Effect of exposure environment on the interactions between acid gas (H_2S and CO_2) and pozzolan-amended wellbore cement under acid gas co-sequestration conditions

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Abstract

Laboratory experiments were conducted to determine the effect of exposure environment on the integrity of pozzolan-amended Class H cement under geologic acid gas co-sequestration conditions. Cement was exposed to two potential subsurface storage environments: (1) a supercritical mixture of CO_2 / H_2S and (2) a CO_2 / H_2S saturated brine. Results show that cement alteration is dependent on the amount of pozzolan addition. The alteration rate and mechanism also differ for the two exposure scenarios. Cement containing 35% pozzolan amounts by volume (hereafter referred to as 35 vol% pozzolan cement) exposed to the aqueous environment was more vulnerable to alteration, compared with the same pozzolan content cement exposed to a supercritical mixture of CO_2 / H_2S (21 mol% H_2S). Specifically, 35 vol% pozzolan cement exposed to the aqueous environment exhibited a higher level of mineral dissolution (e.g., C-S-H, $3\text{CaO}\cdot\text{SiO}_2$, $2\text{CaO}\cdot\text{SiO}_2$, etc.) and a higher degree of sulfur alteration than the same pozzolan content samples exposed to the supercritical mixture of CO_2 - H_2S (21 mol% H_2S). Different from

the 35 vol% pozzolan cement, the cement containing 65% pozzolan by volume (hereafter referred to as 65 vol% pozzolan cement) was more susceptible to alteration in the supercritical CO₂/H₂S (21 mol% H₂S) environment, compared with the same pozzolan content cement exposed to the aqueous environment. Increasing the H₂S mol % in the supercritical phase from 21 mol % to 40 mol % increased the alteration of cement exposed to both exposure environments. The 65 vol% pozzolan cement was more resistant to H₂S and CO₂ alteration than the 35 vol% pozzolan cement if the H₂S content was high (i.e., 40 mol%), while the 35 vol% pozzolan cement was more resistant to H₂S and CO₂ alteration than the 65 vol% pozzolan cement if the H₂S content was relatively low (i.e., 21 mol%). It was observed that while the two related exposure environments resulted in different degrees of cement alteration, the exposure environments did not result in the formation of different minerals.

Key words: Carbon Sequestration, Cement, Fly Ash, Acid Gas, CO₂, H₂S

Nomenclature

Abbreviation	Description
35:65	Pozzolan-amended cement with 35 vol% pozzolan additives and 65 vol% Class H Portland cement
65:35	Pozzolan-amended cement with 65 vol% pozzolan additives and 35 vol% Class H Portland cement
aq-exposed	Samples exposed to CO ₂ and H ₂ S saturated brine
sc-exposed	Samples exposed to a supercritical mixture of CO ₂ and H ₂ S

Note to the editor: this nomenclature is provided to condense the text and get rid of long descriptors used in the text.

1. Introduction

An effective approach to reduce atmospheric CO₂ emissions is to capture CO₂ from large industrial processes involving combustion of fossil fuels, and inject the captured CO₂ into deep geological formations (e.g., hydrocarbon reservoirs and deep saline aquifers) (Holloway, 1997; Bachu, 2000; IPCC, 2007; Duguid and Scherer, 2010; Zhang and Bachu, 2011). In addition to pure CO₂ injection, acid-gas (a mixture of CO₂ and H₂S) injection is also on the rise (Bachu and Gunter, 2004; Machel, 2005), so as to reduce atmospheric emissions of toxic H₂S and reduce the cost to conduct surface desulfurization (Bachu et al., 2003). Acid gas injection is mainly employed to store H₂S and CO₂ separated from sour natural gas (Bachu and Carroll, 2005; Bachu et al., 2005). It could also be used to sequester H₂S and CO₂ from pre-combustion capture of carbon from coal-fired power plants (Kutchko et al., 2011). In 2009, there were over 40 wells used for acid-gas injection in Alberta, Canada (Bachu and Watson, 2009). Compared with pure CO₂ injection, the co-injection of CO₂ and H₂S enables reaction of H₂S with cement to produce pyrite and ettringite (Jacquemet et al., 2008; Kutchko et al., 2011), and an abundant amount of H₂S in the bulk solution enables the bulk solution to maintain low pH, even after most CO₂ is consumed by CO₂-cement interaction. As a result, there is a need to study the degradation of wellbore cement under the conditions of acid gas co-injection.

When a CO₂/H₂S mixture is injected into the subsurface, it may either remain as a separate free gas phase (scenario I) or dissolve in the subsurface formation fluid (scenario II) (Bruant et al., 2002; White et al., 2003). Buoyancy will cause the CO₂ to rise and spread laterally beneath the desired caprock (White et al., 2003). When the CO₂ contacts the formation fluid, it will dissolve and lower the pH of the fluid (White et al., 2003). The exposure experiments described herein

were designed to simulate both scenarios by which the injected fluid can contact the cement sheath in existing wells.

