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SO_2–CO_2 and pure CO_2 reactivity of ferroan carbonates at carbon storage conditions

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ABSTRACT

Carbon dioxide captured and stored geologically from industrial sources such as coal fired and oxyfuel power stations or cement processing may contain impurity gases such as SO_2. Carbonates including siderite and ankerite are some of the most reactive minerals present in siliciclastic reservoirs. The reactivity of crushed siderite–ankerite to pure supercritical CO_2 and impure SO_2–CO_2 dissolved in water was compared in a combined experimental and kinetic modelling study. Ankerite dissolution and fine-grained Fe-bearing mineral precipitation was observed with pure CO_2–water reaction at 80 °C and 200 bar. Dissolved Ni, Cr, and Zn concentrations initially increased but subsequently decreased by 192 h. The solution pH was predicted to be buffered from 3.1 to 4.4, with siderite and trace Fe-oxide precipitation. With the presence of SO_2 in the CO_2 stream, greater ankerite dissolution and additionally siderite dissolution were observed and predicted initially. Solution pH initially decreased on gas injection and was subsequently buffered from 2.5 to 5 during reaction, with the predicted pH 3.9. Gypsum and amorphous FeS were precipitated along with an Fe–Mn carbonate cement, potentially re-precipitated siderite. Dissolved Cr concentration initially increased but subsequently decreased by 192 h, with Cr signatures observed in precipitated FeS. Conversion of ankerite or calcite to gypsum initially (rather than anhydrite) could decrease rock porosity. Theoretically complete conversion of 10% ankerite or 15% calcite could reduce horizontal permeability in potential CO_2 storage cap-rock by 3–170 mD favourably self-sealing and reducing gas migration. Changes to rock permeability through geochemical reactions however require validation data from experimental measurements. These results have implications for the co-injection of flue gas impurities during CO_2 storage in reservoirs containing ferroan carbonates.

1. Introduction

CO_2 captured and processed from flue gas (e.g. coal fired and oxyfuel power stations, gas or cement processing) may contain up to 5% of impurity gases (co-contaminants) including N_2, SO_2, O_2, Ar, NO_X, H_2S, and H_2O (IEAGHG, 2011; Last and Schmick, 2011). The cost of carbon capture and separation, and hence storage, has been predicted to be reduced if CO_2 can be stored safely together with these impurities avoiding some of the purification processes (Glezakou et al., 2012). Acid gas injection with up to 20% H_2S has been demonstrated safely in Canada for many years, however experimental and modelling studies investigating the reactivity of SO_2, O_2, NO_2 and other gas phase impurities are limited compared to pure CO_2 studies (Bachu and Gunter, 2005; Dawson et al., 2015; Heeschen et al., 2011; Pearce et al., 2013, 2015).

Carbonates are generally the most reactive minerals often already present in potential CO_2 storage reservoirs in trace to moderate amounts, siderite and ankerite are also often associated with petroleum maturation and are present in gas bearing shales in for example the Cooper Basin, Australia. Ferroan carbonates such as siderite and ankerite have been observed in target CO_2 storage reservoirs including the Frio Sandstone, USA, Upper Stuttgard Formation in the Northeast German Basin, Cardium Formation, USA, and in the Otway Basin, Surat Basin, and Vlaming Sub-Basin in Australia (Daniel, 2005; Farquhar et al., 2013; Kharaka et al., 2006; Shevalier et al., 2009; Watson and Gibson-Poole, 2005; Watson et al., 2004). For example, Fe–Mg–siderite and Ca–Fe–Mn ± Mg ankerites along with calcite have been identified in trace amounts in the low salinity upper Precipice Sandstone, a target for CO_2 sequestration, and as cements in the Evergreen Formation, Westgrove Ironstone Formation, and Hutton sandstone in the Surat Basin, Queensland, Australia in trace to moderate amounts (Farquhar et al., 2015, in preparation).

