Characterization of the Pore Structure of Well Cement under Carbon Capture and Storage Conditions by an Image-Based Method with a Combination of Metal Intrusion

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ABSTRACT: To more quantitatively and subtly analyze effects of carbonation on the pore structure of well cement by supercritical CO$_2$ under carbon capture and storage (CCS) conditions, a digital scanning electron microscopy-backscattered electron (SEM-BSE) image analysis with a combination of nontoxic low-melting point metal intrusion is used to characterize the exposed cements to humid supercritical CO$_2$ for 10 and 20 days. The porous area fraction (PAF) and pore size distribution (PSD) profiles obtained by slicing operation are used to describe the pore structure variation along the corrosion direction in a two-dimensional (2D) plane. The results show that the image-based method with the combination of metal intrusion is an effective method for characterizing the layer structure of exposed cement and getting quantitative information about the pore structure. From the surface to the core, the main altered layers in exposed cement for 10 days include the partially leached layer, the carbonated layer, and the calcium hydroxide (CH)-dissolved layer. For the exposed cement for 20 days, the main altered layers include the porous leached layer, the partially leached layer, the carbonated layer, and the carbonated transition layer. The nonporous carbonated layer can effectively block the flow parallel to the corrosion direction, while the porous leached layer can facilitate the flow perpendicular to the corrosion direction. Findings from this study will provide valuable information for understanding the effects of carbonation on the pore structure of well cement under CCS conditions.

INTRODUCTION

Climate change is one of the biggest urgent challenges that human beings are facing today, which is mainly attributed to the increase in carbon dioxide (CO$_2$) emission from fossil fuels.$^{1,2}$ Carbon capture and storage (CCS) remains the only technology solution to mitigate the release of CO$_2$ into the atmosphere.$^{1-5}$ The core of CCS is to capture CO$_2$ from power generation and industrial processes and to inject CO$_2$ in geological formations (such as depleted oil or gas reservoirs, unminable coal beds, or saline aquifers) for storage over centuries and thousands of years in a supercritical state (a state where pressure and temperature is greater than 7.38 MPa and 31 °C, respectively).$^{1,6-8}$

For a geologic carbon storage project, the wellbore is the key channel for both storing CO$_2$ and monitoring its reservoir migration. Therefore, the long-term integrity of wellbore is a critical issue for the success of using CCS.$^{2,9,10}$ However, Portland-based well cement, the main sealing material preventing fluid migration and providing mechanical support, is known to be susceptible to CO$_2$ attack as illustrated in the following reaction steps, leading to degradation of wellbore integrity and potentially providing leakage pathways for CO$_2$. $^{1,12}$

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Step 1: Formation of carbonic acid

\[
\text{CO}_2(g) + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3^{(aq)} \leftrightarrow \text{H}_3^+(aq) + \text{HCO}_3^-(aq)
\]
\[
\leftrightarrow 2\text{H}_3^+(aq) + \text{CO}_3^{2-}(aq)
\]

(1)

Step 2: Carbonation of the hydration products

\[
\text{Ca(OH)}_2(s) + 2\text{H}_3^+(aq) + \text{CO}_3^{2-}(aq) \leftrightarrow \text{CaCO}_3(s) + 2\text{H}_2\text{O}
\]

(2)

\[
\text{CSH}_x(s) + \text{H}_2\text{O} \leftrightarrow \text{SiO}_2(\text{amorphous})
\]

(3)

Step 3: Bicarbonation and calcium leaching

\[
\text{CaCO}_3(s) + \text{CO}_2^{(aq)} + \text{H}_2\text{O} \leftrightarrow \text{Ca}^{2+} + 2\text{HCO}_3^-(aq)
\]

(4)

\[
\text{H}_3^+(aq) + \text{CaCO}_3(s) \leftrightarrow \text{Ca}^{2+} + \text{HCO}_3^-(aq)
\]

(5)

Step 4: Decalcification of CSH

\[
\text{CSH} + \text{H}_2\text{CO}_3^{(aq)} \leftrightarrow \text{CaCO}_3 + \text{SiO}_2(\text{amorphous}) + \text{H}_2\text{O}
\]

(6)

Carbonic acid formed when CO2 is dissolved in pore solution of cement or formation of water (eq 1). Then, aqueous CO2 species react with portlandite (Ca(OH)2) and calcium silicate hydrate (CSH) to form CaCO3 (eqs 2 and 3), which are the two main hydration products of hydrated well cement and account for 15–20 wt % and ~70 wt %, respectively. This process is called as carbonation and is known to reduce cement porosity for CaCO3 precipitation in innate pores of cement.15 As the diffusion of the aggressive fluid continues, an abundance of HCO3− leads to the transformation of calcium carbonated to calcium bicarbonate (eqs 4 and 5). Due to higher solubility of Ca(HCO3)2, this process causes calcium to be leached out of the cement matrix gradually. With the dissolution of CaCO3y, the remaining CSH phases will be reacted with H2CO3 to buffer the pH and to form CaCO3 together with amorphous silica gel (eq 6). Amorphous silica gel is porous and lacks structure. Eventually, Ca-leaching will lead to significant changes in the microstructure and properties of well cement.12,14,15

Cement-based materials are a porous medium with a wide range of pore sizes from the micrometer to the nanoscale. The mechanical and transport properties of cement, such as permeability, Young’s modulus, and strength, are strongly correlated with the pore structures.16,17 Meanwhile, it has been well confirmed by numerous laboratories and modeling studies that carbonation of cement is limited by the diffusion of reactants and products, which eventually results in a series of reaction fronts and forms a multilayer structure with different mineral compositions and pore structures in the diffusion direction.11,12,18–20 Therefore, a deep understanding of the effects of carbonation on the pore structure of oil well cement by supercritical CO2 is critical to study the effects of carbonation on wellbore cement integrity under CCS conditions.

