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CEMENT DEGRADATION IN CO_2-SATURATED WATER AND THE IMPACT OF LIQUID TO SOLID RATIO: AN EXPERIMENTAL AND THERMODYNAMIC MODELLING STUDY

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Key words: Oil Well Cement, Degradation Behaviour, Thermodynamic Simulations, CO_2-Saturated Water, Liquid to Solid Ratio (L/S)

Abstract: Cement is an important sealing material for geological CO_2 storage (GCS) reservoirs. The durability of cement exposed to CO_2-saturated water environments is critical for the long-term integrity of GCS structures, as groundwater and CO_2 interact with cement, which may significantly affect its microstructure and mechanical properties. In this study, Class G oil well cement was exposed to CO_2-saturated water under various liquid-to-solid ratios (L/S), temperatures, and pressures for up to four months. After the exposure, the carbonation depths and the mineral compositions of the specimens were analysed using XRD and EDS techniques. The results revealed that exposure to CO_2-saturated water caused the formation of distinct carbonation zones in the specimens. Especially, the dissolution of cement might occur under specific conditions, and it could result in a significant decrease in mechanical properties. This could pose a serious threat to the integrity of the cement, where the influence of the L/S ratio was found critical. Higher L/S ratios led to marked dissolution of the cement, accelerating the loss of mechanical properties. While in the cases of lower L/S ratios, abundant calcium carbonate precipitation was observed in the cement specimens, leading to densification of microstructure and strength enhancement, which might instead help to maintain structural integrity. Furthermore, thermodynamic modelling based on GEMS was performed to provide an evaluation of cement mineral composition changes. The importance of L/S ratio, temperature, and pressure on cement degradation in CO_2-rich environments was emphasised, and the critical L/S corresponding to cement dissolution at different environments was revealed. The findings of this research implied that the local exposure conditions are very important for the structural integrity and sustainability of GCS structures in the long term.

1 INTRODUCTION

Geological carbon storage (GCS) is a pivotal strategy in mitigating climate change by storing CO_2 in deep geological formation reservoirs. The success of GCS systems relies heavily on the long-term performance of wellbore sealing materials. Oil well cement (OWC) plays a critical role as the primary sealing material against CO_2 leakage. It must withstand extreme conditions, e.g. high temperature, high pressure, cyclic stresses, exposure to various water/brine solutions, etc. Once its durability is compromised, CO_2 leakage can occur and imperil the integrity of reservoirs, causing substantial environmental and economic consequences [1].

OWC is exposed to challenging environments in GCS applications. In addition to being subjected to carbonation reactions with CO_2, the high temperature, high pressure as well as the interactions at the metal-cement-geological interfaces further complicate the degradation behaviour of OWC [2]. Extensive research has investigated how these factors influence key properties, e.g. degradation depth, mineral composition, microstructural, and mechanical performance. In actual reservoirs, except in the relatively dry zones near injection points, OWC is often exposed to water environments with inhomogeneous flow characteristics and chemical compositions. The water includes groundwater from overlying formations, carried water from injected CO_2, or residual fluids from enhanced oil recovery (EOR) processes [3]. The chemical pathways of CO_2-cement interactions in such conditions inevitably affect the mechanical and durability properties of OWC.

The volume ratio of the liquid-to-solid (L/S) of the water/brine solutions in contact with cement has been acknowledged as a key parameter. High L/S ratios often correspond to high fluid mobility, accelerating dissolution processes, while low L/S ratios can lead to localised carbonation product accumulation, potentially densifying the cement structure [4-6]. Despite these insights, the mechanisms underlying these contrasting effects remain poorly understood, especially under long-term and varying exposure conditions. Although prior studies have highlighted the influence of temperature on CO_2 solubility and carbonation rates, their combined effects with L/S ratios have yet to be systematically analysed.

This study aims to fill in this knowledge gap by investigating the influence of L/S ratios on the carbonation and dissolution behaviours of Class G OWC. Experimental techniques, including scanning electron microscopy coupled with energy-dispersive spectroscopy (SEM-EDS) and X-ray diffraction (XRD), were employed to determine the mineralogical composition and microstructural evolution. Additionally, thermodynamic simulations using the GEMS were conducted to predict degradation trends under varying conditions. By elucidating the mechanisms through which L/S ratios affect cement degradation, this research provides critical insights for predicting OWC performance in GCS applications, especially for the sections exposed to (ground) water, ultimately leading to the design of the reservoirs with long-term integrity and sustainability.

