



Effect of oxygen co-injected with carbon dioxide on Gothic shale caprock–CO₂–brine interaction during geologic carbon sequestration

Hun Bok Jung, Wooyong Um, Kirk J. Cantrell *

Pacific Northwest National Laboratory, Richland, WA 99354, United States

ARTICLE INFO

Article history:

Received 3 April 2013

Received in revised form 18 June 2013

Accepted 20 June 2013

Available online 29 June 2013

Editor: J. Fein

Keywords:

Gothic shale

Carbon sequestration

Oxygen

Pyrite oxidation

Metal mobilization

ABSTRACT

Co-injection of oxygen, a significant component in CO₂ streams produced by the oxyfuel combustion process, can cause a significant alteration of the redox state in deep geologic formations during geologic carbon sequestration. The potential impact of co-injected oxygen on the interaction between synthetic CO₂–brine (0.1 M NaCl) and shale caprock (Gothic shale from the Aneth Unit in Utah) and mobilization of trace metals was investigated at ~10 MPa and ~75 °C. A range of relative volume percentages of O₂ to CO₂ (0, 1, 4 and 8%) were used in these experiments to address the effect of oxygen on shale–CO₂–brine interaction under various conditions. Major mineral phases in Gothic shale are quartz, calcite, dolomite, montmorillonite, and pyrite. During Gothic shale–CO₂–brine interaction in the presence of oxygen, pyrite oxidation occurred extensively and caused enhanced dissolution of calcite and dolomite. Pyrite oxidation and calcite dissolution subsequently resulted in the precipitation of Fe(III) oxides and gypsum (CaSO₄·2H₂O). In the presence of oxygen, dissolved Mn and Ni were elevated because of oxidative dissolution of pyrite. The mobility of dissolved Ba was controlled by barite (BaSO₄) precipitation in the presence of oxygen. Dissolved U in the experimental brines increased to ~8–14 µg/L, with concentrations being slightly higher in the absence of oxygen than in the presence of oxygen. Experimental and modeling results indicate the interaction between shale caprock and oxygen co-injected with CO₂ during geologic carbon sequestration can exert significant impacts on brine pH, solubility of carbonate minerals, stability of sulfide minerals, and mobility of trace metals. The major impact of oxygen is most likely to occur in the zone near CO₂ injection wells where impurity gases can accumulate. Oxygen in CO₂–brine migrating away from the injection well will be continually consumed through the reactions with sulfide minerals in deep geologic formations.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Carbon capture, utilization and storage (CCUS) is a critical technology under consideration for the mitigation of global warming by storing billions of tons of carbon dioxide (CO₂) annually emitted from stationary industrial sources into deep geologic formations. Among various possible CO₂ storage reservoirs for geological carbon sequestration (GCS), deep saline aquifers appear to be the most promising option because they are nearly ubiquitous worldwide with an estimated potential storage volume of up to 10,000 Gt CO₂, while deep saline aquifers typically do not meet drinking water standard due to high total dissolved solids (TDS) (>10,000 ppm TDS) (Bruant et al., 2002). In addition, deep saline aquifers are often located near major CO₂ sources. The injected CO₂ will form a supercritical fluid in deep geologic reservoirs (>~800 m) where temperatures and pressures are greater than 31 °C and 7.4 MPa, respectively (Bachu,

2003; White et al., 2003). Because of the buoyancy effect resulting from the difference in density between supercritical CO₂ and saline groundwater, injected CO₂ could escape upward into overlying formations and potentially to the land surface if zones of high permeability were to exist (Gasda et al., 2004). Therefore, an impermeable caprock formation (e.g., shale) overlying a permeable geological reservoir is required to keep the buoyant CO₂ within the storage formation and ensure permanent geological carbon storage. Argillaceous rocks (e.g. mudstones, clays, and shales) and evaporites (e.g. salts and anhydrite) are commonly identified caprocks for geologic carbon sequestration (Griffith et al., 2011; Song and Zhang, 2013).

The lower boundary of the caprock will be in contact with CO₂ saturated water or supercritical CO₂ during geologic carbon storage. Depending on the phase of CO₂, there are generally three pathways for CO₂ entry into the caprock: capillary breakthrough as supercritical CO₂, molecular diffusion as either supercritical CO₂ or dissolved CO₂, and CO₂–brine migration through the caprocks (Liu et al., 2012). Diffusion of CO₂ into the caprock of limited porosity is often slow even for high concentration gradients, and may be limited to thin basal layers of the caprock (Gaus et al., 2005; Lu et al., 2009; Alemu et al., 2011). High rates of CO₂ injection may cause over-pressurization of

* Corresponding author at: Pacific Northwest National Laboratory, P.O. Box 999, K6-81, 902 Battelle Boulevard, Richland, WA 99354, United States. Tel.: +1 509 371 7175; fax: +1 509 371 7249.