Presently, some analytical methods, such as nitrogen gas adsorption, mercury intrusion porosimetry (MIP), X-ray microtomography (XMT), and image-based analysis (based on scanning electron microscopy-backscattered electron (SEM-BSE) imaging on polished epoxy-impregnated cement), have been applied to characterize pore structure changes of well cement and to evaluate the degradation of cement by supercritical CO2.18,21–24 However, there are some limitations for these methods. As mentioned above, a multilayer structure with different mineral compositions and pore structures will be formed in the carbonated cement, which directly relates to the performances of exposed cement.11,12,18–20 Nevertheless, MIP and BET methods usually can just offer composite results due to the larger sample size.25 Still, they cannot provide any information on variations of the pore structure of different layers on a fine scale. An additional limitation of MIP and BET methods is they cannot offer a visible interpretation of pores, such as connectivity and shape. Image analysis based on BSE imaging is an effective way to offer quantitative information about the pore structures of porous materials, such as cement-based materials on a fine scale.26,27 During the image analysis, thresholding is particularly important to differentiate the background from the image objects of interest.28,29 However, for the traditional epoxy resin-impregnated cement, the contrast and gray-level differences between epoxy resin and hydration products are small, making it difficult to distinguish epoxy-filled pores individually and obtain trustworthy data.30–32 Therefore, image analysis based on epoxy impregnation was normally used to prove some qualitative information on the pore structure of cement in previous research studies.

It has been well demonstrated that the replacement of metal to epoxy can significantly improve the contrast and resolution of pores under BSE imaging because of the massive atomic number difference between the metal and the cement matrices.31–34 In order to more quantitatively and subtly analyze effects of carbonation on the pore structure of well cement by supercritical CO2, in this paper, the well cement along the corrosion direction in a two-dimensional (2D) plane were analyzed. Findings from this study will provide valuable information for understanding the effects of carbonation on the pore structure of well cement under CCS conditions.

### EXPERIMENTAL METHODS

#### Materials

Conventional density cement slurry was designed to conduct the experiments, as shown in Table 1. Field’s metal (purchased from Rotometals, Inc.), a nontoxic low-melting point metal, was selected to perform intrusion. The relevant chemical composition and physical properties of well cement based materials are a porous medium with a wide range of pore sizes from the micrometer to the nanoscale. The mechanical and transport properties of cement, such as permeability, Young’s modulus, and strength, are strongly correlated with the pore structures.16,17 Meanwhile, it has been well confirmed by numerous laboratories and modeling studies that carbonation of cement is limited by the diffusion of reactants and products, which eventually results in a series of reaction fronts and forms a multilayer structure with different mineral compositions and pore structures in the diffusion direction.11,12,18–20 Therefore, a deep understanding of the effects of carbonation on the pore structure of oil well cement by supercritical CO2 is critical to study the effects of carbonation on wellbore cement integrity under CCS conditions.

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### Table 1. Formulation of the Cement Sample

| materials and composition | class G well cement | silica fume | filtrate reducer | disperser | water/solid ratio | density (g/cm³) |
|---------------------------|---------------------|-------------|-----------------|-----------|-----------------|---------------|
| BWOC = by weight of cement.
Field’s metal are listed in Table 2. A low-viscosity transparent epoxy resin (purchased from Kemet, Inc.) was used to prepare the epoxy resin-impregnated samples.

| Material     | Composition by weight | Melting Point (°C) | Contact Angle (°) | Yield Strength (MPa) | Density (g/cm³) |
|--------------|-----------------------|--------------------|-------------------|----------------------|-----------------|
| Field’s metal| 32.5% Bi, 51% In, 16.5% Sn | 62 | <33.4 | 8 |

Sample Preparation and Exposure. First, the cement slurry was prepared by a high-speed warning mixer (TCH-4060A, Tongchun Oil Instrument Company, China) according to API Recommended Practice 10B. Then, the slurry was cast in cylindrical molds (25 mm inner diameter × 25 mm length) and cured in an autoclave for 28 days at 20 MPa and 60 °C. The curing conditions were selected to simulate the Shenhua CCS field conditions in the Ordos Basin of China.

After the curing and demolding processes, as shown in Figure 1, the samples were placed into a kettle to expose to humid supercritical CO₂. The exposure experiment was also performed at 20 MPa CO₂ and 60 °C. The exposed durations were selected as 10 and 20 days. Then, X-ray diffraction was applied to test the XRD patterns of the cement pastes with different curing conditions at a scanning rate of 0.08 °/s in the range (2θ) from 10° to 70°.

Field’s Mental Intrusion and Epoxy Resin Impregnation. After exposure, the exposed samples for 10 and 20 days were removed from the kettle, respectively, and cut into slices with both the altered region and the unaltered region approximately 5 mm × 5 mm × 5 mm using a diamond blade saw. Then, the sectioned samples were placed in a vacuum oven for 1 week at 60 °C to remove liquid from the pores.

