

Research Article

Micro-CT Characterization of Wellbore Cement Degradation in SO_4^{2-} -Bearing Brine under Geological CO_2 Storage Environment

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In order to explore the process of acid- and CO_2 -induced degradation of wellbore cement and the development of pre-existing leakage channels in wellbore cement under sulfate-rich geological CO_2 storage conditions, wellbore cement samples were immersed in SO_4^{2-} -bearing brine solution for 7 days, and the samples after reacting with the low and circumneutral pH solutions were scanned by a micro-CT scanner. $\text{HCl}+\text{Na}_2\text{SO}_4$ solution was used to simulate the low-pH condition in deep formation waters and the possible existence of high sulfate ion content in deep formation waters. The acidification and carbonation results were compared, and the results given different pH values and different curing conditions were compared as well. The results show that the degradation of cement was related to the pH value of the reaction solution. There was a significant dissolution in the exterior of the cement sample after exposure to the low-pH solution, but the dissolution surrounding a penetrating borehole at the center of the sample (mimicking a leakage pathway within the wellbore cement in geological CO_2 storage environment) was limited. Comparison between acidification and carbonation results in this study shows formation of a thick carbonate layer due to cement carbonation, and this layer was not observed in the acidification result. As for different curing conditions of cement samples, no significant difference in cement alteration depth was observed for the acidification case. For the carbonation case, precipitations in the borehole occurred in the cement sample cured at ambient pressure, while the cement sample cured at high pressure did not produce any precipitation in the borehole. This study provides valuable information on how low pH-induced corrosion and HCO_3^- -induced cement carbonation contribute to structure evolution of wellbore cement in SO_4^{2-} -bearing brine under geological CO_2 storage environment.

1. Introduction

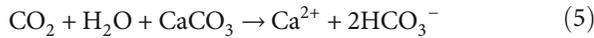
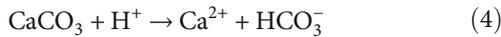
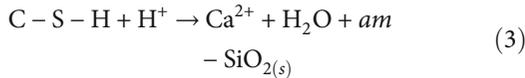
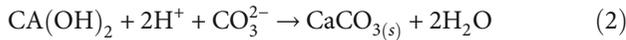
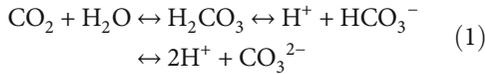
Industrialization accelerates CO_2 emissions into the atmosphere, which causes increase of CO_2 concentration in the atmosphere. CO_2 concentration increased from 280 ppm (parts per million) in the preindustrial era to 400 ppm in 2014, with global surface temperature increasing by 0.85°C (the year of 1880 to 2012) [1]. In order to effectively slow down the pace of the greenhouse effect, the emissions of CO_2 to the atmosphere need to be controlled. CCUS (CO_2 capture, utilization and storage) as an important approach

to reduce CO_2 emissions is receiving increasing attention. In this approach, anthropogenic CO_2 is injected into geologic formations such as depleted oil and gas reservoirs, deep saline aquifers, and unminable coal beds. Among these formations, deep saline aquifers have, by far, the largest potential for CO_2 storage [2].

In the process of geological CO_2 storage, one of the primary risks of interest is the degradation of wellbore cement integrity in existing and abandoned wells exposed to sequestered CO_2 , which could lead to leakage of CO_2 from the storage reservoir [3]. The leakage pathways of CO_2 through

existing and abandoned wells include the interface between wellbore cement and casing, the interface between wellbore cement and formation rock, connected leaking pathway in cement as a result of cement degradation, and the interface between cement plug and casing [4]. Once a leakage channel is formed, the injected CO₂ will go up along the leakage channel to the overlying rock layer or even to the surface, which will cause contamination of groundwater and disturb the soil ecosystem [5–7]. Therefore, it is necessary to investigate the corrosion process of wellbore cement under the condition of CO₂ storage.

During the process of drilling, cement slurry is injected into the circular ring between formation rock and casing when the casing is devolved, so as to secure the casing and to prevent reservoir fluid from flowing into the annular between the formation rock and casing. Portland cement is the most widely used wellbore cement, and there are four major crystalline compounds in it: tricalcium silicate (Ca₃SiO₅), dicalcium silicate (Ca₂SiO₄), tricalcium aluminate (Ca₃Al₂O₆), and tetracalcium aluminoferrite (Ca₄Al₂Fe₂O₁₀). Those compounds form calcium-silicate-hydrate (C-S-H) and calcium hydroxide (Ca(OH)₂) when the compounds of Portland cement are mixed with water [8]. When CO₂ is injected into the reservoir and comes into contact with the wellbore cement, the carbonation reaction of equations (1)–(6) will occur. The carbonation will consume calcium-silicate-hydrate and calcium hydroxide to generate calcium carbonate precipitation and formation of amorphous silicates and amorphous silica [8, 9].