Some of the risks associated with acid gas injection have been identified and evaluated (Kutchko et al., 2011; Jacquemet et al., 2012; Zhang et al., 2013), but more studies are needed to understand better and quantify the risks. One risk associated with acid gas injection is the potential for injected CO₂ and H₂S to escape along the wellbores in the injection area. The process for leakage of injected CO₂ and H₂S along the wellbore can be described as follows: after supercritical CO₂-H₂S is injected into the storage aquifer, the supercritical CO₂-H₂S plume can migrate in the storage aquifer, driven by the pressure gradient. The interaction between wellbore cement and injected CO₂ and H₂S may cause degradation of wellbore cement and form leakage pathways for CO₂ and H₂S to escape along the wellbore (Figure 1). Based on recent studies involving CO₂ (Kutchko et al., 2008; Kutchko et al., 2009), the degree of cement alteration from supercritical CO₂-H₂S—cement interaction (scenario I) is expected to be different from that of CO₂-H₂S saturated brine—cement interaction (scenario II).

This paper is focused on the effect of the two exposure scenarios (scenario I and scenario II depicted in Figure 1) on the integrity of commonly-used wellbore cement amended by pozzolan additives. It builds on previously published work (Zhang et al., 2013; Zhang et al., 2014) which focused on exposure of pozzolan-amended cements to aqueous solutions in equilibrium with a supercritical mixture of CO₂ and H₂S (21 mol%). The present study investigated the alteration of pozzolan-amended cement in contact with a supercritical CO₂ and H₂S mixture, and the

alteration of pozzolan-amended cement under a high mol% H₂S environment (i.e., 40 mol% H₂S) in a supercritical CO₂ and H₂S mixture. Lab experiments were conducted simulating the exposure conditions of 1) cement—supercritical CO₂/ H₂S interaction, and 2) cement—brine (saturated with CO₂ and H₂S) interaction. After exposure, the cement samples were characterized by scanning electron microscopy-back scattered electron (SEM-BSE) analysis, scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) analysis, and X-ray diffraction (XRD).

The overall objective of this study was to examine the effects on wellbore cement integrity of the two different but related exposure scenarios. The extent of cement alteration and formation of minerals under the two exposure scenarios were investigated. The innovative aspects of this work include: 1) study of the effect of pozzolan additives commonly used in cement preparation on the resistance of cement to CO₂ and H₂S attack; 2) study of the effect of exposure environment (e.g., CO₂ and H₂S in supercritical phase, and CO₂ and H₂S in brine) on the degree of cement alteration; and 3) study of the effect of H₂S content in acid gas on cement alteration.

2. Materials and methods

2.1 Detailed sample preparation, loading and exposure procedures

The pozzolan-cement samples were prepared according to American Petroleum Institute (API) Recommended Practice (RP) 10B (section 17.4) (American petroleum institute, 1997). Two pozzolan : cement ratios (35:65 and 65:35 percent by volume) were used during the mixing process and the two ratios chosen represent the minimum and maximum pozzolan : cement ratios typically employed (Nelson, 1990; Kutchko et al., 2009). Samples with 35 vol% pozzolan

content are hereafter referred to as 35:65 samples, and samples with 65 vol% pozzolan content are hereafter referred to as 65:35 samples. Both “35:65” and “65:35” are the standard notations used in cement industry to describe pozzolan content in pozzolan-amended cement. The cement used in this study was Class H cement, which is API designated wellbore cement. The pozzolan used in this study was a Type F fly ash provided by Halliburton Inc. Type F fly ash, which consists mainly of siliceous spherical particles (typical composition of Type F fly ash can be seen in Table S-1), is the most commonly used cement additive in wells (Nelson, 1990; Kutchko et al., 2009). Pozzolan is added to reduce the density of the slurry and reduce the amount of cement needed, and pozzolan contents of up to 65 vol% have been determined sufficient to maintain low permeability and mechanical strength of cement (Brandl et al., 2010). The samples with 35 vol% pozzolan content (35:65 samples) had a water/solid ratio of 0.51, and the samples with 65 vol% pozzolan content (65:35 samples) had a water/solid ratio of 0.56. Pozzolan-cement samples were cast in the form of cylindrical rods (12 mm diameter $\times$ 130 mm) and were cured in a 1wt% NaCl solution with a pressure of 15 MPa and a temperature of 50 °C. The NaCl concentration of 1 wt% was chosen to be consistent with earlier studies (Kutchko et al., 2007; Kutchko et al., 2011). The total curing time was 28 days, which is consistent with standard industry practice (Kutchko et al., 2007). The curing conditions were chosen to simulate a geologic sequestration depth of approximately 1300 m (Kutchko et al., 2011). Curing cement at an increased pressure and temperature results in a change in the microstructure and distribution of Ca(OH)_2 in cement, which was found to increase the resistance of cement to CO_2 attack (Kutchko et al., 2007). More details about cement preparation and curing can be found in Zhang et al. (2013).