2 MATERIALS AND METHODOLOGY

Class G OWC was used in this study, prepared with a water-to-cement (w/c) ratio of 0.44. No supplements or additives were added to the mix. The chemical composition of the cement is presented in Table 1, as well as the mineral phases determined by the Bogue calculation. The loss on ignition (LOI) was measured using thermogravimetric analysis (TGA) under a nitrogen atmosphere at 1000°C. The OWC was mixed in a high-speed mixer to form a fresh cement slurry, which was subsequently cast into cubic moulds and cured following a two-step regime [7]. Initially, the specimens were cured covered with a plastic film at room temperature for 24 hours. After demoulding, the specimens were then submerged in preheated tap water in sealed containers at 75°C for the remaining 14 days. This curing regime has been validated in the authors' prior studies to achieve hydration products, hydration degree, and carbonation resistance comparable to those obtained under high temperature and high pressure conditions (75°C and 20 MPa). The volume ratio of cement to curing water was kept constant to minimise the differences caused by leaching in the cement specimens.

Table 1: Chemical composition of HSR Class G cement specimens (in mass %)

Oxide	Content	Mineral	Content
SiO_2	20.75	C_3S	52.32
Al_2O_3	4.45	C_2S	19.98
Fe_2O_3	5.04	C_3A	3.27
CaO	62.35	C_4AF	15.34
MgO	1.06	C_4AF+2C_3A	21.87
SO_3	2.35		
K_2O	0.72		
Na_2O	0.23		
LOI	2.21		

The cured specimens were subjected to carbonation under controlled conditions simulating GCS environments. The investigated factors included L/S ratio (10–200), temperature (20°C and 75°C), and pressure (0.1 MPa and 20 MPa). Maximum exposure durations reached four months, conducted within an autoclave. High pressure was created by pumping CO_2 into the autoclave, and the pressure loading/unloading rates were carefully regulated to prevent damage caused by abrupt pressure changes, which could induce pore pressure imbalances within the cement matrix.

Characterisation of the carbonated specimens was performed using XRD and SEM-EDS. XRD was conducted with a Rigaku Smart-Lab diffractometer with Cu-Kα radiation (λ=0.154059 nm), operated at 40 kV and 180 mA. XRD data were recorded in the range of 5°–70° (2θ) with a step of 0.01° and a speed of 2° per minute. The absolute content of identified crystalline phases was determined using software TOPAS.

SEM-EDS test was performed to obtain the element distribution on the cross-section of the cement. The instrument used for this test was TESCAN CLARA, ultra-high-resolution SEM. All images and analysis were taken at an accelerating voltage of 20 kV and current of 10 nA. The cross-section of specimen was pre-polished by 120 and 400 grit for five minutes and cleaned by ultrasonic cleaner for one minute, before submerged into the isopropanol and start the stop hydration process. All SEM specimens were platinum-coated for 15 nm by using LEICA EM SCD 500 to increase the electrical conductivity.

Thermodynamic modelling was performed using the Gibbs Energy Minimization Software (GEMS), utilising the Nagra-PSI and CEMDATA 18 databases [8]. The C-S-H phase adopted in this work used the CSHQ model [9].