The experiment results of carbonation reaction between wellbore cement and CO₂ can be divided into two main categories [10, 11]: (1) a rapid process and (2) a slower and limited penetration of CO₂ with time. The difference in results reported by different studies is caused by different reaction temperatures, pressures, ion concentrations, fluid properties, cement types, and so on. Barlet-Gouédard et al. [12, 13] conducted an experiment between cement and supercritical CO₂ and another reaction experiment between cement and a saturated CO₂ aqueous solution at 90°C and 28 MPa to study the evolution of cement chemical properties over time. The results showed that Portland cement could not effectively limit the corrosion of supercritical CO₂ or saturated CO₂ aqueous solution. In the presence of CO₂, wellbore cement was rapidly and widely degraded and had been

peeled off after six months. Jung and Um [14] conducted one reaction experiment between cement and dry or wet supercritical CO₂ and another reaction experiment between cement and saturated CO₂ solution at 50°C and 10 MPa. The study found that the cement alteration was significantly more extensive with CO₂-saturated synthetic groundwater than dry or wet supercritical CO₂. The degree of carbonation of cement may vary significantly depending on the phase of CO₂, but the wellbore cement exposed to different CO₂ phases can still maintain wellbore integrity. After carbonation of wellbore cement, four areas can be formed on its surface [15]: a dissolution front, a carbonated zone, a portlandite-depleted zone, and an unreacted zone. If the amount of precipitation in the calcium carbonate sedimentary area is sufficient, the sediment can hinder the further corrosion of CO₂ and block the potential leakage channel [16–18], thus preventing the CO₂ from moving upward. The resulting calcium carbonate precipitation that can block the leakage channel depends on the aperture size of the leaking channel and the length of time the CO₂ stays in the crack channel. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) characterization showed that under the condition of small fracture width and long hydraulic residence time, significant calcium carbonate deposition would occur on the fracture channel and then clog the fracture. While under the condition that the fracture width is large and the hydraulic residence time is short, the hydraulic condition is not conducive to the deposition of calcium carbonate, because the high-velocity water flow washes away calcium carbonate precipitants. As a result, calcium carbonate precipitants fail to fill in the fracture and the self-healing mechanism does not work [19, 20]. Field studies have also looked at the self-healing effects of fractured channels. Carey et al. [21] has studied Portland cement recovered from oil wells with a history of 55 years (the time for oil wells to be exposed to CO₂ for 30 years) and found that the recycled cement shows evidence of CO₂ migration along the casing-cement and cement-shale interfaces. The study concluded that, despite evidence of CO₂ migration along the well, the wellbore cement could prevent significant leakage of CO₂ from the reservoir for a long time (at least decades), thus maintaining the integrity of the wellbore and providing an effective barrier to fluid and CO₂ flow. Crow et al. [22] conducted downhole and laboratory experiments to study the isolation performance of a 30-year-old natural CO₂ production well. It is found that CO₂ has been migrated to the cement, but the fluid migration along the wellbore is very small and no corrosion occurs in the casing. Therefore, wellbore cement can be used to establish an effective barrier system for long-term storage of CO₂.

In addition to the injection of pure CO₂ for storage, some researchers also simulated storage environments to inject impurities such as H₂S and SO₂ into the reservoir together with CO₂ [3, 23–29]. In the process of fossil fuel processing and sulfur-containing natural gas purification, impurity gases such as H₂S and SO₂ will be released with the release of CO₂, and the impurity gas needs to be removed before the CO₂ is injected into the underground reservoir. Due to the fact that the cost of removing impurities is high,

TABLE 1: Summary of curing conditions and reaction conditions of the cement samples.

Sample no.	Cement curing condition		pH	Cement reaction condition		
	Pressure (MPa)	Temperature (°C)		Pressure (MPa)	CO ₂	Temperature (°C)
Cement #1	17	62	3	Ambient	No	62
Cement #2	17	62	7	Ambient	No	62
Cement #3	17	62	3	17	Yes	62
Cement #4	Ambient	62	3	Ambient	No	62
Cement #5	Ambient	62	3	17	Yes	62

