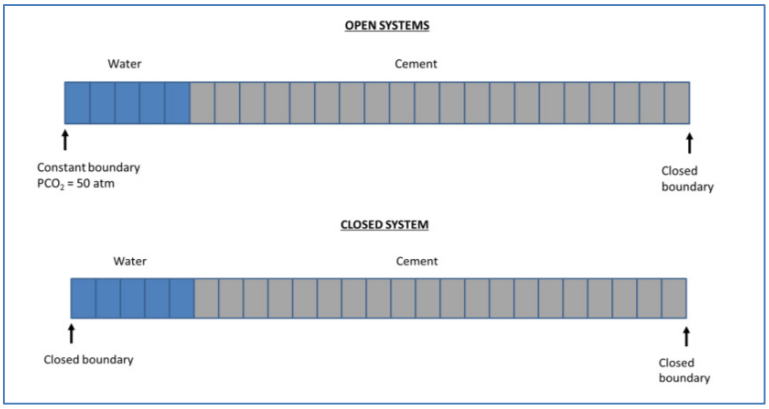

Fig.4. Schematic illustration of the two system models: *open* and *closed*

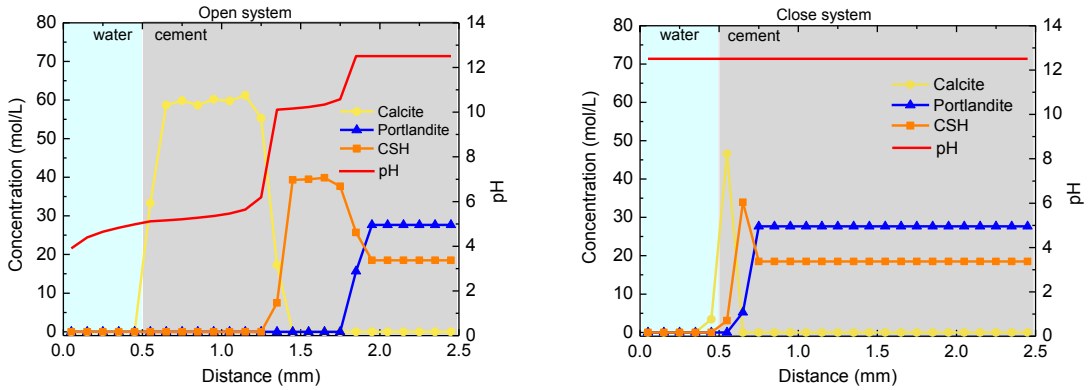

Fig. 5. Calcite, Portlandite and C-S-H concentration variations along the solution and the cement interface for a) open and b) closed system after 275 min of reaction.

The open system model showed that after 275 minutes of reaction with constant CO_2 supply three regions in the cement matrix can be distinguished, cf. Fig. 5. The region nearest to the water/cement interface was most abundant with calcite. This region was approximately 0.8 mm thick and was depleted from C-S-H and portlandite. The second region ranging between 0.8 and 1.5 mm from the water/cement interface was most abundant in C-S-H and depleted from portlandite. In the third region located deeper than 1.5 mm from the interface portlandite was the most abundant phase. However, no or very little precipitation of calcite in the water cells was observed. pH in the water surrounding the cement was around 4-5 and increases gradually inside the cement, i.e. in the calcite-rich region pH was around 6 and increased further to approximately 10 in the C-S-H rich region. In the region dominated by portlandite and unaffected by reaction with CO_2, the pH is approximately 12.5.

Similarly, the results from the closed system model also showed the expected sequence of minerals near the interface, namely, calcite, C-S-H, portlandite, but the calcite and C-S-H rich regions were much narrower compared to the results obtained with the open system. The unaffected portlandite rich region started already from a depth of

0.25 mm from the interface. The pH in the closed system after 275 minutes of reaction was constant around 12.5 throughout the entire system. In this system calcite precipitated also in the water phase.

The carbonation processes have previously been suggested by Kutchko et al. to proceed by following mechanisms[2]. First the carbon dioxide dissolves in water and reacts with water to form carbonic acid. This results in lowering the pH of the solution. When this acidic solution containing carbonic acid diffuses into the cement matrix, the dissociated acid reacts with portlandite and C-S-H. As a result of these reactions calcium carbonate precipitates inside the cement matrix. It has been shown that calcium carbonate can also precipitate inside defects such as voids, cracks, pores etc. and thus result in a decrease of cement porosity and permeability[8,17]. This effect has been referred to in the literature as self-sealing or self-healing[6].