E-mail address: kirk.cantrell@pnnl.gov (K.J. Cantrell).

the reservoirs relative to the ambient hydrostatic pressure and may open faults and fracture zones, creating pathways for CO₂–brine migration (Rutqvist and Tsang, 2002). In a carbon storage site, caprock may contain faults or fractures from a few meter-scale to kilometer-scale. In the presence of caprock fractures, upward CO₂ leakage from the reservoir formation to the overlying underground sources of drinking water (USDWs) could occur at high rates, and result in contamination from mobilized trace metals and intrusion of saline groundwater (Little and Jackson, 2010; Wilkin and Digiulio, 2010). There is field evidence indicating upward flow of brine to shallow aquifers through high permeability conduits such as fracture zones and faults at the Chimayo site in New Mexico, and at a site in north-eastern Pennsylvania (Marcellus shale formation) (Keating et al., 2012; Warner et al., 2012). Major effects of CO₂ leakage into an overlying aquifer include decreased pH due to carbonic acid formation, increased alkalinity due to weathering reactions that consume protons, increased TDS, and increased concentrations of inorganic and organic contaminants. Trace metals/metalloids can be released by interactions between metal oxyhydroxides or metal sulfide minerals in the reservoir rock or caprock and the acidic CO₂-rich brine (Kharaka et al., 2006; Wigand et al., 2008; Keating et al., 2010; Little and Jackson, 2010).

Coal-fired power plant effluent or flue gas may contain a number of gas impurities such as hydrogen sulfide (H₂S), methane (CH₄), nitrogen (N₂), nitrous oxide (NO_x), sulfur dioxide (SO₂), and oxygen (O₂) (Koenen et al., 2011). The gas impurities in a liquefied CO₂ stream can interact with saline groundwater and reservoir rock as well as caprock during geologic carbon sequestration. Nonetheless, only a few studies have focused on the effect of gas impurities such as SO₂, NO₂, and H₂S on saline groundwater, reservoir rock, and caprock (Knauss et al., 2005; Crandell et al., 2010; Wilke et al., 2012), while most experimental, modeling, and field studies have investigated pure CO₂–rock interactions (Wang and Jaffe, 2004; Kharaka et al., 2006; Wigand et al., 2008; Wilkin and Digiulio, 2010; Wilke et al., 2012). From a geochemical perspective, O₂, H₂S, SO₂, and NO_x are considered the most important gaseous impurities (Koenen et al., 2011) because these impurities can influence the pH of the formation water and disturb the redox condition of brines in contact with the reservoir rock and caprock. The concentration of O₂ in typical flue gas streams ranges from 3 to 12 vol.% (Lee et al., 2009), and substantial amounts of oxygen can still be present in CO₂ streams after capture, particularly for oxyfuel combustion plants. For example, the effluent CO₂ stream from a CanmetENERGY (Ottawa, Ontario, Canada) oxyfuel fluidized bed pilot plant combustor contained gas impurities that included 5.2 vol.% O₂, 221 ppm CO, 1431 ppm SO₂, and 243 ppm NO (Jia et al., 2007). The IEA Greenhouse Gas R&D Programme (IEAGHG, 2004) has provided an additional estimate of oxyfuel combustion plant effluent impurities: 5.8 vol.% N₂, 4.7 vol.% O₂, 4.47 vol.% Ar, 100 ppm NO_x, 50 ppm SO₂, 20 ppm SO₃, and 50 ppm CO.

A number of previous experimental studies have focused on changes in the major ion composition and mineralogical alteration during the interaction between caprock and pure CO₂–brine or supercritical CO₂ (Credoz et al., 2009; Alemu et al., 2011; Liu et al., 2012; Wilke et al., 2012). Although oxygen is a common component in CO₂ streams and co-injection of oxygen can significantly alter the redox state of deep geologic formation, few studies have investigated the effect of co-injected oxygen on the CO₂–brine–rock interaction. During geologic carbon sequestration, oxidative dissolution of sulfide minerals in the reservoir rock or caprock can occur in the presence of dissolved oxygen (Lowson, 1982; Moses et al., 1987; Evangelou and Zhang, 1995), and subsequently release trace metals into the brine (Keating et al., 2010; Little and Jackson, 2010). This study focuses on understanding the potential impacts of co-injected oxygen in the CO₂ stream on the CO₂–brine–shale caprock interaction and mobilization of trace metals from shale caprock (Gothic shale from the Aneth Oil Field, Utah) during geological carbon sequestration. Because of the