After drying, the samples were divided into two parallel groups. Field’s metal intruded into one group, and the other group was impregnated by epoxy resin for comparison. While preparing the metal-intruded samples, the dried samples were placed into a heated chamber with melted Field’s metal at 90 °C first. For the melted Field’s metal is a nonwetting liquid to cement (one having a contact angle greater than 90° as shown in Table 1) and can only intrude capillary pores under pressure, the relationship between the pressure and capillary diameter could be described as Washburn’s equation (eq 7), which also is the basic principle of the MIP test.

\[
P = \frac{-4\gamma \cos \theta}{d}
\]

where \(P\) is pressure, \(\gamma\) is the surface tension of the liquid, \(\theta\) is the contact angle of the liquid, and \(d\) is the diameter of the capillary. Therefore, a pressure up to 400 MPa was gradually applied to the chamber at a rate of 16 MPa/min to drive the liquid metal into pores of samples and maintained for 20 min, which is equal to the highest intrusion pressure of most commercial MIP instruments at present. Then, the chamber was cooled to room temperature while still under pressure, and the liquid metal was finally solidified and fixed in the pores of cement during this process. After cooled, the Field’s metal-intruded samples were finely polished down to 0.1 mm grit.

For the epoxy resin impregnation process, the parallel samples used for metal intrusion were impregnated under vacuum with epoxy resin. Subsequently, the impregnated samples were kept in ambient for 2 days until the epoxy was totally solidified. Then, the samples were also finely polished down to 0.1 mm grit.

BSE Images and Image Analysis. A Megallen 400 SEM (FEI, USA) was used to perform SEM-BSE imaging on the finely polished and carbon-coated samples. Each BSE image is a 256 gray-level image with a 6144 × 4096 pixel-square size. Then, the BSE images were further analyzed by software ImageJ to produce binary images. First, the scale was set based on the scale bar on the BSE image. Then, the image data was converted into 8-bit grayscale, with the range of grayness from 0–255. Binary images of the pores were obtained by thresholding of pores. The epoxy or metal-filled pores, identified as black pixels in the binary image, were

![Figure 1. Schematic of the experimental setup and sample loading.](image1.png)

![Figure 2. Schematic of slicing operation.](image2.png)
analyzed using the inbuilt algorithm of software ImageJ. Solid inclusions within pores were considered in the calculation of pore fraction.

In order to analyze the variety of the pore structure of exposed cement with corrosion direction, several sets of adjoining BSE images with similar magnification (×500), brightness, and contrast were recorded along the CO2 penetrating direction first. Under the magnification of ×500, the size of a pixel is 0.067 μm × 0.067 μm. Then, the metal-intruded pores were identified in a single threshold to produce a binary image. Afterward, each set of BSE images and corresponding binary images were stitched together in turn to get the 2D panoramas of exposed cement.

The actual porosity or pore volume of cement is a concept in the three-dimensional (3D) plane; however, it is evident that the binary image only shows the distribution of the pores in a two-dimensional (2D) plane. Therefore, the porous area fraction (PAF) is adopted, which is defined by the area of the pores divided by the total area of the investigated sample. For the epoxy impregnation method, it can be seen from Figure 4a that a weaker but discernable contrast between hydrated products (CSH, Ca(OH)2, AFt, etc.), epoxy-filled pores, and unhydrated cement grains (C3S, C2S, C3A, etc.) was obtained due to the anhydrous phases having a higher average atomic number than the hydrates and epoxy. The relatively high brightness of unhydrated grains contributes to analysis of the mineral phase composition, hydration degree, and hydration process of cement by image analysis on the basis of the gray level.9,10 However, for image analysis on the pore structure, the gray level differences between epoxy-impregnated pores (especially the small capillary pores in porous CSH gel as shown in Figure 4a) and surrounding hydrated products is indistinguishable as shown in Figure 4b because the atomic number of elements in epoxy (composed of C6H1O8, etc.) is just slightly lower than other elements in the cement (Si14, Ca20, O8, Al13 etc.), making the epoxy-impregnated pores, especially the small pores in CSH gel, and the edges of pores not clear.33 Consequently, it is difficult to differentiate the pores and hydrated products clearly.

For porous media, the pore shape factor (PSF) is another important parameter to describe the 2D pore structure. This parameter is usually used to analyze the morphological characteristics of pores, which reflects the roundness degree of pores.39 The PSF of circular pores equals one, as a referring value. Also, a complex pore shape has the lower pore shape factor. For example, the PSF for rectangular pores and triangular pores are 0.883 and 0.362, respectively. Yang et al.30 reported the calculation method of the pore shape factor of pores. In this work, based on the SEM-BSE images, the pore shape factors of different layers of exposed cement were analyzed using software ImageJ.