3 EXPERIMENTAL RESULTS AND ANALYSIS

3.1 Carbonation under wet supercritical CO_2 and CO_2-saturated water

Figure 1 presents cross-sections of the cement specimens carbonated in an autoclave at 75 ° C and 20 MPa, showing a notable carbonation progression. Within the autoclave, two distinct environments were created: wet supercritical CO_2 (wet SC-CO_2) in the upper section and CO_2-saturated water in the lower section. Cement carbonation behaviours differed significantly between these two conditions. In wet SC-CO_2, carbonation primarily proceeded using the water from the initial mix and water vapour accompanying CO_2 penetration. The cement in CO_2-saturated water maintained water saturated due to the immersion. Therefore, the carbonation behaviour exhibited substantial differences. Overall, wet SC-CO_2 resulted in lower carbonation depths and slower carbonation rates, especially in the early period. The transition from the carbonated zones and uncarbonated zones appeared clear and sharper, indicating a rapid and concentrated carbonation. By contrast, CO_2-saturated water condition demonstrated faster initial carbonation rates, achieving significant depths within the first month. The carbonation front is less clear and so called "paleofronts" [10] can be observed in the carbonated zone. These regions were believed to comprise well-crystallised calcium carbonate and amorphous silica with a relatively high density [11], indicating an enhanced Ca dissolution process in CO_2-saturated water condition. Additionally, the increase in carbonation depth appeared to decelerate after the first month, suggesting greater resistance to further CO_2 penetration into cement.

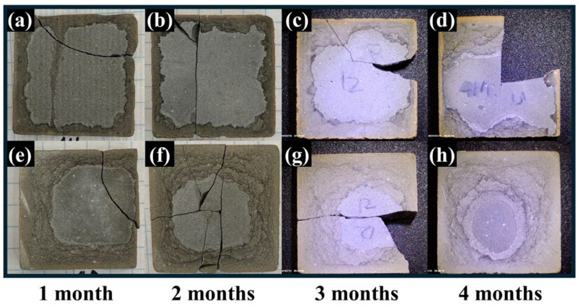


Figure 1: Cross-section of cement carbonated at 75°C and 20 MPa within four months where (a–d) wet SC-CO_2; (e–h) CO_2 saturated water.

Another notable observation was the colour transformation. After three months or more, the outer layer of specimens in wet SC-CO_2 condition transitioned from cement's typical grey to an orange colour. Such a colour change deviates from the "orange" layers reported in [12], but aligns more closely with those described in [2]. The phase composition of this layer is believed to predominantly consist of polycrystalline calcium carbonate, with the colour change attributed to the transformations in Fe-bearing phases, such as maghemite or amorphous materials.

SEM-EDS line scans were performed to evaluate the progression of carbonation over time, focusing on the distributions of Ca, Si, and Ca/Si ratio. The Ca/Si ratio was smoothed using the Savitzky-Golay filter for enhanced clarity. As depicted in Figure 2, the variations of the Ca/Si ratio along depth indicated accelerated dissolution and carbonation. For wet SC-CO_2 conditions, the Ca/Si ratio near the exposed surface (close to the depth of 0) did not exhibit a notable decline. Strengthened Ca signals with relatively high Ca/Si ratio were even observed in certain areas, likely resulting from calcium carbonate accumulation. In contrast, specimens exposed to CO_2-saturated water displayed a pronounced reduction in the Ca/Si ratio near the surface, with Ca intensity gradually converging towards Si intensity when measured in counts per second (CPS). Based on the Ca/Si ratio, four distinct zones were identified across the cross-section: an uncarbonated zone, a portlandite precipitation zone, a calcium carbonate deposition zone, and a cement dissolution zone, progressing outward from the interior, which aligned with the previous studies [13]. Specimens under wet SC-CO_2, however, predominantly displayed only the first three zones. It should also be noted that, Figure 2 highlighted the exposed surface and shallow-depth regions, because presenting the entire profile in a single figure is challenging as the substantial carbonation depth involved.