In our experiments the self-healing process led to partial sealing of artificially made voids. After 20 h of CO_2 exposure, 22 and 40 % of the 0.5 and 0.2 mm diameter cavities were filled by precipitated calcite, respectively. If there were enough portlandite and C-S-H in the cement matrix and there were an unlimited CO_2 supply, we estimate that the 0.5 and 0.2 mm cavities would have been sealed after 3.8 and 2 days, respectively. Calcium carbonate precipitated not only inside the voids but also in the cement bulk. It has been observed both as a brighter zone in μ-CT scans as well as in the SEM-BSE images (zone III, Fig. 3). Importantly, no precipitation was observed neither in the solution surrounding the cement sample nor at the external sample surfaces, see Fig. 2. In order to understand why the calcite precipitates only in the voids but not at the external sample surfaces, conceptual numerical simulations were performed. In case of an open system, where CO_2 supply is constant and unlimited, the pH in the solution surrounding the cement sample is kept low (see Fig. 5a, red line). The low pH does not support calcite precipitation but rather the dissolution of calcite[18]. The numerical simulation results confirm that no or very little calcium carbonate precipitate is present in the solution at cement sample surfaces in the case where CO_2 supply is unlimited (Fig. 5a, yellow line). Contrary to this, some precipitation of calcite in the aqueous solution occurs close to the water/cement interface in the case with closed system boundary conditions. The main reason for this is that the limited supply of CO_2 enables a much higher pH of 12.5 in the entire water/cement system. At this pH, the activity of the CO_3^{2-} ion is much higher relative to the open boundary system, and therefore calcite precipitation takes place at much lower Ca^{2+} concentrations. Thus, calcium ions released inside the cement due to dissolution of portlandite and C-S-H will in both cases diffuse back into the water, but while low pH in the open boundary case prevents the calcium ions from precipitating as calcite, the high pH in the closed boundary system results in calcite precipitation near the interface[18].

The experimental conditions at the external sample surfaces and in the surrounding solution, with unlimited availability of CO_2, correspond to the *open* model system. On the other hand inside the void the availability of CO_2 is limited by the diffusion along the length of the void. This system thus resembles more the closed system although it is not an ideal closed system because CO_2 can be constantly supplied to the void, however with a significantly reduced rate compared with at the external surfaces. This mechanism also provides a possible explanation why the carbonated layer near the external surfaces was observed to be thicker than the thickness of the carbonated layer around the void. In case of limitations of mass exchange the carbonation process goes more slowly and is more prone to provide self-healing. The limitations of CO_2 supply can be either geometrical or flow dependent. Brunet et al. have made a study to identify key controlling parameters and offer general guidelines to predict when self-sealing occurs[19]. Their focus was on reactive transport rather than static carbonation conditions but they have also identified that the interplay between the two parameters fracture volume and the flow rate of the brine drives either sealing or opening of the existing voids/fractures. Based on their studies and the results presented here, we conclude that both under static and flow conditions both fracture geometry and mass transport associated with flow rate (under flow conditions) or diffusive transport (under static conditions) are the parameters that determine whether self-healing will occur or not.

4. Conclusions

Carbonation of well cement has been investigated using X-ray computed micro-tomography, BSE-SEM and chemical reaction simulations. The cured Portland G well cement sample was exposed to CO_2 saturated brine at 100 bars at room temperature. The samples had artificially made cylindrical cavities with a diameter of 0.5 and 0.2 mm. The carbonation processes included self-healing of the voids, carbonation of the bulk cement and leaching of $CaCO_3$. It was shown that at batch conditions $CaCO_3$ precipitated in the voids leading to partial sealing of the cavities. Simulations were performed to quantify the differences in carbonation under conditions of ample or no CO_2 supply. It has been shown that in open systems where CO_2 supply is quick and unlimited, calcium carbonate precipitation is unlikely. On the other hand if CO_2 transport is limited by e.g. slow diffusion in a static system, calcium carbonate precipitation was likely to occur. The effect was found to be closely related with pH changes that are associated with carbonic acid consumption. Self-healing of defects inside the well is promoted in the case of impeded CO_2 supply, while in the case of unlimited CO_2 availability leaching of the cement is more probable.

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