## RESULTS AND DISCUSSION

A Comparison between Epoxy Impregnation and Metal Intrusion. Figures 4 and 5 respectively show the typical BSE images, gray-level histograms, and binary images of pores (black) of epoxy-impregnated and Field’s metal-intruded unexposed cement. According to the principle of BSE imaging, the intensity of the BSE signal and the brightness of an image is mainly a function of the atomic number of the atoms in the sample. For the epoxy impregnation method, it can be seen from Figure 4a that a weaker but discernable contrast between hydrated products (CSH, Ca(OH)2, AFt, etc.), epoxy-filled pores, and unhydrated cement grains (C3S, C2S, C3A, etc.) was obtained due to the anhydrous phases having a higher average atomic number than the hydrates and epoxy. The relatively high brightness of unhydrated grains contributes to analysis of the mineral phase composition, hydration degree, and hydration process of cement by image analysis on the basis of the gray level.9,10 However, for image analysis on the pore structure, the gray level differences between epoxy-impregnated pores (especially the small capillary pores in porous CSH gel as shown in Figure 4a) and surrounding hydrated products is indistinguishable as shown in Figure 4b because the atomic number of elements in epoxy (composed of C6H1O8, etc.) is just slightly lower than other elements in the cement (Si14, Ca20, O8, Al13 etc.), making the epoxy-impregnated pores, especially the small pores in CSH gel, and the edges of pores not clear.33 Consequently, it is difficult to differentiate the pores and hydrated products clearly.

In contrast to the epoxy-impregnated cement, Figure 5a shows that the metal-filled pores appeared as apparently bright signals in the BSE images because Field’s metals (In49, Sn50, Bi50, etc.) in the pores strongly deflected electrons to the BSE detector for their high atomic number compared with elements in the cement. Therefore, the pores filled by metal in the BSE

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Figure 3. Schematic for the $d_p$ calculation.

For noncircular pores, $d_p$ is the diameter of a circular pore with an equivalent area and is given as follows:

$$d_p = \sqrt{\frac{4P_{area}}{\pi}}$$

where $P_{area}$ is the area of the pore from the image analysis.

Using the slicing operation, the pore size distribution (PSD) of each section and the PSD profile along with the corrosion direction can be obtained.

Figure 4. Typical BSE image (a), the gray-level histogram (b), and a binary image (c) of pores (black) of epoxy-impregnated cement.
image are white color. In order to clearly observe the pore characterization, the BSE image is analyzed by binary image analysis; the pores are colored using black color.

A magnified view (Figure 5b) illustrates that both the large capillary pores and small capillary pores in porous CSH gel are well filled with metal and showed much higher resolution and contrast. The high resolution and contrast of pores can guarantee a significant gray level difference between metal-filled pores and solid phases (hydration products, unhydrated cement grains, etc.). Moreover, it is clearly shown that the geometry of pores in cement is irregular and complicated. As shown in Figure 5c, there is a separate peak for metal-filled pores in paste, which was quite beneficial to distinguish the pores from cement during image analysis. As demonstrated in Figure 5d, the analysis can successfully distinguish the pores (black pixels in the binary image) from the cement (white pixels). The comparison demonstrated that BSE image analysis in combination with Field’s metal intrusion is an effective...
technique for characterizing the pore structure of cementitious materials in a 2D scale.

**CO₂ Corrosion of Cement Paste.** Figure 6 shows the pictures and XRD results of cement pastes cured for 28 days and exposed for 10 and 20 days in CO₂ condition. Comparing the pictures (see Figure 6a), the macroscopic morphology of the unexposed cement did not have obvious difference. However, with the cement paste exposed CO₂ condition, the macroscopic morphology was changed obviously, and with an increasing exposed time, the depth of the corrosion layer in the cement paste increased.

Figure 6b,c presents the XRD patterns of the cement paste with different layers exposed for 10 and 20 days in CO₂. From these results, Ca(OH)₂ in the form of portlandite was the main crystalline phase in the unexposed sample. Meanwhile, the unexposed cement and the inner unaltered cement had similar XRD patterns, which proved that their chemical compositions were almost similar. The XRD patterns of inner unaltered cement of exposed samples show that their main crystalline phase was only portlandite, and there was no peak of CaCO₃ for the CO₂ attack did not penetrate into this section. Compared with the inner unaltered cement, all altered layers of cement pastes exposed for 10 and 20 days revealed the characteristic peak of CaCO₃ in the form of calcite, aragonite, and vaterite, and the intensity of peaks corresponding to portlandite is decreased for the carbonation of portlandite. It has been mentioned that the formation of aragonite and vaterite is seemingly related to high decalcification of cement.²⁹

**Effects of CO₂ Corrosion on 2D Distribution of Porous Area Fraction and Pore Size.** The 2D porous area fraction (PAF) and pore size distribution (PSD) profiles of the exposed sample for 10 and 20 days along with the corrosion direction obtained by slicing operation are shown Figures 7 and 8, respectively.

As can be seen from Figures 7 and 8, the PAF curve can be divided into several distinct regions with different pore size distribution characteristics, which corresponds to the BSE and binary images in Figures 9 and 10. For the exposed sample for 10 days, the PAF of the innermost unaltered cement was ~25%, and the main pore size is concentrated in the range of 1–10 μm. In the CH-dissolved layer, both the PAF and the ratio of pores with size >10 μm were increased significantly.

The largest PAF was close to 45%. In contrast to the CH-dissolved layer, the PAF of the carbonated layer was decreased significantly due to CaCO₃ precipitation in cement pores. Also, the ratio of pores in the range of >5 μm was also markedly decreased. In some slices, the ratio of pores >10 μm even went down to 0. This phenomenon indicates that CaCO₃ is more inclined to precipitate in the pores with larger pore sizes.⁴³ It could be attributed that larger pores have more pore solution with dissolved Ca(OH)₂ for carbonation and better connectivity for species migration. This is supported by the work of Putnis et al. who found that precipitation in bigger pores is more energetically favored than in micropores.⁴³ For the partially leached layer, the PAF was slightly increased to ~15% caused by Ca-leaching as expressed in eqs 5 and 6. In terms of pore size, the proportion of pores with sizes in a range of 1–5 μm showed the largest growth.