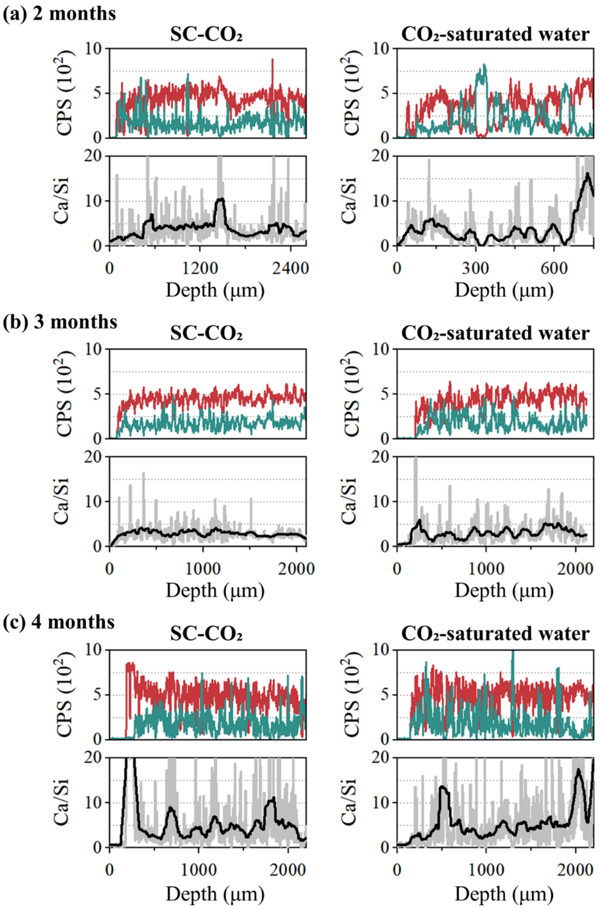


Figure 2: EDS line scan results of carbonated cement at wet SC-CO_2 and CO_2-saturated water within a period of four months (red: Ca, green: Si, grey: Ca/Si, black: smoothed Ca/Si).

XRD analysis was performed on the surface (hydrated cement), middle layer (carbonated or precipitation layer), and outer layer (cement dissolution) of carbonated specimens to determine phase compositions and study the underlying mechanisms driving differential carbonation behaviour. Figure 3 shows that the interior of the specimens primarily contained portlandite and unhydrated particles. In the middle layer, reduced hydration product peaks and the appearance of the carbonation product peaks indicated partial carbonation of the hydration products. This pattern was consistent across both environments, showing minimal variation. However, in the outer layer, specimens exposed to the wet SC-CO_2 condition exhibited a significant presence of calcium carbonate in the form of aragonite. By contrast, those carbonated in the CO_2-saturated water condition predominantly formed highly crystalline calcite. It suggested that CO_2-saturated water conditions promote the formation of calcite phase, while wet SC-CO_2 conditions and elevated temperatures favour aragonite formation. Furthermore, calcite peaks under CO_2-saturated water were concentrated around 29°, displaying high consistency. Conversely, under wet SC-CO_2, the strongest peak appeared at 25°, with other peaks showing relatively similar intensities, indicating a lower consistency. The density differences between the carbonation products—with calcite having a lower density (2.7 g/cm³) compared to aragonite (2.9 g/cm³)—likely explain why the presence of aragonite reduces the densification effect of carbonation on the cement matrix. This phenomenon may account for the continued progression of carbonation with wet SC-CO_2, leading to variations in transport properties and carbonation depths over time.

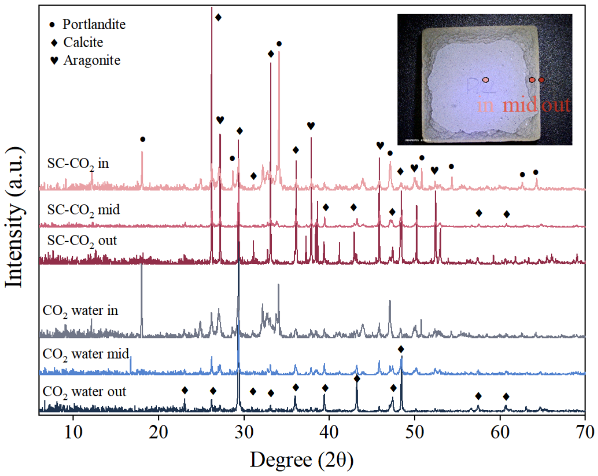
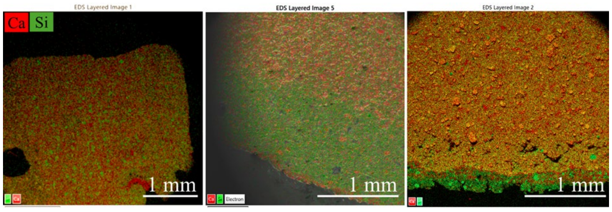


Figure 3: XRD patterns.