Once cured, the hardened pozzolan-amended cement samples were cut into 12 mm diameter $\times$ 60 mm cylindrical rods and placed in 30 mL glass vials. These in turn were placed in a sample holder with a top deflector plate to prevent the CO₂ and H₂S from blowing directly onto the sample vials during the CO₂ and H₂S filling process. The glass vials were half-filled with a supercritical CO₂-H₂S mixture (scenario I, hereafter referred to as “sc-exposed”) and half-filled with 1 wt % NaCl brine (scenario II, hereafter referred to as “aq-exposed”), so as to mimic the exposure environments of cement—brine interaction and cement—supercritical mixture interaction. Figure 2 shows a schematic of the sample loading design. The exposure experiments were conducted in a 1000 mL stainless steel vessel (Model 4653, Parr Instruments, Moline, IL), and the exposure times were 2.5 days and 28 days. The inner diameter of the vessel was 6.35 cm (2.5 inches) and the interior height of the vessel was 33 cm (13 inches). A supercritical mixture of CO₂ and H₂S (the H₂S : CO₂ ratio of the mixture was adjusted for different test conditions) was pumped into the stainless steel vessel and the pressure and temperature were kept at 150 bar (15.0 MPa) and 50°C, respectively. In the experiments presented in this paper, two H₂S : CO₂ ratios--21 mol % H₂S : 79 mol % CO₂ and 40 mol % H₂S : 60 mol % CO₂--were used for the supercritical mixture. The 21 mol % H₂S : 79 mol % CO₂ experiment presented in this paper is the same as the experiment presented in Zhang et al.(2013), and is included for comparison purposes. The H₂S : CO₂ ratios used are representative of compositions encountered in the field, as the composition of the acid gas licensed for injection in western Canada can vary from 2 mol% H₂S—98 mol % CO₂ to 85 mol% H₂S—15 mol % CO₂ (Bachu et al., 2003). Details about the CO₂ and H₂S pressurizing system and the temperature control system can be found in Hawthorne et al. (2011) and Zhang et al.(2013). It is important to note that under the pressure and temperature conditions described, there could be presence of water in the supercritical mixture in

contact with brine. Therefore, the supercritical phase employed was a “humid” supercritical CO₂-H₂S phase.

After exposure, the cement samples were removed from the vials and cut into slices approximately 1 cm thick using a Buehler IsoMet low speed diamond blade saw. The slices were dried using a N₂ dessicator at 1 atm and room temperature. Once dry, the cement was characterized by the SEM-BSE, SEM-EDS and XRD techniques. The unexposed samples (samples that were not exposed to CO₂ and H₂S) were cured under conditions identical to those of the exposed samples, and the unexposed samples were cut, dried and characterized using the same process as that used for the exposed samples.

2.2 SEM-BSE imaging and SEM-EDS analysis

SEM-BSE analysis was used for direct observation of the cement before and after exposure to CO₂-H₂S using a Quanta™ 600 Scanning Electron Microscope (FEI Inc, Hillsboro, OR). Before analyses, the slices cut from samples were roughly polished with the use of a silicon carbide paper and then finely polished with the use of a low-relief polishing cloth, coated with 1 µm particle size diamond polishing paste. Polishing of samples is necessary because rough-textured surfaces diminish the image quality by reducing contrast and loss of feature definition (Stutzman and Clifton, 1999).

SEM-electron dispersive spectroscopy (EDS) analysis has been widely applied in cement characterization studies (Cocke et al., 1992; Mollah et al., 1994; Kutchko and Kim, 2006; Chen

et al., 2010). Several modes (spot mode, line mode and area mode) are available for SEM-EDS analysis (Edwards et al., 2012). In this work, both the spot and the line mode were utilized to yield the best information regarding sample characterization. The line mode, which yields the weight average of the target element along an EDS measurement line, was used to minimize the effect of sample heterogeneity. Figure S-1 in Supporting Information shows a schematic depicting how the EDS line analysis was conducted. The sulfur wt% was obtained using the average of sulfur wt % values obtained at points along the EDS measurement line. All EDS measurement lines were aligned on the center radius of the sample and the position of each measurement line was described as the distance between the measurement line center and the outer edge of the sample.

The sulfur alteration index (Zhang et al., 2014) was used to evaluate the degree of sulfur alteration of the exposed cement compared with unexposed cement sample. The equation developed to calculate the sulfur alteration index is:

$$I = \frac{1}{N} \sum_{i=1}^N \left(\frac{S_i - S_b}{S_i} \right) \quad (1)$$

where I is the sulfur alteration index of the sample, N is the total number of points analyzed by SEM-EDS, S_i is the sulfur content at point i , and S_b is the average background sulfur content obtained from unexposed samples. For the unexposed 35:65 sample, S_b was equal to 0.59 ± 0.23 %, and for the unexposed 65:35 sample, S_b was equal to 0.48 ± 0.35 % (Zhang et al., 2014). If S_i is smaller than S_b in a measurement, the term $(S_i - S_b)/S_i$ is set to be zero. The range for the

sulfur alteration index is between 0 and 1; the higher the index value, the higher the degree of sulfur alteration.