it is considered that the impurity gas and CO₂ can be coinjected into the reservoir. In fact, there were already field engineering practices wherein H₂S and CO₂ were coinjected into the reservoir for storage [30]. Researchers conducted an experiment of wellbore cement and H₂S and CO₂ mixed gas after coinjecting into a reservoir and found that due to the local porewater pH buffering, ettringite was observed in the interior region of the cement and pyrite in the carbonated rim of the cement [23]. In addition, in the case of CO₂ and H₂S coinjection, the anticorrosion capacity of wellbore cement and pure cement mixed with different amounts of pozzolan is different [3, 25, 31]; compared with pure wellbore cement, cement mixed with 35 vol% pozzolan has similar erosion resistance to CO₂ and H₂S, while pozzolan-amended cement with 35 vol% of pozzolan has better anticorrosion performance than cement with 65 vol% of pozzolan. There is no reported work on the reaction between wellbore cement and SO₂-CO₂ mixed gas in the reservoir, while the studies of reservoir rock reaction with the mixed gas of SO₂ and CO₂ have been done [26, 27, 29, 32]. After being injected to the reservoir, SO₂ will form sulfuric acid with water and O₂ and then react with reservoir rock. The amount of silicate and carbonate dissolved in reservoir rocks after the mixed gas of SO₂ and CO₂ injection is greater than that of pure CO₂ injection. Wang et al. [28] studied the potential effect of SO₂ as an impurity on the CO₂ injection capacity of a saline sandstone aquifer in Western Canada and found that the injection of SO₂ increased the precipitation of sodium chloride and calcium sulfate. The permeability of reservoir rock, which is closely related to the injection ability of CO₂, will reduce because of the precipitation of salt; therefore, the influence of SO₂ should be considered in evaluating the injection ability of CO₂.

CO₂-induced corrosion on wellbore cement under the condition of CO₂ geological storage is attributed to a combination of carbonation and acidification. In order to study the contribution of acidification and carbonation to wellbore cement corrosion, we designed the experiment of the reaction between wellbore cement and different kinds of reaction solution. Considering that some deep strata contain high sulfate ion content, HCl+Na₂SO₄ solution was selected to make the low-pH and sulfate-rich solution to react with cement samples, so as to study the contribution of acidification to cement degradation. The purpose of this paper is (1) to obtain pore structure characterization of the acidification reaction between wellbore cement and low-pH solution by using X-ray micro computed tomography (CT) to study the corrosion process of cement in low-pH envi-

ronment, (2) to compare acidification results at different pH conditions for 7 days, (3) to compare the acidification result of the cement sample reacting with HCl+Na₂SO₄ solution with the carbonation result of the cement sample reacting with CO₂-saturated brine, and (4) to compare acidification and carbonation results of the cement samples cured at different conditions. The research results provide valuable information on how low-pH-induced corrosion and HCO₃⁻-induced cement carbonation contribute to structure evolution of wellbore cement in SO₄²⁻-bearing brine under the geological CO₂ storage environment.

2. Experimental Methods

The cement slurry was prepared using Class G Portland cement and a water-to-cement (*w/c*) ratio of 0.4 according to API Recommended Practice 10B [33], and the slurry was poured into a cylindrical mold with a diameter of 10 mm and a length of 30 mm after being stirred with the constant speed stirrer. In order to simulate cracks or voids in wellbore cement, a small glass tube (ϕ 1.0 mm) was inserted into the middle of the cement to simulate the leakage channel in the cement sample.

Cement samples were demoulded after 4~6 h and then were cut into two pieces with a height of approximately 15 mm. The samples after cutting (10 mm diameter \times 15 mm height) were used in the experiments. The samples were placed in a solution containing 1 wt% NaCl and 0.036 wt% Na₂SO₄ (238 ppm SO₄²⁻) for curing, and the conditions of curing were divided into two types: (1) in an atmospheric pressure water bath and (2) in a high pressure (17 MPa) vessel. Both curing conditions had a temperature of 62°C and a curing time of 7 d. The curing solution contained a SO₄²⁻ concentration of 238 ppm, which was designated based on the fluid chemistry of brine with high sulfate content from a typical CO₂ storage formation. Details of the experimental fluid are available in [34]. The curing solution also contained 1 wt% NaCl, which is typical in cement degradation studies under geologic CO₂ storage conditions [8, 15, 31, 34]. For high pressure curing, the samples were labeled as cement #1, cement #2, and cement #3; for atmospheric pressure curing, the sample was labeled as cement #4. As for after-curing reaction conditions, different reaction solutions were made and all of the reaction solutions contained 238 ppm sulfate concentration to mimic SO₄²⁻-bearing brine in a typical SO₄²⁻-rich CO₂ storage formation [34]. Details of the curing conditions and the reaction conditions are displayed in Table 1, and the experimental diagram is shown in Figure 1.

