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Mineral changes in cement-sandstone matrices induced by biocementation

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ABSTRACT

Prevention of wellbore CO_2 leakage is a critical component of any successful carbon capture, utilization, and storage program. *Sporosarcina pasteurii* is a bacterium that has demonstrated the potential ability to seal a compromised wellbore through the enzymatic precipitation of $CaCO_3$. Here we investigate the growth of *S. pasteurii* in a synthetic brine that mimics the Illinois Basin and on Mt. Simon sandstone encased in Class H Portland cement under high pressure and supercritical CO_2 (P_{CO2}) conditions. The bacterium grew optimum at 30 °C compared to 40 °C under ambient and high pressure (10 MPa) conditions; and growth was comparable in experiments at high P_{CO2}. *Sporosarcina pasteurii* actively induced the biomineralization of $CaCO_3$ polymorphs and $MgCa(CO_3)_2$ in both ambient and high pressure conditions as observed in electron microscopy. In contrast, abiotic (non-biological) samples exposed to CO_2 resulted in the formation of surficial vaterite and calcite. The ability of *S. pasteurii* to grow under subsurface conditions may be a promising mechanism to enhance wellbore integrity.

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1. Introduction

Carbon sequestration pilot programs are being conducted to evaluate the injection of carbon dioxide (CO_2) into deep geological formations to mitigate the rise in atmospheric CO_2 concentrations. During carbon sequestration, it is essential to maintain wellbore integrity to prevent the injected CO_2 from leaking either into adjacent formations or being released back into the atmosphere (e.g. McGrail et al., 2006). Several pathways exist in which CO_2 leakage could lead to groundwater or surficial aquifer contamination, but the probability of CO_2 leakage is greater at the cement-host lithologies interface, around the annulus, and at the cement plug (e.g. Duguid et al., 2011; Gasda et al., 2013).

Class G or H Portland cement paste is used in oil and gas wells and is composed of unhydrated calcium silicates, calcium aluminoferrites, magnesium oxide phases, and hydrated phases such as calcium hydroxide ($Ca(OH)_2$) or semi-amorphous calcium silicate hydrate (known as C–S–H in cement nomenclature) (Taylor, 1997). Carbon dioxide injected during carbon capture and storage (CCUS) exists as a supercritical fluid at depths greater than 800 m where critical pressures (>7.38 MPa), and temperatures (>31.1 °C) exist. Several studies have documented alteration of hydration products in the cement paste in the presence of supercritical CO_2 and CO_2-saturated brine (e.g. Kutchko et al., 2008; Barlet-Gouedard et al., 2009). Furthermore, poor bonding or emplacement of cement combined with supercritical CO_2 conditions may reduce the effectiveness of carbon capture. The reaction of CO_2 with cement is provided below with Eqs. (1)–(5) (Kutchko et al., 2008). This is a two-step process where the formation of carbonic acid results in the dissolution of $Ca(OH)_2$, and subsequently the conversion of C–S–H into amorphous silica gel.

$$CO_{2(g)} \rightarrow CO_{2(aq)} \tag{1}$$

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow \mathrm{HCO_3}^- + H^+ \leftrightarrow \mathrm{2H}^+ + {CO_3}^{2-} \tag{2}$$

$$Ca(OH)_{2(s)} \rightarrow Ca^{2+}{}_{\mathrm{(aq)}} + 2OH^-{}_{\mathrm{(aq)}} \tag{3}$$

$$Ca^{2+}{}_{\mathrm{(aq)}} + \mathrm{HCO_3}^-{}_{\mathrm{(aq)}} + \mathrm{OH}^-{}_{\mathrm{(aq)}} \rightarrow CaCO_{3(s)} + \mathrm{H_2O} \tag{4}$$

$$2H^+ + {CO_3}^{2-} + \text{C-S-H}_{(s)} \rightarrow CaCO_{3(s)} + H_2O_{(aq)} + \text{am-SiO}_{2(s)} \tag{5}$$

Microbially induced mineralization is a potential mechanism to control fluid migration or seal wellbores via the bioprecipitation of calcium carbonate (Dejong et al., 2013; Phillips et al., 2013). The use of *Sporosarcina pasteurii* to improve oil recovery by modifying preferred flow paths in oil-bearing formations was proposed by Ferris and Stehmeier (1992) and most recently Phillips et al.