2.3 Qualitative XRD analysis

Qualitative XRD analysis was applied to determine mineral phases in pozzolan-amended cement samples after exposure under both experimental scenarios. To conduct a qualitative XRD analysis, fine powders of the sample were loaded onto a sample holder. The powders were evenly distributed inside the notch of the sample holder and the top surface of the powders was made flat by placing a glass slide at the top of powders and tapping the slide. The whole sample holder was then placed into the test chamber of a PANalytical X'pert Pro PW 3040/60 diffractometer (PANalytical, Almelo, The Netherlands) for XRD analysis. The testing time for one sample was 40 min and the testing range (2θ range) was from 5° to 70° .

3. Results

3.1 SEM—BSE characterization of 35:65 and 65:35 samples exposed to 21 mol% H₂S

SEM-BSE analyses showed that the sc-exposed 35:65 samples exhibited similar thickness of the carbonate layer and similar distribution of pore space to the aq-exposed 35:65 samples in the exterior region after 28 days of exposure (Figures 3-a and 3-b). Hereby the exterior region refers to the region from the cement-brine interface to 1 mm away into the cement from the interface. Both the sc-exposed and the aq-exposed 35:65 samples had similar distribution of unhydrated cement grains and pore space in the interior region after 28 days of exposure (see Figure S-2 in

Supporting Information) . Compared with the unexposed samples (cured under identical conditions as the exposed samples, Figure S-3), both sc-exposed and aq-exposed 35:65 samples had a thin carbonate ring (confirmed by SEM-BSE images of other studies, e.g., Kutchko et al., 2007; Kutchko et al., 2011; Jacquemet et al., 2012) around the exterior while the interior region of both samples seemed to be unaltered, though there might be ettringite formation in the interior region (Kutchko et al., 2011). Formation of sulfide phase (pyrite) was observed in aq-exposed samples by SEM observation and the results were recorded in Zhang et al.(2013). Formation of pyrite was also observed in sc-exposed samples by SEM observation (see Figure S-4 in Supporting Information).

Different from the 35:65 samples, both the exterior and interior regions of the 65:35 samples were observed to be altered in the SEM-BSE images as a result of CO₂ and H₂S exposure. In the exterior region, the sc-exposed samples had a higher degree of alteration than the aq-exposed samples (Figures 3-c and 3-d), which is shown by the abundance of pore spaces in the sc-exposed samples. The interior region of sc-exposed 65:35 samples had a similar degree of alteration to that of aq-exposed 65:35 samples (with respect to pore space distribution and disappearance of unhydrated cement grains, see Figure S-5 in Supporting Information). Formation of both pyrite and ettringite was observed in the interior region of aq-exposed samples and the results were recorded in Zhang et al. (2013). Formation of pyrite was also observed in the exterior region of sc-exposed samples by SEM observation (see Figure S-4 in Supporting Information). A summary of SEM-BSE characterization results for both the 35:65 and 65:35 samples is provided in Table 1.

3.2 SEM—EDS results of sc-exposed and aq-exposed samples (21 mol % H₂S)

SEM-EDS results of both the sc-exposed and aq-exposed 35:65 samples showed S wt % values decreasing from the interface to the interior of the sample (Figure 4a). The S wt % values in the interior regions of samples were higher than the background S wt %, confirming that sulfur was able to penetrate to the interior of samples within a short time (2.5 days) for both sc-exposed and aq-exposed environments. SEM-EDS line analysis results of the 35:65 samples were consistent with SEM-EDS mapping results (Figure 5), which showed high abundance of sulfur in the exterior region and low abundance of sulfur in the interior region. EDS elemental spectra (Figure 5) showed that pyrite was formed in the exterior region, while ettringite was formed in the interior region. In contrast, decrease of S wt% from the exterior to the interior was not apparent for the 65:35 samples (Figure 4b), due to the fast penetration of H₂S to the interior of these samples.