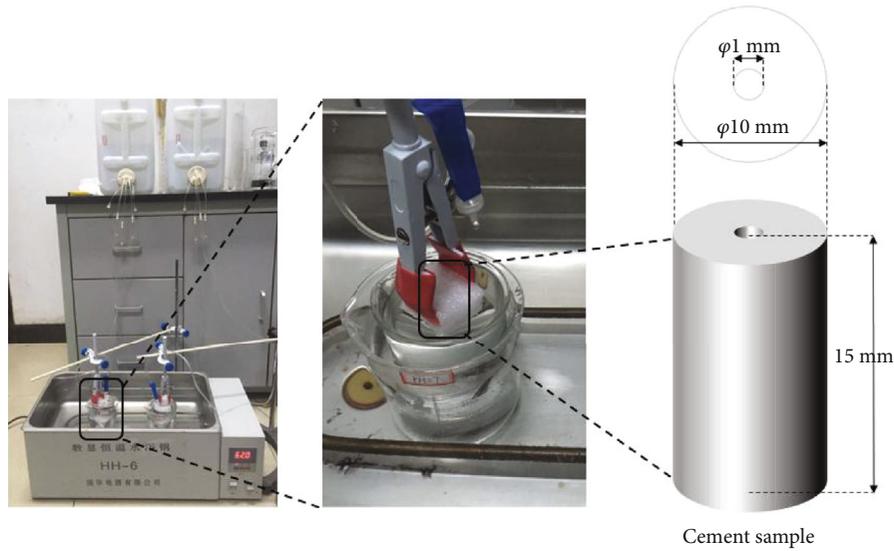


FIGURE 1: Experimental set-up.



FIGURE 2: CT scanner external view (a) and internal view (b).

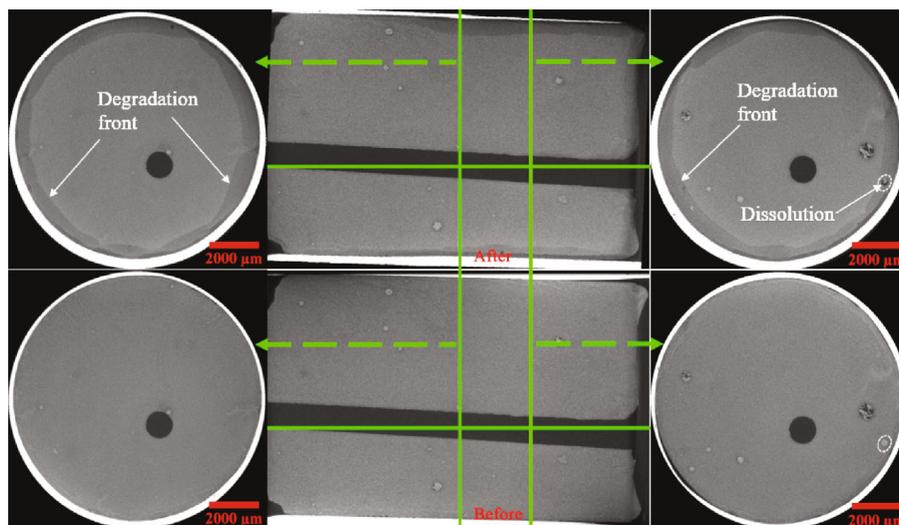


FIGURE 3: CT images of horizontal and vertical slices of the cement sample (#1) before and after reaction.

In the reaction experiment, one end of the cylindrical cement sample was immersed in the reaction solution for 7 days. The sample was embedded in the foam block which was sand-

wiched on the iron frame, while the beaker containing the reaction solution was placed in the open tank. One end of the cement (~5 mm) was immersed in the reaction solution.

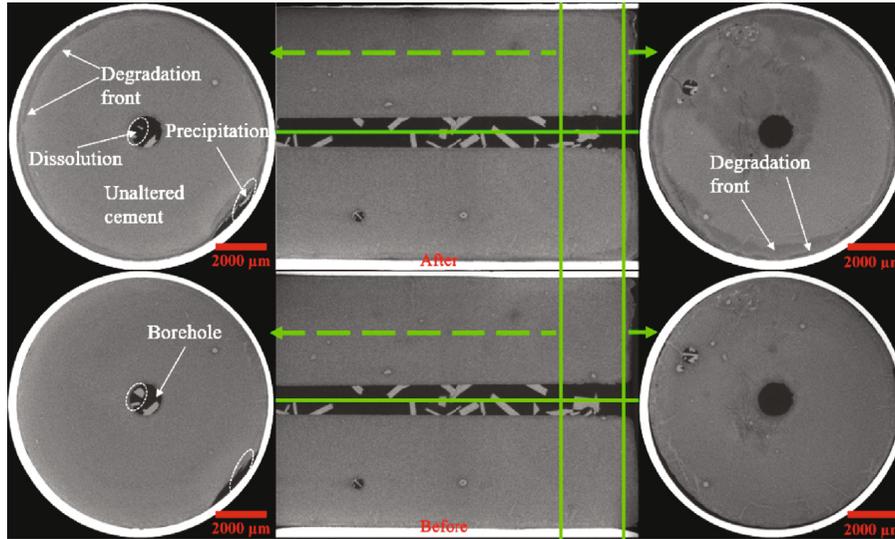


FIGURE 4: CT image of horizontal and vertical slices of cement sample (#2) before and after the reaction.