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(2013) reviewed the utilization of biomineralization to increase wellbore cement integrity. *Sporosarcina pasteurii* produces urease as a metabolic byproduct and in the presence of urea and Ca^{2+}, deposition of calcium carbonate occurs (Fujita et al., 2000; Fujita et al., 2008; Mitchell and Ferris, 2006; Mitchell et al., 2008, 2010; Colwell et al., 2005; Phillips et al., 2013, 2015). Exploitation of this reaction in engineered systems is useful to strengthen unconsolidated porous media (Van Paassen, 2011) and reduce permeability of sandstone fractures (Phillips et al., 2015). Mitchell et al. (2013) found *S. pasteurii* to be metabolically active and capable of precipitating calcium carbonate in saline and porous synthetic media in the presence of supercritical CO_2 at 7.5 MPa and 32 °C. This work showed that bacterial ureolysis (hydrolysis of urea) led to increased pH (up to 9.1) and nucleation of calcite. The total amount of calcite precipitated was limited by mass transport of Ca^{2+} ions and urea.

Microbially produced urease catalyzes the hydrolysis of urea into carbonic acid and ammonia; carbonic acid and ammonia dissociate in water to form ammonia, hydroxide, and bicarbonate ions. Provided there is a calcium source, this reaction will lead to the subsequent precipitation of calcium carbonate as described in Eq. (6) (Mitchell et al., 2013). For *S. pasteurii* to be used at the field scale to effectively seal wellbores, its growth and ability to produce urease needs to be evaluated at conditions that will be found in wellbore environments, specifically high temperature, salinity, and pressure.

$$CO(NH_2)_2 + 2H_2O + Ca^{2+} \leftrightarrow 2NH_4{}^{+} + CaCO_3 \qquad (6)$$

Class H Portland cement is commonly used in wellbores making it amenable to the reaction above in the presence of calcium enriched brine. Well temperatures can exceed 40 °C and pressure increases with depth. Phillips et al. (2015) demonstrated in laboratory experiments that pressures (4.5 MPa) in wells would not be detrimental to *S. pasteurii*'s ability to seal cracks in the cement. Further, moderate temperature (32 °C) and pressure (7.5 MPa) did not preclude this species from mediating the precipitation of $CaCO_3$ (Mitchell et al., 2013). However, much is left to be learned about the synergistic impacts of temperature, brine, and pressure on the growth and ability of *S. pasteurii* to precipitate $CaCO_3$ under the conditions where fractured sealing would be most beneficial to supercritical CO_2 storage. In both of the previously cited papers, the medium used to test the efficacy of *S. pasteurii* was a nutrient rich solution that is unlike the brine found in those aquifers most likely to be used for supercritical CO_2 injection. We investigate the mineralogical changes induced by *S. pasteurii* in cement bonded to Mt. Simon sandstone immersed in high salinity brine at various temperature and pressure conditions, and in the presence of supercritical CO_2. Supporting experiments were conducted on bacteria growing in a nutrient rich broth and brine, as well as precipitation on membrane filters and cement-sandstone samples to test the limiting factors on the growth of *S. pasteurii* in subsurface conditions.

2. Experimental methods

2.1. Sample preparation

Table 1
Top 5 salt species used to represent the Mt. Simon sandstone from the Illinois Basin at the expected 1220–1250 m depth (Hazen well data, Illinois State Geological Survey, 2010).