Table 2 shows the sulfur alteration index values of the sc-exposed and aq-exposed 35:65 and 65:35 samples exposed to 21 mol% H₂S. For the 35:65 sample, after a short exposure time (2.5 days), both exposure scenarios had similar sulfur alteration indices ($I = 0.49$ for the aq-exposed sample and $I = 0.51$ for the sc-exposed sample). However, when the exposure time became longer (28 days), the aq-exposed sample exhibited a significantly higher sulfur alteration index than the sc-exposed sample ($I = 0.64$ for the aq-exposed sample and $I = 0.53$ for the sc-exposed sample), implying that the CO₂/H₂S-saturated brine environment was more aggressive to 35:65 cement than the supercritical mixture environment. For the 65:35 sample, the aq-exposed sample

also had a higher sulfur alteration index than the sc-exposed sample after 2.5 and 28 days of exposure, implying that the H₂S-induced alteration of 65:35 cement was more favorable in the CO₂-H₂S saturated brine environment than in the supercritical CO₂-H₂S environment.

3.3 Qualitative XRD analysis of sc-exposed and aq-exposed samples (21mol % H₂S)

The qualitative XRD analysis results showed that both aq-exposed and sc-exposed samples had very similar mineral compositions in the exterior and interior regions for the same time of exposure based on similar XRD spectra (see Figures S-6 and S-7). Representative minerals identified in the XRD images included aragonite (three characteristic peaks at $2\theta = 26^\circ$, 27° and 33°), quartz (one characteristic peak at $2\theta = 26.5^\circ$) and calcite (one strong characteristic peak at $2\theta = 29.3^\circ$). For all samples tested, strong aragonite and calcite peaks were observed in the exterior region, which indicates that CO₂-induced alteration occurred in the exterior region of both sc-exposed and aq-exposed samples. For the 65:35 samples tested, aragonite and calcite peaks were also observed in the interior region, while for 35:65 samples tested, no aragonite or calcite peaks were observed in the interior region. That is to say, CO₂ penetrated faster in the 65:35 samples than in the 35:65 samples, which caused alteration in the interior region of the 65:35 samples. This result is also consistent with results for exposure to pure supercritical CO₂ (Kutchko et al., 2009), which showed a faster penetration rate of CO₂ in 65:35 samples than 35:65 samples. Pyrite was expected to form due to interaction between H₂S and Fe-rich particles in all samples and conditions, but peak overlap with aragonite (at $2\theta = 33^\circ$) made it difficult to identify by XRD. Ettringite was observed in the interior of both 35:65—aq exposed and 35:65—sc exposed samples (XRD spectrum peaks are at $2\theta = 9^\circ$ and 13°), consistent with data reported by Kutchko et al.(2011).

3.4 SEM—BSE characterization of 35:65 and 65:35 pozzolan-cement samples exposed to 40 mol% H₂S

The sc-exposed 35:65 samples from both the 40 mol% H₂S environment and the 21 mol% H₂S environment had a carbonate layer in the exterior. However, the carbonate layer thickness of the 35:65 sample exposed to 40 mol% H₂S was greater than that of the 35:65 sample exposed to 21 mol% H₂S (0.3 mm vs. 0.1 mm, Figure 6). Next to the carbonate layer, there was a thick decalcification zone in the sc-exposed 35:65 sample from the 40 mol% H₂S environment. The zone next to the decalcification zone consisted of smaller carbonate-rich regions, decalcified regions and unaltered cement grains.

The entire aq-exposed 35:65 sample from the 40 mol% H₂S environment was carbonated, and the degree of carbonation of the aq-exposed 35:65 sample was higher than that of the sc-exposed 35:65 sample. There was also a wide distribution of decalcified zones throughout the aq-exposed 35:65 sample (Figure 6). As a result, a large area of the aq-exposed sample (40 mol% H₂S) was altered by CO₂ and H₂S due to fast penetration the interior region of the sample. The degree of alteration of the aq-exposed sample was higher than that of the sc-exposed sample, which can be seen from the advancement of the decalcified zones to the interior region of the aq-exposed sample.

As for the 65:35 samples, both the aq-exposed and the sc-exposed samples had similar SEM-BSE images in the exterior region (with respect to carbonate layer thickness and decalcified zone thickness). There was a thick carbonate layer (~0.35 mm) formed in the exterior region of both

the aq-exposed and the sc-exposed samples, and a darker decalcified zone next to the carbonate layer. Different from the 35:65 samples, the frontier of the decalcified zone only reached 0.66 mm away from the interface for the sc-exposed sample, and 0.50 mm away from the interface for the aq-exposed sample. The interior region for both samples remained unaltered (Figure 7).

4. Discussion

4.1 Correlation between acid gas—cement interaction and exposure environment

Results presented in Section 3 indicated that for the 35:65 sample, the CO₂/H₂S-saturated brine environment yielded greater alteration than the supercritical CO₂/H₂S environment (for both 21 mol% and 40 mol% H₂S scenarios). For the 65:35 samples, SEM-BSE results showed that supercritical CO₂/H₂S yielded greater alteration for the 21 mol% H₂S scenario, and sulfur alteration index results showed that brine saturated with CO₂ and H₂S yielded greater H₂S-induced alteration. The 65:35 samples exhibited the same resistance to CO₂/H₂S-saturated brine as for supercritical CO₂/H₂S mixture for the 40 mol% H₂S scenario. To explain these results, there is a need to review cement chemistry regarding interaction between minerals in cement and acid gas.