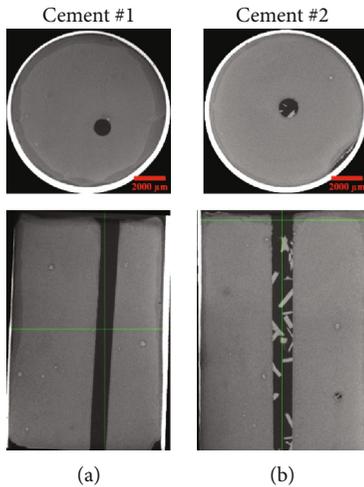


FIGURE 5: Horizontal and vertical CT slices of cement reacted with different pH solutions: (a) cement reacted with pH = 3 solution; (b) cement reacted with pH = 7 solution.

One end of the infusion tube was connected to the PVC water tank which was filled with the reaction solution; the other end was fixed on the beaker which the reaction solution was transported to. The droplet drop-down rate was not strictly controlled, but the experimental set-up was able to maintain a constant pH level in the reaction solution, ensuring continuous supply of the reaction solution in the beaker and eliminating the need to replace the reaction solution in the beaker. pH was measured using a pH meter during the reaction experiment (pH = 3 HCl and 238 ppm sulfate solution) to determine whether the solution pH remained at 3 during the experiment. Based on the measurement, the pH of the reaction fluid in contact with cement remained at 3 after the 7-day reaction.

With the use of a Zeiss Xradia 410 X-ray Computed Tomography (CT) scanner (Figure 2), the structural changes of the cement sample before and after the reaction can be obtained. The micro-CT was operated at 80kV and 10 W,

and the preexposure scans of the samples yielded images with a voxel resolution of 10.48 microns, which was the same as that of the postexposure scans. The sample was placed on a sample stage for a 360-degree rotation scan, and 1801 images were obtained. The raw CT images were postprocessed by an image processing software, ImageJ. For fast visualisation, the images were resampled at a $2 \times 2 \times 2$ -binning.

3. Results and Discussion

This section firstly presents the structural changes of cement samples after reacting with pH = 3 HCl and 238 ppm sulfate solution (hereafter referred to as acidification) and then makes comparison between the cases given different pH values (pH = 3 and pH = 7). After that, cement acidification results are compared with results of cement reacting with CO₂-saturated brine under a CO₂ pressure of 17 MPa (hereafter referred to as carbonation). In the end, the cases given different curing conditions are compared.

3.1. Base Case: Cement Reacting with pH=3 HCl and 238 ppm Sulfate Solution. The structural changes of the cement sample (cement #1 in Table 1) after the reaction with pH = 3 HCl and 238 ppm sulfate solution for 7 d were investigated by micro-CT scanner. The results are shown in Figure 3, in which two green arrows point to horizontal sections of two locations. CT images of vertical and horizontal slices in Figure 3 show that the cement sample was dissolved at the edge of the sample at different degradation thicknesses after submerging in the pH = 3 HCl and 238 ppm sulfate solution for 7 d, and the degradation front can be observed clearly, which indicated that cement was degraded at some degree in the low-pH solution. In the right horizontal slice, a very small preexisting particle in the degradation zone was dissolved after reaction.

In our system, precipitation of gypsum may occur if the reaction solution contains enough SO₄²⁻, according to equation (7). However, the precipitation occurred neither in the

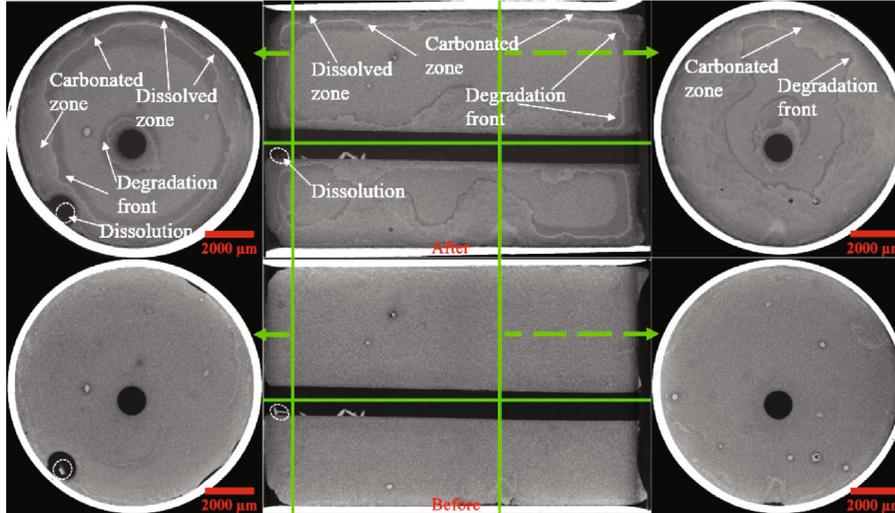
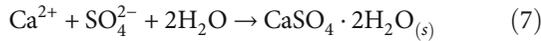