3.2 L/S Effect

Cross-sections of cement carbonated in the autoclave for four months (Section 3.1) did not reveal the severe degradation zones associated with cement dissolution as reported in other studies [13]. The high temperature, high pressure, and immersion conditions employed in the study were similar to those used in previous research, yet the observed Ca dissolution levels and carbonation outcomes showed great discrepancies. A possible explanation is that the L/S ratio under immersion conditions remained below the critical value required for significant dissolution of Ca from the cement or carbonation products. Calculations revealed that the L/S ratios for CO_2-saturated water and wet SC-CO_2 were 6.3 and 0.8, respectively. Despite the eightfold difference, the L/S seems still inadequate to make substantial differences in cement dissolution.

To validate the hypotheses, experiments were conducted using increased L/S ratios, which were subjected to carbonation under ambient temperature and pressure in immersion conditions. SEM-EDS mapping results of carbonated specimens were shown in Figure 4, increasing the L/S ratio to 80 led to the appearance of severe degradation zones characterised by strong Si signals and weak Ca signals. When the L/S ratio was further increased to 200, the Ca signal in the outermost degradation zone diminished further, indicating more severe degradation, with Ca almost completely dissolved into the surrounding solution. This left behind amorphous silica gel dominated by Si element. It indicated that the L/S ratios significantly increase the dissolution process and further affecting the degradation behaviours.



(a) L/S=6.3 (b) L/S=80 (c) L/S=200

Figure 4: EDS mapping results of cement cross-section under increasing L/S ratios at 20°C and 0.1 MPa.

3.3 Exposed Surface Area of the Cement

Another hypothesis is that the surface area of cement exposed to the solution is relatively small, requiring times longer than four months to generate significant differences. The effect of the exposure surface area on carbonation rates was also evaluated by using original and quarter-sized cement specimens. Increasing exposed surface area facilitated ion exchange and material transport between cement and the surrounding solution. Larger surface areas increased ion and material fluxes within a given timeframe, enhancing reaction kinetics. Additionally, larger specimen sizes increase the core-to-surface distance, which reduced the concentration gradient and retarded reactions. Comparing two specimens, small-sized ones had a relative exposed surface area 1.72 times greater than larger-sized ones. As illustrated in Figures 5, the carbonation cross-section of the larger specimens showed simultaneous decreases in Ca and Si intensities at a depth of approximately 1200 μm, with the Ca/Si ratio stabilising beyond this point. The depth affected by carbonation was thus limited to 1200 μm. By contrast, the carbonation depth in smaller specimens reached 1950 μm, with an increase of 62.5%. The increase in relative exposed surface area led to a significant degradation of cement, which was primarily indicated by the formation of cement dissolution zones rather than portlandite dissolution zones. The Ca/Si ratio initially increased in the carbonation precipitation zone but subsequently declined rapidly and stabilised, resulting in clearer regional demarcations in Figure 5. These findings highlight that calcium carbonate dissolution primarily governs the extent of carbonation. The increased relative exposed surface area allows for faster CO_2 and water penetration, as well as the reaction kinetics.

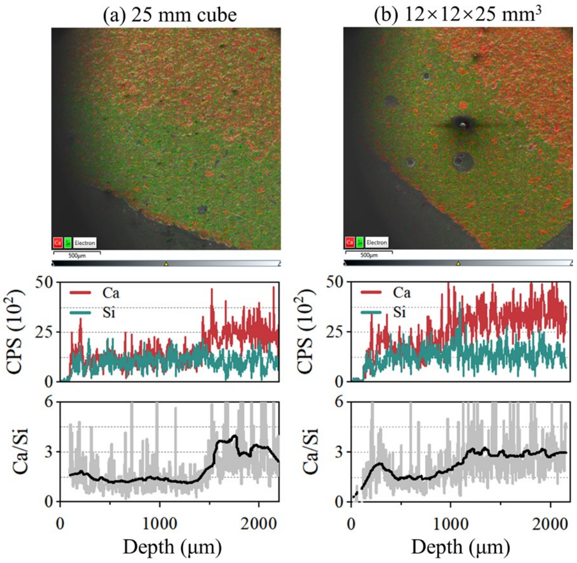


Figure 5: EDS line scan results of carbonated cement of (a) 25 mm cube and (b) 12×12×25 mm^3.