For the exposed sample for 20 days, the innermost unaltered cement, the carbonated layer, and the partially leached layer showed similar PAF and PSD characteristics to the exposed sample for 10 days. The differences show that the PAF of the carbonated transition layer was gradually increased along with the corrosion direction, and the fraction of pores >10 μm showed a relatively significant reduction. As to the outermost porous leached layer, both the PAF and the fraction of pores >10 μm showed a sharp increase because the main component in this layer was amorphous silica gel as a result of complete decalcification of CSH phases.³⁵

**Effects of CO₂ Corrosion on the Pore Structure of Exposed Cement.** The 2D panoramas of exposed cement for 10 and 20 days by image analysis in combination with Field’s metal intrusion are presented in Figures 9 and 10. As can be seen from Figures 9(a-1,a-2) and 10(a-1,a-2), several noticeable heterogeneous altered layers with different pore structures along with the corrosion direction can be identified clearly on the rim region of exposed cement.

For the exposed cement for 10 days, the altered zone consists of a partially Ca-leached layer, a carbonated layer, a CH-dissolved layer, and inner unreacted cement in order from the surface to the core. It should be noted that the high heterogeneity of cement makes it very difficult to form and determine the clear interface between layers. The zoomed-in views (Figure 9(b-1,b-2) show that the outermost partially leached layer is more porous than the carbonated layer (Figure
9(c-1,c-2) due to the calcium carbonate partly dissolved in the presence of excess carbonic acid to form water-soluble calcium bicarbonate and results in leaching of calcium ions from the cement matrix, gradually (eqs 4 and 5). It should be noted that, however, the structure of the partially leached layer is still much denser than the unreacted cement (Figure 9(e-1,e-2)). Compared with the inner unreacted cement, Figure 9(c-1,c-2) shows that the PAF of the carbonated layer is decreased dramatically due to the precipitation of calcium carbonate in pores of this layer, which is the product of the reaction between CH diffusing out of the cement and aqueous CO$_3^{2-}$ diffusing into the cement. In addition to CH, CSH is also susceptible to carbonation to form calcium carbonate and amorphous silica gel, while there is enough CH to buffer the pH. It is commonly reported that the volume of calcium carbonate is larger than that of the primary reactants (CH and CSH). Consequently, the formation of the dense carbonated layer can hinder the further penetration of carbonic acid solution into the cement. In the meantime, however, some intrusion pressure-induced cracks appear on this layer. Feldman found that the mercury in the MIP test can break down fragile walls within the microstructure of pastes with extremely low porosity when intrusion pressure is above 70 MPa. Therefore, the cracks were excluded from the image analysis.
In addition, this phenomenon gives us a hint that the intrusion pressure-induced cracks may cause undecidable errors while applying the MIP method to carbonated cement. In contrast to the carbonated layer, both the amount of small capillary pores and the connectivity of pores in CH-dissolved layers are increased sharply as shown in Figure 9(d-1,d-2). The reason for this alteration is attributed to the outward portlandite dissolution and CSH decalcification to buffer the pH and the calcium concentration decrease in the outer carbonated layer. It is reported that the dissolution rate of portlandite is typically faster than CSH by as much as four orders of magnitude. Therefore, the increase of pores was mainly attributed to the outward dissolution of portlandite crystals. A zoomed-in view of the inner unreacted cement (Figure 9(e-1)) illustrates that the porous CSH gel, capillary pores, and unhydrated cement grains are the three main
morphologies in unreacted cement.\textsuperscript{31,34} Visually, the porous CSH gel makes up the major portion of unreacted cement and possesses a massive amount of small capillary pores with diameters less than a few hundred nanometers. In contrast, the size of capillary pores is much larger but the number is much lower. The unhydrated gains, as clearly shown in Figure 9(e-1,e-2), also occupy a large portion of the area, which normally have a larger size and are surrounded by a thin shell of inner CSH.\textsuperscript{17}

Compared with the exposed cement for 10 days (Figure 9), the altered region of exposed cement for 20 days shows some different features, which is more porous in general as shown in Figure 10. An apparent difference is that a porous leached layer is generated in the outermost of the sample due to almost complete Ca-leaching in this layer, and the partially leached layer (Figure 10(c-1,c-2)) moved toward. As shown in Figure 10(b-1,b-2), the diameter of pores is bigger and the connectivity is better in the porous leached layer. Another noticeable difference is that no CH-dissolved layer can be observed between the inner unaltered cement and concatenated layer. Instead of the CH-dissolved layer, a carbonated transition layer (Figure 10(e-1,e-2) with fewer pores and smaller pore size than the unaltered cement (Figure 10(f-1,f-2), appears. As shown in Figure 10(e-1,e-2), the area fraction of small capillary pores in the carbonated transition layer is gradually decreased in the opposite corrosion direction, while many large capillary pores still remain. This difference could be attributed to the formation of a dense carbonated layer in the initial exposure stage, which reduced the inner diffusion rate of CO$_2$ and finally led to a decrease in the outward dissolution rate of CH.