Similar to neat cement (cement without additives), CO₂ mainly reacts with Ca(OH)₂ and amorphous C-S-H (expressed here as Ca₃Si₂O₇·3H₂O) in pozzolan-amended cement to form CaCO₃ (Richardson, 1988; Papadakis, et al., 1989; Zhang and Bachu, 2011). It is important to note that C-S-H does not have a defined formula, and Ca₃Si₂O₇·3H₂O is just an expression for convenience.

The addition of pozzolan results in reactions (Kutchko et al., 2009), which convert most Ca(OH)_2 into amorphous C-S-H. As a result, in pozzolan-amended cement, C-S-H is the main Ca source to produce CaCO_3 .

Similar to neat cement, H_2S mainly reacts with Fe(III) from hydration products of Fe(III)-bearing minerals in pozzolan-amended cement (expressed here as $\text{Fe(OH)}_3(\text{am})$) to produce Fe^{2+} and SO_4^{2-} . H_2S can then react with Fe^{2+} to form pyrite, and SO_4^{2-} can react with Ca^{2+} and Al(OH)_4^- to form ettringite (Kutchko et al., 2011).

For H_2S —cement interaction, several ionic species are involved in the interaction process. Therefore, an aqueous environment is more conducive to H_2S —cement interaction than a supercritical mixture environment. As to CO_2 —cement interaction, the reactions require the dissolution of CO_2 into the pore water of cement paste (Papadakis et al., 1989; Zhang and Bachu, 2011), and the carbonation process requires ionic species (e.g. Ca^{2+} , CO_3^{2-} , H^+) as intermediates. As no ionic species occur in supercritical H_2S - CO_2 , an aqueous environment is more conducive

to CO₂—cement interaction than a supercritical mixture environment. In our experiment, water is able to get dissolved in supercritical H₂S-CO₂ and ionic species are present in the dissolved water, therefore sc-exposed samples are still able to react with CO₂ and H₂S.

Compared with 35:65 samples exposed to pure supercritical CO₂ (Kutchko et al., 2009), the alteration depth was much less for 35:65 samples exposed to supercritical CO₂-H₂S. To be specific, the pure CO₂ results showed a complete carbonation of the whole sample (12 mm diameter × 130 mm cylinders) within 14 days of exposure (Kutchko et al., 2009), while the CO₂-H₂S results show that the inner frontier of the carbonate zone was only 0.4 mm away from the interface into the cement (Figure 3). The faster advancement of the carbonate frontier in samples exposed to pure CO₂ may be explained as follows. The presence of H₂S results in more dissolution of interior materials (providing dissolved Ca) than the CO₂-only scenario, and dissolved Ca is able to migrate to the exterior of cement. More dissolved Ca results in more precipitation of carbonate species in the exterior region, which causes a reduction of the effective diffusion coefficient of CO₂ compared with the CO₂-only scenario. Due to a reduction of the effective diffusion coefficient of CO₂, the advancement of the carbonate frontier in samples exposed to H₂S-CO₂ is slower than that in samples exposed to pure CO₂. Furthermore, we hypothesize that the fast penetration of H₂S to the interior of samples may result in adsorption of H₂S to surfaces of cementitious materials (Vollertsen et al., 2008), and a subsequent inhibition of carbonation.

For the aq-exposed 35:65 sample from the 40 mol% H₂S environment, there is a development of decalcified and carbonated regions in a patchy pattern. An explanation of this phenomenon is that no protective layer was formed in the exterior of the sample, and thus CO₂ was able to penetrate to the interior of the sample. As cement materials may not be uniformly distributed in the interior of this sample, carbonated regions can only be seen in the regions close to cement materials which provide Ca²⁺ for calcite precipitation. In contrast, regions with high content of pozzolan do not have sufficiently high content of cement materials, and thus such regions do not have calcite precipitation due to a lack of Ca²⁺ supply.

Both this study and previous studies (Jacquemet et al., 2008; Jacquemet et al., 2012) predict carbonation of calcium silicate hydrates, formation of a dense carbonate layer in the exterior of cement, and ferrite sulfidation. Different from this study, a re-dissolution of calcite on the surface of the calcite-rich layer was not observed by Jacquemet et al.(2012), probably due to a higher temperature used in their experiment (120°C vs. 50°C in this study), which makes formation of calcite more thermodynamically favorable. The absence of dissolution of the exterior calcite in Jacquemet et al.(2012) is also favored by the low W/R ratio used by Jacquemet et al., which favors a buffering of the exterior brine.