3.4 Temperature Effects

Environmental factors significantly affect cement carbonation behaviour as well. With every 100 m increase in depth, the temperature rises by approximately 3°C, reducing the solubility of CO_2 and the pH of the solution. This results in a relative scarcity of H^+ ions at higher temperatures and a decline in degradation rates, leading to significant differences in carbonation behaviour at different depths of oil wells. CO_2-saturated water tested at 25°C and 75°C exhibited pH values of 4.2 and 5.8, respectively, with the EDS results of carbonated cement shown in Figure 6. At 75°C, the specimen surface featured regions with weak Ca and strong Si signals, but the overall Ca/Si ratio was relatively high, indicating milder degradations. The surface also exhibited stronger Ca signals with no detectable Si, suggesting precipitation of free calcium carbonate from the solution. It demonstrated that cement did not undergo significant degradation due to carbonation under high temperatures alone and may even exhibit improved carbonation resistance. In contrast, carbonation at 20°C revealed a distinct four-zone structure, presenting higher risks of severe degradation. At 75°C, the simultaneous reduction of Ca and Si occurred at a depth of approximately 800 μm, compared to 500 μm at 25°C, suggesting that water dissolution plays a stronger role at higher temperatures. Although carbonation risks are reduced, dissolution-induced degradation poses a greater threat to cement performance at elevated temperatures.

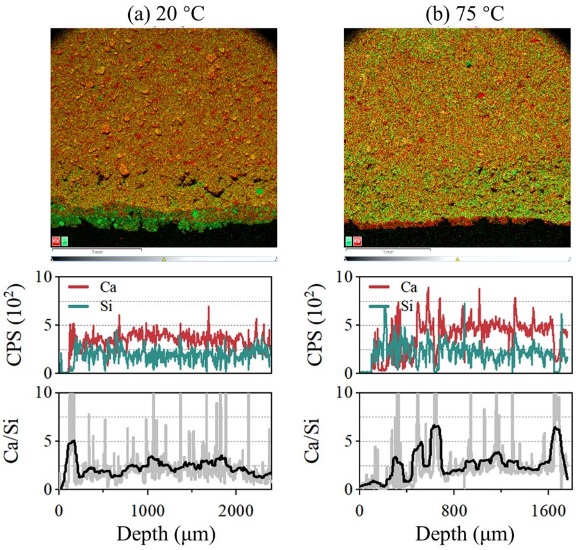
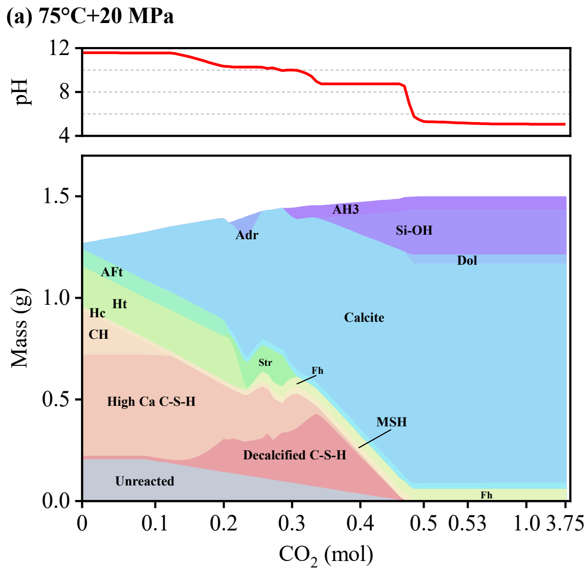


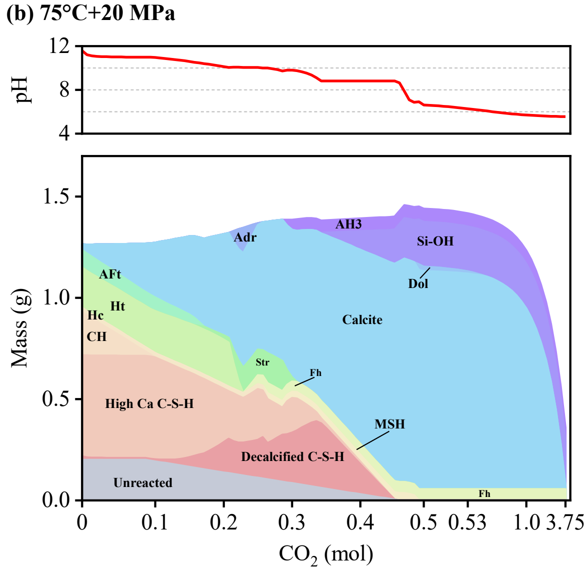
Figure 6: EDS line scan results of carbonated cement at (a) 20°C and (b) 75°C.