In addition, the results of PSF analysis of exposed cement for 10 days (Figure 9(b-3, c-3, d-3, and e-3) show that the PSFs of both the carbonated layer and the CH-dissolved layer are lower than that of the inner unreacted cement, which means that the pore irregularity of the two altered layers is increased. According to Yang et al.,\textsuperscript{40} the irregular pores usually had a larger pore wall–fluid contact area than that of circular pores, and this may generate more immobile fluid and diminish the effective area of the flow path. For the partially Ca-leached layer, the PSF is almost equal to the inner unreacted cement.

The results of PSF analysis of exposed cement for 20 days (Figure 10(b-3, c-3, d-3, e-3, and f-3) also show that the average PSFs of both the carbonated layer and the CH-dissolved layer are lower than that of the inner unreacted cement. Meanwhile, the average PSF is slightly decreased. For the porous leached layer, although the PAF increased significantly, the average PSF has decreased compared to the unreacted cement. Therefore, in the following studies, more efforts may be paid to research the effects of PAF, PSD, and PSF variation on the migration of CO$_2$-rich fluids in oil well cement.

**Implications for Understanding Well Cement Carbonation.** The above results show that the carbonation of cement is a complicated process with both mineral phase and pore structure (porosity and pore size) changes at the same time. Obviously, PAF corresponds directly to the local porosity and permeability of altered cement. In general, the PAF profiles of the exposed sample for 10 and 20 days indicated a two-stage evolution of well cement porosity: an initial sealing stage induced by formation and precipitation of CaCO$_3$ as shown in Figure 9, followed by a stage of increasing porosity corresponding to decalcification of CaCO$_3$ and CSH as shown in Figure 10. The first stage usually occurs only in the first few days of exposure. However, the second stage may last very long time until the cement is completely destroyed because the carbonation of cement is a diffusion-dominated process, and the dense carbonated layer can severely block the inward diffusion of carbonic acid and the further alteration of cement.\textsuperscript{55,49,50}

As a result of the formation of the layer structure, the exposed cement matrix shows porosity and a permeability variation from the surface to the innermost unaltered cement. This variation will have different effects on the integrity of CCS wells in different directions.\textsuperscript{6,51,52} When the diffusion direction of flow is parallel to the corrosion direction, the permeability of the exposed cement shows a reduction because the CaCO$_3$ precipitation layer acts as a barrier to the flow. The averaged permeability increases for the flow perpendicular to the corrosion direction due to the permeability increase in the porous leached layer and the CH-dissolved layer.

Many transport models have been developed to simulate the interaction between cement and CO$_2$ or CO$_2$-saturated brine, and porosity is an essential parameter in these models.\textsuperscript{35,34} The results of this paper show that the overall porosity and pore size distribution of exposed cement is not suitable for analyzing the diffusion process of carbonic acid fluid in the cement matrix because each layer has different pore structure characteristics. Using the method of digital BSE image analysis with a combination of Field’s metal intrusion, it is possible to deduce the 3D porosity and connectivity of pores from the 2D sections.\textsuperscript{30} This future work may greatly facilitate the optimization of the transport models and kinetics models and ultimately contribute to a more accurate analysis of the integrity of well cement under CCS conditions.

**CONCLUSIONS**

The results demonstrated that digital BSE image analysis with a combination of Field’s metal intrusion is an effective method for characterizing the layer structure of exposed cement under CCS condition and getting quantitative information about the pore structure (PAF and PSD) of each layer. Based on the method, the variation characteristics of the pore structure of exposed cement for 10 and 20 days under the simulated CCS condition were analyzed. From the surface to the core, the main altered layers in exposed cement for 10 days include the partially leached layer, the carbonated layer, and the CH-dissolved layer. For the exposed cement for 20 days, the main altered layers include the porous leached layer, the partially leached layer, the carbonated layer, and the carbonated transition layer. The partially leached layer and the carbonated transition layer had not been reported in previous studies. The results indicated an initial sealing stage related to precipitation of calcium carbonate that tends to plug larger pores, followed by a dissolution stage marked by a significant increase of porosity.

By slicing operation, the 2D PAF and PSD profiles of the exposed sample along with the corrosion direction were obtained. Compared to the unaltered cement, the partially leached layer, the carbonated layer, and the carbonated transition layer showed a reduction in PAF and the fraction of bigger pores. On the contrary, both the CH-dissolved layer and the porous leached layer exhibited a sharp increase in PAF and the fraction of lager pores, although by different mechanisms. The nonporous carbonated layer can effectively block the flow parallel to the corrosion direction, while the
porous leached layer can facilitate the flow perpendicular to the corrosion direction.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

**Notes**

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**REFERENCES**

(1) Pires, J. C. M.; Martins, F. G.; Alvim-Ferraz, M. C. M.; Simões, M. Recent developments on carbon capture and storage: An overview. Chem. Eng. Res. Des. 2011, 89, 1446–1460.

(2) Zhang, M.; Bachu, S. Review of integrity of existing wells in relation to CO2 geological storage: What do we know? Int. J. Greenhouse Gas Control 2011, 5, 826–840.

(3) International Energy Agency Technology roadmap: carbon capture and storage; OECD Publishing: 2009, DOI: 10.1787/9789264088122-en.