Simulated Mt. Simon Sandstone Illinois Basin Brine	Quantity, g/L
$NaHCO_3$	**0.84**
NaCl	**59.36**
$MgCl_2$	**5.71**
Na_2SO_4	**2.84**
$CaCl_2$	**18.85**
Total	**87.60**

To simulate *in situ* (down hole pressure and temperature) conditions in the experiments, we used a sandstone sample cored from the Mt. Simon formation, prepared raw Class H Portland cement, and prepared a brine solution to match that of the fluids in a target CO_2 injection site in the Mt. Simon formation. The brine was comprised of NaCl, $CaCl_2$, $MgCl_2$, and trace salt species (Table 1; based on Hazen core data, Illinois State Geological Survey). All sample conditions are described in Table 2. The Mt. Simon sandstone is a coarse grained sandstone that overlies Precambrian granite and underlies fine-grained Eau Claire Formation (c.f., Bonneville et al., 2013). A core sample from the Mt. Simon Formation acquired 1198 m below land surface (provided by J. Szecsody, Pacific Northwest National Laboratory) was sub-cored into 1.3 cm diameter cylinders.

The raw Class H Portland cement powder (Lafarge) contained 64.5 wt.% tricalcium silicate (Ca_3SiO_5), 11.77 wt.% dicalcium silicate (Ca_2SiO_4), 13.24 wt.% calcium aluminoferrite (Ca_4AlFeO_5), 2.94 wt.% MgO, 2.8 wt.% $SO_4{}^{2-}$, and 0.16 wt.% total alkali content (Na_2O). This cement has no tricalcium aluminate ($Ca_3Al_2O_6$). The cement powder contained 0.62% free lime (CaO). The [water] loss on ignition (LOI) was computed to be 0.73, a value that is within acceptable ASTM limits. The cement slurry was prepared using a water-rock (w/c) ratio of 0.38 composed of 500 g dry cement powder and 190 mL of distilled water according to American Petroleum Institute (API) Recommended Practice RP10-B. The sandstone sub-cores were encased in a cement slurry, cured for 24 h in a humidity controlled room, removed from the mold, and subsequently immersed in a 30 °C Mt. Simon brine bath to cure for 28 days at 1) ambient pressure or 2) at 10 MPa (hydraulic or $P_{CO2} = 10$ MPa) to simulate the expected pressure at the target injection site. All cores were cured at the pressure that they would be subjected to during the respective experiments. After the curing period, the cement-sandstone cores were cut into 1.3 cm slices for detailed imaging and characterization at ambient and high pressures and at variable temperatures, as described below.

2.2. Culture growth experiments at ambient conditions

Sporosarcina pasteurii (strain 11859) used for all experiments was obtained from the American Type Culture Collection (ATCC). We tested growth in 1) both a nutrient-rich broth, 2) in calcium-enriched Mt. Simon brine, and 3) on cement-sandstone cores immersed in Mt. Simon brine. An additional experiment quantified growth on membrane filters placed on top of an agar made with the nutrient-rich broth. The ideal growth medium for this strain (referenced as 'ATCC medium') is composed of 20.0 g yeast extract and 10.0 g ammonium sulfate in 1.0 L 0.13 M Tris Buffer (pH 9.0). The Tris Buffer was autoclaved (sterilized) prior to adding the yeast extract and ammonium sulfate, and then filter-sterilized using 0.2 μm syringe filters. All glassware used throughout the experiment was heat sterilized by autoclave. Early in the experiments, we observed rapid and abiotic precipitation of $MgHPO_4$ when an inoculum in ATCC medium was added to the brine as a result of brine-medium interactions (see sections 3.1 and 4.1). To prevent formation of $MgHPO_4$ crystals in subsequent experiments, an aliquot (0.5 mL to 1.0 mL) of the inoculum was centrifuged (1200 rpm for 10 min) to pellet the bacteria and then the supernatant medium was replaced with brine. The cell pellets were rinsed at least 3× with brine to remove all traces of the ATCC medium prior to inoculating the brine solution. Sterilized Mt. Simon brine was augmented with 1 or 10 g per liter of urea, as this substrate is needed for the hydrolysis reaction to occur over a 7 day period.