4 THERMODYNAMIC MODELLING

Thermodynamic modelling using GEMS simulated the changes in mineral composition of cement phases under carbonation conditions.

The initial composition of the cement was determined using the properties listed in Table 1, with the degree of hydration estimated to be 80%. The results of the simulations indicated that pressure effects on hydration were negligible, while temperature exerted a significant influence, primarily on mono-carbonate hydrate and ettringite phases. These specific hydration effects were not analysed in this study. The exposure conditions were modelled under predefined temperatures and pressures, with CO_2 and water continuously introduced into the system. For a 1 g cement sample, the resulting changes in phase composition are shown in Figure 7, as well as the pH development.





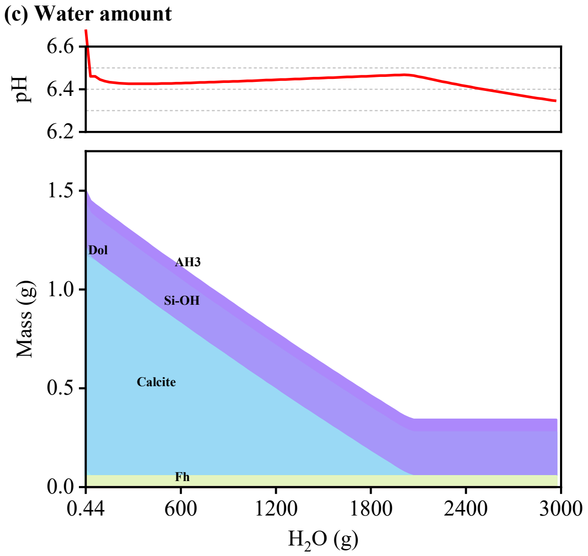


Figure 7: Thermodynamic simulation results (a) dry carbonation (no water evaporation), (b) CO_2 saturated water, and (c) gradually adding water with 5 mol CO_2 (CH = portlandite; Hc = OH-hydrotalcite; Fh = Ferrihydrite-mc; Ht = Si-hydrogarnet; Mc = C4AcH11; Str = Strätlingite; Anh = Anhydrite; Dol = Dolomite-ord; Adr = Hydroandradite; and AH3 = $Al(OH)_3$mic).

The comparison of Figures 7(a) and 7(b) revealed that additional water has minimal impact on the carbonation before the complete carbonation of cement hydration products, except in the case of soluble phases like portlandite. The water included in the cement mix is sufficient to react with all hydration products. Post-carbonation, the system retains amorphous Si-OH, $Al(OH)_3$, and $Fe(OH)_3$ in amorphous form, with the primary role of excess water being the dissolution and transport of calcite and $Ca(HCO_3)_2$.

Figure 7 (c) also shows that under carbonation conditions of 75°C and 20 MPa, the complete dissolution of calcite requires approximately 1410 g of water, whereas at ambient conditions (20°C and 0.1 MPa), it requires approximately 2040 g, representing a 1.5-fold difference. It is important to note that these simulations assume sufficient CO_2 availability, indicating that factors influencing CO_2 solubility, such as temperature and pressure, also have significant impacts on carbonation and dissolution behaviour.

5 DISCUSSIONS

The findings of this study provide critical insights into the degradation behaviour of Class G cement under varying conditions. The impact of the L/S ratio on the cement degradation is particularly pronounced. At higher L/S ratios, the accelerated dissolution of Ca phases (e.g. portlandite, C-S-H) leads to significant Ca depletion, which compromises the structural integrity of the cement. This phenomenon can be attributed to the increased availability of water as a solvent, enhancing ion transport and reaction kinetics. Conversely, lower L/S ratios favour the precipitation of carbonates, i.e. calcite, which densifies the cement matrix and potentially mitigates further degradation. This densification effect highlights the dual role of carbonation in both protecting and compromising the properties of cement materials, depending on specific conditions. These results align with thermodynamic predictions, where the critical L/S for initiating cement dissolution is strongly influenced by temperature and the CO_2 partial pressure.