(4) Liu, Y.; Chen, S.; Guan, B.; Xu, P. Layout optimization of large-scale oil-gas gathering system based on combined optimization strategy. Neurocomputing 2019, 332, 159–183.

(5) Wang, Z.; Bai, Y.; Zhang, H.; Liu, Y. Investigation on gelation nucleation kinetics of waxy crude oil emulsions by their thermal behavior. J. Pet. Sci. Eng. 2019, 181, 106230.

(6) Kutchko, B. G. Effect of Carbon dioxide on the Integrity of Well Cement under Geologic Sequestration Conditions. PhD dissertation, Carnegie Mellon University, Pittsburgh, Pennsylvania, 2008.

(7) Leung, D. Y. C.; Caramanina, G.; Maroto-Valer, M. M. An overview of current status of carbon dioxide capture and storage technologies. Renewable Sustainable Energy Rev. 2014, 39, 426–443.

(8) Kenarsari, S. D.; Yang, D.; Jiang, G.; Zhang, S.; Wang, J.; Russell, A. G.; Wei, Q.; Fan, M. Review of recent advances in carbon dioxide separation and capture. RSC Adv. 2013, 3, 22739–22773.

(9) Viswanathan, H. S.; Pawar, B. J.; Stauffer, P. H.; Kaszuba, J. P.; Carey, J. W.; Olsen, S. C.; Keating, G. N.; Kavetski, D.; Guthrie, G. D. Development of a Hybrid Process and System Model for the Assessment of Wellbore Leakage at a Geologic CO2 Sequestration Site. Environ. Sci. Technol. 2008, 42, 7280–7286.

(10) Sweatman, R. E.; Santra, A. K.; Kulakofsky, D. S.; Calvert, D. G. Effective zonal isolation for CO2 sequestration wells. In SPE International Conference on CO2 Capture, Storage, and Utilization; Society of Petroleum Engineers: 2009.

(11) Kutchko, B. G.; Strazisar, B. R.; Lowry, G. V.; Dzombak, D. A.; Thalow, N. Rate of CO2 attack on hydrated class H well cement under geologic sequestration conditions. Environ. Sci. Technol. 2008, 42, 6237–6242.

(12) Kutchko, B. G.; Strazisar, B. R.; Dzombak, D. A.; Lowry, G. V.; Thalow, N. Degradation of Well Cement by CO2 under Geologic Sequestration Conditions. Environ. Sci. Technol. 2007, 41, 4787–4792.

(13) Ashraf, W. Carbonation of cement-based materials: challenges and opportunities. Constr. Build. Mater. 2016, 120, 558–570.

(14) Jacquemet, N.; Pironon, J.; Saint-Marc, J. Mineralogical Changes of a Well Cement in Various H2S-CO2-(Brine) Fluids at High Pressure and Temperature. Environ. Sci. Technol. 2008, 42, 282–288.

(15) Yuanhua, L.; Daijiang, Z.; Dezhi, Z.; Yuanguang, Y.; Taihe, S.; Kuanzhai, D.; Chengqiang, B.; Deping, Z.; Feng, W. Experimental studies on corrosion of cement in CO2 injection wells under supercritical conditions. Corros. Sci. 2013, 74, 13–21.

(16) Aligizaki, K. K. Pore Structure of Cement-Based Materials: Testing, Interpretation and Requirements; CRC Press: 2005, DOI: 10.1201/b19074.

(17) Scrivener, K.; Smellings, R.; Lothenbach, B. A Practical Guide to Microstructural Analysis of Cementitious Materials; CRC Press: 2018, DOI: 10.1201/b19074.

(18) Rimmelé, G.; Barlet-Gouédard, V.; Porcherie, O.; Goffé, B.; Brunet, F. Heterogeneous porosity distribution in Portland cement exposed to CO2-rich fluids. Cem. Concr. Res. 2008, 38, 1038–1048.

(19) Laudet, J.-B.; Garnier, A.; Neuville, N.; Le Guen, Y.; Fourmaintreaux, D.; Rafai, N.; Burlion, N.; Shao, J.-F. The behavior of oil well cement at downhole CO2 storage conditions: Static and dynamic laboratory experiments. Energy Procedia 2011, 4, 5251–5258.

(20) Matteo, E. N.; Scherer, G. W. Experimental study of the diffusion-controlled acid degradation of Class H Portland cement. Int. J. Greenhouse Gas Control 2012, 7, 181–191.

(21) Jung, H. B.; Um, W. Experimental study of potential wellbore cement carbonation by various phases of carbon dioxide during geologic carbon sequestration. Appl. Geochem. 2013, 35, 161–172.

(22) Jung, H. B.; Jansik, D.; Um, W. Imaging wellbore cement degradation by carbon dioxide under geologic sequestration conditions using X-ray computed microtomography. Environ. Sci. Technol. 2013, 47, 283–289.

(23) Um, W.; Rod, K. A.; Jung, H. B.; Brown, C. F. Geochemical alteration of wellbore cement by CO2 or CO2+H2S reaction during long-term carbon storage. Greenhouse Gases: Sci. Technol. 2017, 7, 852–865.

(24) Guo, T.; Tang, S.; Liu, X.; Xu, J.; Rui, Z. Physical Simulation of Hydraulic Fracturing of Large Size Tight Sandstone Outcrops; Society of Petroleum Engineers: 2020.