The pozzolan-amended cement (Type F fly ash + class H Portland cement) used in our study is less resistant to CO₂ and H₂S attack compared with class G Portland cement used in Jacquemet et al.(2012). Significant integrity loss of the 35:65 cement is apparent in the SEM-BSE image (Figure 6b) for exposure to brine saturated with 40 mol% H₂S and 60 mol% CO₂ (total pressure

is 150 bar). Alteration of the 65:35 cement in the interior is also apparent in the SEM-BSE image (Figure 3c) for exposure to brine saturated with 21 mol% H₂S and 79 mol% CO₂. However, the interior of class G Portland cement was not altered after 60 days of exposure to brine saturated with H₂S and CO₂, even given a “harsher” exposure environment (66 mol% H₂S and 34 mol% CO₂, total pressure is 500 bar) (Jacquemet et al., 2012). A possible explanation is that the class G cement used in Jacquemet et al. (2012) was amended with silica flour, which enhances the resistance of the cement to CO₂ and H₂S alteration.

In summary, the nature of CO₂-cement and H₂S-cement reactions, which involves dissolved species, explains the SEM-BSE and sulfur alteration index results indicating that the aq-exposed 35:65 samples were altered more than the sc-exposed 35:65 samples. SEM-BSE results of the aq-exposed and sc-exposed 35:65 samples from the 40 mol% H₂S environments also support the conclusion that the aqueous environment is more conducive to both H₂S—cement and CO₂—cement interactions than the supercritical CO₂-H₂S mixture environment. Sulfur alteration index results for the 65:35 samples also showed that the aq-exposed 65:35 samples were altered more by H₂S than the sc-exposed 65:35 samples. As to the impact of pozzolan content, lower pozzolan content samples (i.e., 35:65 samples) were more resistant to CO₂ and H₂S alteration than high pozzolan content samples (i.e., 65:35 samples). However, SEM-BSE results also showed inconsistent behaviors. For example, sc-exposed 65:35 samples were altered more than aq-exposed 65:35 samples. Aq-exposed 65:35 samples were altered more than aq-exposed 35:65 samples when exposed to 21 mol% H₂S supercritical mixtures, while aq-exposed 65:35 samples were altered less than aq-exposed 35:65 samples when exposed to 40 mol% H₂S supercritical

mixtures. The inconsistent behavior is attributable to the complicated nature of the pozzolan-cement-brine-supercritical CO₂ and H₂S system, and there is no simple explanation.

5. Conclusions

For 35:65 samples, the aqueous environment (e.g., brine saturated with CO₂ and H₂S) was more conducive to CO₂ and H₂S attack. The same samples exposed to a supercritical mixture of 79 mol% CO₂ and 21 mol% H₂S showed no significant integrity loss. For samples exposed to 21 mol% H₂S, 35:65 samples were more resistant to H₂S and CO₂ alteration than 65:35 samples. The formation of a protective CaCO₃ layer in the exterior of 35:65 samples exposed to 21 mol% H₂S protects the interior of the cement from CO₂ and H₂S induced alteration. For 65:35 samples exposed to 21 mol% H₂S, the supercritical mixture of CO₂ and H₂S caused greater alteration than brine, and the alteration of samples in both environments was significant in both the exterior and the interior regions. As no protective CaCO₃ layer was formed in 65:35 samples exposed to 21 mol% H₂S, there was a loss of materials and an increase of pore space in the interior of 65:35 samples exposed to 21 mol% H₂S. However, if H₂S content in acid gas was raised to 40 mol%, the 65:35 samples seemed to be more resistant to H₂S and CO₂ alteration than 35:65 samples. A protective carbonate layer would be formed in the exterior of 65:35 samples, due to enhanced dissolution of Ca-bearing minerals in the interior region. Further investigations are needed to explain why an increase of H₂S content can result in release of more Ca²⁺.

Overall, both pozzolan content in wellbore cement and H₂S content in acid gas affect wellbore cement integrity under geologic co-sequestration conditions. There is great potential for the interior to experience pore space-increasing alteration with very high pozzolan content under

both exposure environments, and there is a low potential for the interior to experience pore space-increasing alteration with low pozzolan content under both exposure environments given a H₂S content of 21 mol%. This work, along with other published works (Kutchko et al., 2009; Kutchko et al., 2011; Zhang et al., 2013), suggests that abandoned wells with a volumetric pozzolan : cement ratio of 35:65 or less will have lower risk of degradation from the perspective of interior alteration given a H₂S content of 21 mol% or less. However, this work also shows that given a high H₂S content (e.g., 40 mol%), abandoned wells with a volumetric pozzolan : cement ratio of 65:35 are able to resist interior alteration, due to formation of a protective carbonate layer. In summary, if a protective carbonate layer is able to form in the exterior of the pozzolan-amended cement, the alteration of cement interior will be minimized.