Temperature also plays an important role in affecting the degradation mechanisms. Higher temperatures reduce CO_2 solubility and degree of carbonation. However, it simultaneously accelerates dissolution, particularly for phases with higher solubility, e.g. C-S-H, portlandite. The resulting Ca-depleted regions near the cement surface suggest that dissolution instead of carbonation dominates degradation behaviour. In contrast, at lower temperatures, the higher CO_2 solubility facilitates carbonation and the formation of distinct zones. These zones, characterised by different mineralogical compositions, reflect a complex interaction between CO_2 transport, carbonation, and cement dissolution processes. The preferential formation of aragonite at higher temperatures and calcite at lower temperatures further underscores the sensitivity of mineralogical phases to the thermal conditions.

The observed differences in the degradation behaviours between wet SC-CO_2 and CO_2-saturated water environments are consistent with the hypothesis that exposure conditions significantly influence the reaction pathways. The "paleofronts" observed in higher L/S conditions under SC-CO_2 indicate localised supersaturation and subsequent precipitation of dense carbonate phases, which could impede further progress of the carbonation front. This phenomenon was less pronounced in lower L/S water environments, where $CaCO_3$ precipitation was more evenly distributed and the matrix was more densified, resulting in less pronounced front structures.

Thermodynamic modelling provided additional insights into the underlying mechanisms. It revealed that the presence of excess water primarily acts as a carrier for dissolving and redistributing reactive species rather than directly contributing to carbonation reactions. This finding highlights the critical role of large volumes of water in the cement degradation. Furthermore, the modelling results showed that the critical L/S ratio for cement stability varies with environmental conditions, suggesting that accurate evaluation of the cement performance under GCS conditions must consider the availability of water in the surroundings.

While these findings advance the understanding of cement degradation in CO_2-rich environments, several uncertainties remain. The experimental setup, though designed to replicate key aspects of GCS conditions, may not fully capture the complexities of field-scale interactions. Additionally, the differences in carbonation behaviour of different specimen sizes in Figure 5 suggest that kinetic factors are important in the relevant reactions and that a certain amount of time is required to reach equilibrium with the environment, which may be a point that is not able to be captured in thermodynamic modelling.

6 CONCLUSIONS

In this study, cement degradation in GCS conditions was studied. Particularly under CO_2-saturated water environments, the influence of the liquid-to-solid (L/S) volume ratio (i.e. CO_2-saturated water/cement) on the carbonation behaviour of cement was investigated in detail. The main findings are summarised as follows:

1. The L/S ratio is a critical parameter

affecting the carbonation behaviours of cement in GCS environments and is influenced by factors such as temperature and pressure. The critical water amount required to induce severe degradation under high temperature and high pressure conditions may be 50% lower than that that under ambient conditions.

2. The degradation behaviours of cement in CO_2-rich environments comprises both dissolution and carbonation processes. Important factors influence one or both processes include temperature, pressure, and L/S ratio as well as the relative exposure surface area of the cement. Further systematic studies are required to quantify these effects.

3. Research on the influence of L/S ratio contributes to improving long-term safety assessments of cement sealing systems for GCS reservoirs, particularly under varying groundwater exposure conditions. Comprehensive investigations of reservoir-specific parameters, e.g. temperature, pressure, groundwater flow or volume as well as the chemical compositions, are crucial for assessing the structural and chemical integrity. These factors play a pivotal role in understanding and predicting the cement degradation behaviour.

4. Beyond the specific findings, this study highlights the importance of standardising the L/S ratio in laboratory testing. Variations in L/S ratios across studies may lead to inconsistent outcomes, limiting the applicability of the results to practical problems. Adopting a standardised L/S ratio in experimental protocols would also facilitate meaningful cross-study comparisons, ultimately enhancing their relevance to GCS applications.

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