FIGURE 6: CT image of horizontal and vertical slices of cement sample (#3) before and after reaction.

exterior of the cement nor in the penetrating hole in our experiment. This may be due to limited SO_4^{2-} in the reaction solution. Our future experiments will increase the reaction time (such as 14 d and 28 d) and add enough SO_4^{2-} to observe the structural changes of the cement exterior and penetrating holes and possible gypsum precipitation.



3.2. Comparison 1: Different pH Values of Reaction Solution.

Generally speaking, cement degradation becomes more severe with a lower reaction solution pH. The reaction between the cement sample (cement #2 in Table 1) and pH = 7 Na_2SO_4 solution for 7 days (the concentration of SO_4^{2-} was 238 ppm) was conducted, so as to make comparison with the case of the low-pH solution. As shown in Figure 4, after reaction with the circumneutral solution for 7 d, a very small amount of precipitation was produced at the edge of the reaction area while some of the preexisting particles were dissolved in the penetrating hole. Also, a degradation front can be observed from the horizontal slices.

The horizontal and vertical slices of cement samples reacting with different pH solutions were compared in Figure 5. The degradation front of the cement reacting with the lower pH solution for 7 d was deeper than that reacting with circumneutral solution for 7 d. There was a very small amount of precipitation at the edge of the reaction area for the cement reacting with circumneutral solution, while no precipitation occurred for the cement reacting with the pH = 3 solution.

Comparing Figure 3 with Figure 4, it can be seen that the amount of dissolution after reaction between cement and the pH = 3 solution was significantly higher than that after reaction between cement and the pH = 7 solution, showing that the acid-induced corrosion of cement by the lower pH solution was more significant.

3.3. Comparison 2: Acidification and Carbonation Results after 7 d Reaction.

In order to study the contribution of car-

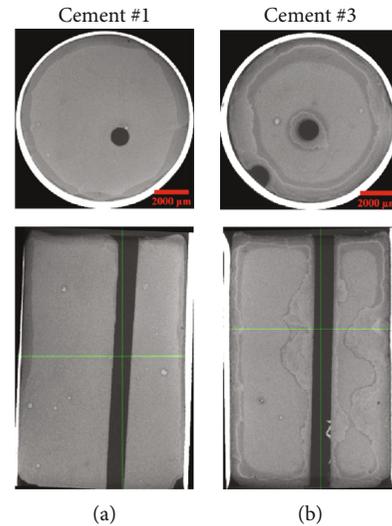


FIGURE 7: Horizontal and vertical CT slices of cement after acidification (a) and carbonation (b) results.

bonation and acidification to cement corrosion, the acidification results of the reaction between cement and the HCl +sulfate solution (cement #1 in Table 1) and the carbonation results of the reaction between cement and the CO_2 -saturated brine (cement #3 in Table 1) were compared. The pH of CO_2 -saturated brine with a temperature of 62°C and a CO_2 pressure of 17 MPa is 3, which is calculated with the use of the reactive transport code CrunchFlow.

Figure 6 shows that the cement was degraded after carbonation. From the edge to the interior of the sample, four zones were observed: exterior dissolved zone, carbonated zone, interior degradation front, and unreacted cement, which was similar to the result of Kutchko et al. [8, 15]. Besides, the cement particles at the edge of the cement and some of the cement particles in the borehole were dissolved as observed in Figure 6.

After the same reaction time (7 d), the main difference between the acidification result and the carbonation result is

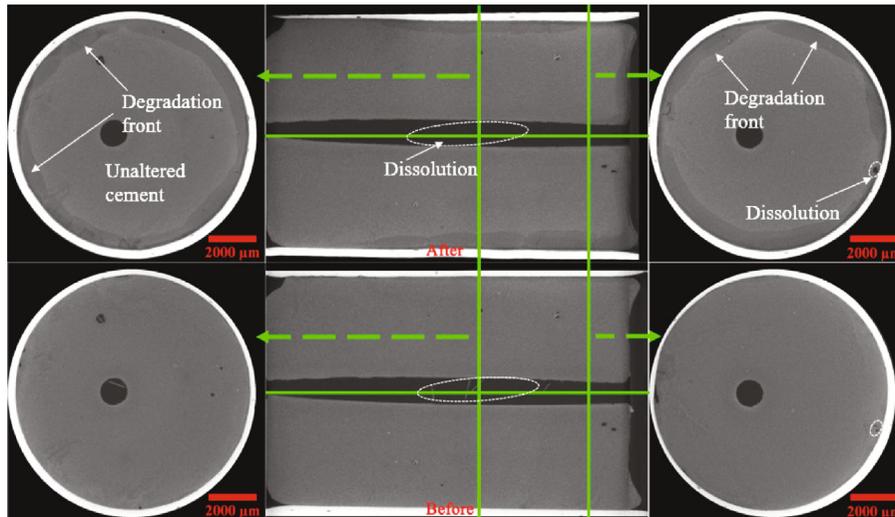


FIGURE 8: CT image of horizontal and vertical slices of cement sample (#4) before and after reaction.