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Table 1: Summary of SEM-BSE results

Cement	Carbonate band	Exterior alteration	Interior alteration
21-79 mol%-H₂S-CO₂			
Supercritical exposed (sc-exposed)			
35:65	yes	moderate	Minimal (no carbonate; ettringite formation was observed by XRD)
65:35	no	severe	yes (carbonate formation was observed by XRD; no ettringite)
Aqueous exposed (aq-exposed)			
35:65	yes	moderate	Minimal (no carbonate; ettringite formation was observed by XRD)
65:35	no	moderate	yes (carbonate formation was observed by XRD; no ettringite)
40-60 mol%-H₂S-CO₂			
Supercritical exposed (sc-exposed)			
35:65	yes	moderate	yes (carbonate formation was observed by XRD; no ettringite)
65:35	yes	moderate	Minimal (no carbonate; ettringite formation was observed by XRD)
Aqueous exposed (aq-exposed)			
35:65	no	severe	severe (carbonate formation was observed by XRD; no ettringite)
65:35	yes	moderate	Minimal (no carbonate;

ettringite formation
was observed by
XRD)

Note:

“Moderate” refers to a state that new minerals can be observed in the SEM-BSE image, but no significant integrity loss (e.g., morphology change and obvious increase of pore space due to significant dissolution of minerals) can be observed.

“Severe” refers to a state that both new minerals and significant integrity loss can be observed in the SEM-BSE image.

For samples exposed to 40 mol% H₂S, aq-exposed 65:35 sample was more resistant to CO₂ and H₂S alteration than aq-exposed 35:65 sample. A possible explanation is, there is formation of both CaCO₃ and FeCO₃ on the surface of aq-exposed 65:35 sample, and the major Fe source for FeCO₃ formation is pozzolan additives. As the 65:35 sample has a high pozzolan content, formation of a FeCO₃-rich carbonate layer is favored. Formation of FeCO₃ under a reduced environment rich in SO₂ or H₂S has been documented in other studies (Palandri and Kharaka, 2005; Garcia et al., 2011). For this study, no experimental evidence is available to support this explanation, and more investigations are needed.

Table 2: Sulfur alteration index values of both 35:65 and 65:35 samples (21 mol% H₂S-79 mol% CO₂)

Sample	I
35:65 2.5 days (aq-exposed)	0.49
35:65 2.5 days (sc-exposed)	0.51
35:65 28 days (aq-exposed)	0.64
35:65 28 days (sc-exposed)	0.53
65:35 2.5 days (aq-exposed)	0.79
65:35 2.5 days (sc-exposed)	0.77
65:35 28 days (aq-exposed)	0.83
65:35 28 days (sc-exposed)	0.76

Figure

Figure 1: Schematic of CO₂ and H₂S interactions with wellbore cement under two exposure scenarios: scenario I is the exposure of wellbore cement to supercritical CO₂ and H₂S; scenario II is the exposure of wellbore cement to brine saturated with CO₂ and H₂S.

Figure 2: Photograph and schematic of the sample exposure unit. Multiple samples can be placed in the apparatus at the same time. The portion of the sample exposed to the brine is referred to as “aq-exposed” and the portion of the sample exposed to supercritical CO₂ and H₂S is referred to as “sc-exposed”.

Figure 3: SEM-BSE images of exterior regions of the 35:65 and 65:35 samples exposed for 28 days, aq-exposed and sc-exposed portions (21 mol % H_2S). P = pore space.

Figure 4: a) S wt % values obtained from SEM-EDS line analysis from the interface to the interior of samples tested. Samples tested were: 35:65 samples exposed to 21 mol% H₂S for 2.5 days, aq-exposed and sc-exposed portions; 35:65 samples exposed to 21 mol% H₂S for 28 days, aq-exposed and sc-exposed portions. b) S wt % values obtained from SEM-EDS line analysis

from the interface to the interior of samples tested. Samples tested were: 65:35 samples exposed to 21 mol% H₂S for 2.5 days, aq-exposed and sc-exposed portions; 65:35 samples exposed to 21 mol% H₂S for 28 days, aq-exposed and sc-exposed portions.

Figure 5: SEM-EDS mapping and EDS elemental spectra showing the formation of S-rich mineral (sample: 35: 65 sample exposed to 21 mol% H_2S for 28 days, aq-exposed portion). Pyrite mainly forms in the exterior region of the sample, and ettringite mainly forms in the interior region of the sample.

Figure 6: SEM-BSE images of the exterior regions of 35:65 samples exposed to 40 mol% H₂S for 28 days, sc-exposed portion (a) and aq-exposed portion (b). Zone A corresponds to the carbonate-rich zone, Zone B corresponds to the decalcified zone, Zone C corresponds to a combination of carbonate-rich zone, decalcified zone and unaltered zone.

Figure 7: SEM-BSE images of the exterior regions of 65: 35 samples exposed to 40 mol% H₂S for 28 days, sc-exposed portion (a) and aq-exposed portion (b). Zone A corresponds to the carbonate-rich zone, Zone B corresponds to the decalcified zone, and Zone C corresponds to the unaltered zone.