(25) Diamond, S. Mercury porosimetry: an inappropriate method for the measurement of pore size distributions in cement-based materials. Cem. Concr. Res. 2000, 30, 1517–1525.

(26) Scrivener, K. L. Backscattered electron imaging of cementitious microstructures: understanding and quantification. Cem. Concr. Compos. 2004, 26, 935–945.

(27) Yang, Z.; Peng, X.-F.; Lee, D.-J.; Chen, M.-Y. An image-based method for obtaining pore-size distribution of porous media. Cem. Compos. 2020, 112, 103681.
(29) Liu, K.; Cheng, X.; Zhang, C.; Gao, X.; Zhuang, J.; Guo, X. Evolution of pore structure of oil well cement slurry in suspension-solid transition stage. Constr. Build. Mater. 2019, 214, 382–398.

(30) Wang, P.; Feng, S.; Liu, X. Application of Backscattered Electron Imaging and Image Analysis in Microstructure Research on Cement-Based Materials. J. Clin. Ceram. Soc. 2011, 10, 1659–1665. (in Chinese)

(31) Chen, S. J.; Tian, Y.; Li, C. Y.; Duan, W. H. A new scheme for analysis of pore characteristics using centrifuge driven non-toxic metal intrusion. Geomech. Geophys. Geo-Energy Geo-Resour. 2016, 2, 173–182.

(32) Chen, S. J.; Li, W. G.; Ruan, C. K.; Sagoe-Crentsil, K.; Duan, W. H. Pore shape analysis using centrifuge driven metal intrusion: Indication on porosimetry equations, hydration and packing. Constr. Build. Mater. 2017, 154, 95–104.

(33) Abell, A. B.; Willis, K. L.; Lange, D. A. Mercury intrusion porosimetry and image analysis of cement-based materials. J. Colloid Interface Sci. 1999, 211, 39–44.

(34) Willis, K. L.; Abell, A. B.; Lange, D. A. Image-based characterization of cement pore structure using wood’s metal intrusion. Cem. Concr. Res. 1998, 28, 1695–1705.

(35) American Petroleum Institute Recommended Practice for testing well cements 10B-2; American Petroleum Institute Publishing: Washington, 2013.

(36) Wu, X.; Cui, Y. Study on 0.1 Mt/a CO2 sequestration in saline formation. Acta Pet. Sin., Pet. Process. Sect. 2010, S1, 236–239. (in Chinese)

(37) Ferreira, T.; Rasband, W. The ImageJ user guide; National Institutes of Health: 2012.

(38) Ridler, T.; Calvard, S. Picture thresholding using an iterative selection method. IEEE Trans. Syst. Man Cybern. 1978, 8, 630–632.

(39) Sun, Y.; Guo, S. Qualitative and Quantitative Characterization of Shale Microscopic Pore Characteristics Based on Image Analysis Technology. Adv. Earth Sci. 2016, 31, 751–763. (in Chinese)

(40) Yang, B.; Kang, Y.; Lu, X.; You, L.; Zhang, H.; Chen, Z. Experimental investigation of the pore shape factor in fluid imbibition model—taking the Longmaxi shale in Sichuan Basin as examples. J. Pet. Sci. Eng. 2020, 193, 107327.

(41) Han, F.; Liu, J.; Yan, P. Comparative study of reaction degree of mineral admixture by selective dissolution and image analysis. Constr. Build. Mater. 2016, 114, 946–955.

(42) Haha, M. B.; De Weerdt, K.; Lothenbach, B. Quantification of the degree of reaction of fly ash. Cem. Concr. Res. 2010, 40, 1620–1629.

(43) Šavija, B.; Luković, M. Carbonation of cement paste: Understanding, challenges, and opportunities. Constr. Build. Mater. 2016, 117, 285–301.

(44) Putnis, A.; Prieto, M.; Fernandez-Diaz, L. Fluid supersaturation and crystallization in porous media. Geol. Mag. 1995, 132, 1–13.

(45) Jacquemet, N.; Pironon, J.; Lagneau, V.; Saint-Marc, J. Armouring of well cement in H2S–CO2 saturated brine by calcite coating—Experiments and numerical modelling. Appl. Geochem. 2012, 27, 782–795.

(46) Santra, A.; Reddy, B.R.; Liang, F.; Fitzgerald, R. Reaction of CO2 With Portland Cement at Downhole Conditions and the Role of Pozzolanic Supplements. In SPE International Symposium on Oilfield Chemistry; Society of Petroleum Engineers: 2009.

(47) Feldman, R. F. Pore structure damage in blended cements caused by mercury intrusion. J. Am. Ceram. Soc. 1984, 67, 30–33.

(48) Baur, I.; Keller, P.; Mavromvatados, D.; Wehrli, B.; Johnson, C. A. Dissolution-precipitation behaviour of ettringite, monosulfate, and calcium silicate hydrate. Cem. Concr. Res. 2004, 34, 341–348.

(49) Raoof, A.; Nick, H. M.; Wolterbeek, T. K. T.; Spiers, C. J. Pore-scale modeling of reactive transport in wellbore cement under CO2 storage conditions. Int. J. Greenhouse Gas Control 2012, 11, S67–S77.

(50) Newell, D. L.; Carey, J. W. Experimental evaluation of wellbore integrity along the cement-rock boundary. Environ. Sci. Technol. 2013, 47, 276–282.