loss of CO₂ transport and storage capacity as well as the increase in pressure requirements and compression work, it is recommended that the total volume of non-condensable gases (N₂, H₂, CH₄, O₂ and Ar) in the CO₂ stream should not exceed 4% (de Visser et al., 2008). Therefore, impurity oxygen in a typical CO₂ stream is likely to be regulated below 4 vol.% prior to the CO₂ injection. However, during the CO₂ injection, impurity oxygen can accumulate in the CO₂–brine near the injection well by diffusion and dissolution into the brine (Koenen et al., 2011). The experiments were thus conducted at 1 vol.% oxygen as well as 4–8 vol.% oxygen to explore the potential reactions of shale–CO₂–brine and metal mobilization under various oxygen concentration scenarios.

2. Materials and methods

2.1. Background of Aneth Oil Field, Paradox Basin, Utah

A core sample of Gothic shale (caprock) overlying the Desert Creek Limestone (reservoir rock) at approximately 1640 m depth was collected from a Texaco well (H-117) located within a carbon sequestration site at the Aneth Oil Field in southeastern Utah. A core from the Aneth Unit H-117 well that contains a nearly complete unslabbed section of Gothic shale was selected for detailed representative analysis of the Desert Creek reservoir caprock. Located in the Paradox Basin of southeastern Utah within the Colorado Plateau, the Greater Aneth is a stratigraphic trap, with fractures and small faults (Griffith et al., 2011). The Greater Aneth has been designated to demonstrate combined enhanced oil recovery (EOR) and CO₂ sequestration under the auspices of the Southwest Regional Partnership on Carbon Sequestration, sponsored by the U.S. Department of Energy. In the Aneth Unit, the Gothic shale is remarkably uniform, consisting of black to gray, laminated to thin-bedded, dolomitic marine shale. The shale ranges in thickness from 5 to 27 ft (1.5 to 8.2 m), averaging 15 ft (3.6 m) and generally thins over the carbonate buildup complex in the Desert Creek zone. Diagenetic products include abundant pyrite and varying amounts of rare to common dolomite/ankerite (Rutledge, 2010). Modest amounts of clay microporosity likely occur, but the permeability is in the nanodarcy range (Rutledge, 2010). Naturally occurring fractures in the shale caprock are documented mostly in the northern Paradox Basin, with some in the southern regions of the basin, ranging from “hairline” to “massive,” and the fractures are filled with secondary precipitates of carbonates, halides, anhydrite, and pyrite (Hite and Lohman, 1973; Tromp, 1995; Tuttle and Klett, 1996).

2.2. Experimental methods

Two sets of experiments were conducted at rock-to-brine ratios of 22 and 33 g/L by reacting 4 or 6 g of Gothic shale with 180 mL of CO₂–brine over a period of 4–6 weeks. The rock-to-brine ratios in these experiments are comparable to that in previous experimental studies, which ranged from ~20 to ~50 g/L (Alemu et al., 2011; Liu et al., 2012; Wilke et al., 2012). Gothic shale was crushed to a sand-sized fraction (0.063–2 mm) to increase reactivity. After thorough homogenization, Gothic shale subsamples were added to pressure vessels (Parr Instrument Company; Model: 4760 with 300 mL capacity) with polytetrafluoroethylene (PTFE) liners containing a synthetic brine (0.1 M NaCl). To minimize corrosion of the pressure vessels made of HC alloy (ferritic Fe–Cr–Ni alloy), the vessel, heads, and fittings were treated with a silicon coating (SilcoTek, Bellefonte, PA). In addition, titanium thermowells were used. After sealing each vessel, the system was purged with pure N₂ gas for 10 minutes to remove atmospheric oxygen. Next, O₂ and CO₂ were injected into the vessel with a high-pressure syringe pump (Teledyne Isco) through a gas inlet valve to produce a range of O₂-to-CO₂ volume percentages (0%, 1%, 4%, and 8%). Pressure and temperature

Download English Version:

<https://daneshyari.com/en/article/6436828>

Download Persian Version:

<https://daneshyari.com/article/6436828>

[Daneshyari.com](https://daneshyari.com)