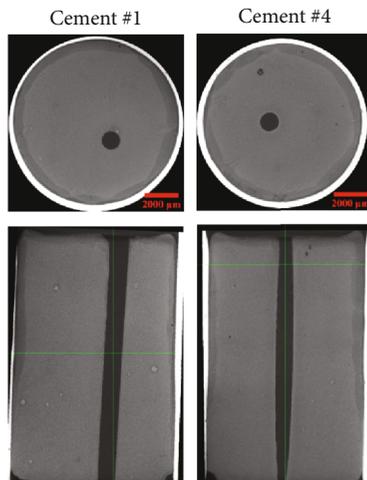


FIGURE 9: Horizontal and vertical CT slices of after-reaction cement samples under different curing conditions.

as follows (Figure 7): the amount of dissolution after carbonation was larger than that of acidification, and a deeper dissolution layer on the exterior of the wellbore cement was formed after carbonation, compared with the case of acidification.

A previous study of cement carbonation conducted by Wang et al. [35] without the presence of SO_4^{2-} shows formation of a thin carbonate layer in the exterior region of cement (see Figure S8 in SI), which can effectively hinder the reaction between wellbore cement and CO_2 . Different from that study, results in our study show formation of a relatively thick carbonate layer, and the degradation front in cement was deeper than the case in Wang et al. [35]. Therefore, the presence of SO_4^{2-} may significantly increase the rate and the extent of cement carbonation. A possible explanation is that the presence of SO_4^{2-} favors the formation of expansive ettringite, which causes damage to the cement matrix and allows fast migration of CO_2 to the interior of cement.

However, heterogeneity of the cement sample and formation of micro channels when preparing the sample may also cause fast cement carbonation. Further experiments will be conducted in a future study to verify the hypothesis that the presence of SO_4^{2-} may significantly increase the rate and extent of cement carbonation.

3.4. Comparison 3: Different Curing Conditions. The samples were cured for 7 d either under high temperature and ambient pressure conditions (62°C and atmospheric pressure) or high temperature and high pressure conditions (62°C and 17 MPa) to explore the effect of cement curing conditions on cement alteration by low-pH solutions. Considering the variation of geologic reservoir conditions, it is worth comparing the structural changes between cement samples cured at different conditions when reacting with the same solution.

The structural changes of the cement sample (cement #4 in Table 1) cured under ambient pressure after the reaction with pH = 3 HCl and 238 ppm sulfate solution for 7 d are shown in Figure 8. Similar to cement #1, there was dissolution at the edge of the sample and the degradation front can be clearly seen. Besides, the preexisting particles in the borehole were dissolved after reaction.

The comparison results of cement samples under different curing conditions can be seen in Figure 9, indicating that the two thicknesses of the cement alteration zone after 7 d exposure to the pH = 3 HCl+ Na_2SO_4 solution were similar regardless of cement curing conditions.

As for carbonation results, comparing the result of cement #3 (Figure 6) with the result of cement #5 (Figure 10, note: cement #5 was cured at ambient pressure while cement #3 was cured at 17 MPa) shows that precipitation occurred in the borehole of cement #5 after carbonation reaction while cement #3 did not have any precipitation in the borehole. Contrary to cement #3, cement #5 was cured at ambient pressure, which means that the binding strength of cementitious materials in cement #5 may be lower than that of cement #3. As a result, the tendency to release calcium ions from the

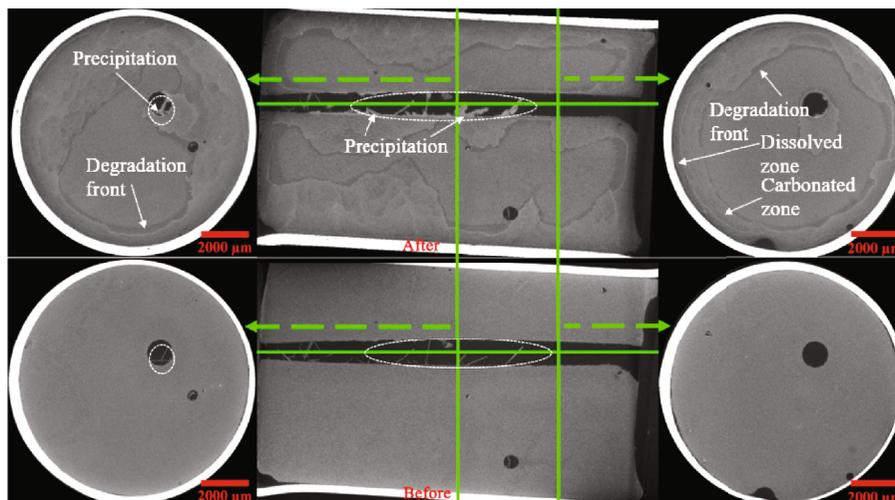


FIGURE 10: CT image of horizontal and vertical slices of cement sample (#5) before and after reaction.

sample cured at ambient pressure when reacting with CO_2 -saturated brine was higher than that from the sample cured at high pressure. Therefore, mineral precipitations (gypsum or calcium carbonate) were more likely to occur in the borehole of cement #5.

4. Conclusion

The experiments of reaction between wellbore cement and different kinds of reaction solutions under SO_4^{2-} -rich geological CO_2 storage conditions were carried out, and the structural changes of cement samples under different reaction and curing conditions were investigated by CT scanning technique. The contribution of acidification and carbonation to cement degradation was studied, and the conclusions are as follows:

- (1) After reaction between cement and solution with different pHs, the amount of dissolution after the reaction between cement and the pH = 3 solution was significantly higher than that after the reaction with the pH = 7 solution, indicating that the degradation of cement is related to the pH value of the solution. The lower the pH value, the faster the reaction and the deeper the degradation depth
- (2) Comparison between the acidification results and the carbonation results shows that carbonation contributes more to cement degradation in the sulfate-rich CO_2 storage environment. The presence of sulfate in the solution speeded up the penetration of CO_2 into cement. However, further investigation is needed to demonstrate whether this speed-up is due to the presence of sulfate, or due to sample heterogeneity and poor initial sample integrity
- (3) Comparison between results of cement samples cured at ambient pressure and high pressure conditions shows that there was no significant difference in cement alteration depth after acidification (no CO_2)

reaction. As for carbonation reaction, precipitations were produced in the borehole of the cement sample cured at ambient pressure while cement sample cured at high pressure did not produce any precipitation

- (4) This study demonstrates the feasibility to use micro-CT to investigate H^+ -induced and CO_2 -induced cement degradation under geologic CO_2 storage conditions, indicating that H^+ -induced cement degradation behaviour is very different from CO_2 -induced cement degradation behaviour

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest regarding the publication of this paper.

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Supplementary Materials

- (1) CT characterization of the reaction between the wellbore cement and pH = 2.5 sulfuric acid solution (cured in 1 wt% NaCl solution with no presence of SO_4^{2-}). Figure S1: CT-

observed structural changes before and after the reaction between cement and pH=2.5 sulfuric acid solution: (top) reaction for 3.5 d; (bottom) reaction for 7 d. From left to right: before reaction, after reaction, and the CT number difference before and after reaction. Figure S2: CT-observed structural changes after reaction between cement and pH=2.5 sulfuric acid solution for 14 d, from left to right: before reaction, after reaction, and the CT number difference before and after reaction. Figure S3: The CT number difference diagram of a cross section in the reaction area between cement and pH=2.5 sulfuric acid before and after reaction. From left to right: reaction for 3.5 d and reaction for 7 d. (2) CT characterization of the reaction between the wellbore cement and pH=3 sulfuric acid solution (cured in 1 wt% NaCl solution with no presence of SO_4^{2-}). Figure S4: CT-observed structural changes after the reaction between cement and pH=3 sulfuric acid solution: (top) reaction for 3.5 d; (bottom) reaction for 7 d; from left to right: before reaction, after reaction, and the CT number difference before and after reaction. Figure S5: CT-observed structural changes after the reaction between cement and pH=3 sulfuric acid solution for 14 d, from left to right: before reaction, after reaction, and the CT number difference before and after reaction. Figure S6: the difference diagram of a cross-section reaction in the reaction area between cement and pH=3 sulfuric acid before and after reaction, from left to right: reaction for 3.5 d; reaction for 7 d. (3) Comparison between acidification and carbonation results after 14 d reaction (cured in 1 wt% NaCl solution with no presence of SO_4^{2-}). Figure S7: CT number difference diagram of the cement sample before and after reaction between cement and pH=2.5 sulfuric acid solution for 14 d. Figure S8: CT number difference diagram of the cement sample before and after reaction between cement and CO_2 -saturated brine for 14 d (modified from Wang et al. [1]). (*Supplementary Materials*)

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