CO_2 injected underground at depths greater than 800 m and temperatures greater than 31 °C exists as a supercritical fluid, which also dissolves in formation water present to form carbonic acid at a pH of ~3–4. Acidic CO_2 rich fluids may be pacified by interaction with existing carbonates e.g. calcite, dolomite, siderite, ankerite. Interaction with CO_2 rich fluids may also induce mineral dissolution, porosity-permeability changes, metal ion release (e.g. Fe, Cr, Ni, Sr, Ba, Zn), and subsequent mineral precipitation (Dawson et al., 2013; Wunsch et al., 2013). Injecting CO_2

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containing SO_2, O_2 and NO_2 has been predicted or observed to result in the formation of acids stronger than carbonic acid, e.g. sulfuric, and nitric acids (Wilke et al., 2012). Co-injection of impurities such as SO_2 has been predicted to reduce formation water pH to as low as 0–1 (Gunter et al., 2000; Knauss et al., 2005; Xu et al., 2007). However, the natural alkalinity of reservoir rock with the presence of trace to moderate carbonates may buffer the initially lowered pH, as has been observed for pure CO_2 injection into the Frio formation, USA (Kharaka et al., 2006). Pure calcite mineral separates and moderate calcite in sandstone core have been observed experimentally to buffer the acidity generated by co-injection of SO_2 with CO_2 to ~pH 6 in two studies (Pearce et al., 2015; Wilke et al., 2012). SO_2 co-injection with CO_2 also has the potential for increased ferroan carbonate mineral dissolution to occur compared to pure CO_2 injection, and hence increased cation release into solution (and potentially reservoir porosity–permeability in the short term). Metal cations from dissolved carbonates may re-precipitate as carbonates, or in the presence of dissolved SO_2, as sulphates or sulphides e.g. Ca-sulphates such as gypsum or anhydrite sequestering injected SO_2 (Bacon and Murphy, 2011). As gypsum has a higher molar volume and anhydrite a lower molar volume than carbonates, conversion of carbonates to sulphates may open or plug overall porosity.

An experimental and geochemical modelling comparison of the reactivity, water impacts, and reaction products of siderite–ankerite to dissolved pure supercritical CO_2, and SO_2–CO_2 at carbon storage conditions is described here.

2. Method

2.1. Materials

A crushed 100–200 μm grain size siderite–ankerite (SiAn) sample from Karnten, Austria, was obtained from BGR, Hannover as part of the GaMin'11 interlab comparison (Ostertag et al., 2014). The sample contained 80 wt.% siderite ($Fe_{0.8}Mn_{0.1}Mg_{0.07}Ca_{0.03}(CO_3)$), 17 wt.% ankerite ($Ca(Fe_{0.7}Mg_{0.2}Mn_{0.1})(CO_3)_2$), and 3 wt.% quartz (determined by X-ray diffraction and point counting), with traces of k-feldspar (and possibly pyrite although not observed in our sub-samples) (Kaufhold and Dohrmann, 2012). The siderite–ankerite sample had an experimentally measured specific surface area (gas absorption using the Brunauer–Emmett–Teller theory) reported as BET (BET SSA) of 0.07 m^2/g, and a geometric specific surface area (geometric SSA) calculated based on grain size information of 0.015 m^2/g.

2.2. Experiments and analytical measurements

The experimental setup, based on modified unstirred Parr reactors, has been described in detail elsewhere (Pearce et al., 2015). In the current experiments, the vessels were maintained at a temperature of 80 ± 1 °C. A 2 g portion of the crushed minerals was contained in a cellulose dialysis membrane (14,000 Da, 25 mm diameter, Thermo fisher Scientific), following the method of Allan and co-workers, which allows the diffusion of aqueous ions between the inner and outer solutions, yet confines solid particles to the inner suspension (Allan et al., 2011). The membrane was rinsed thoroughly in MQ water prior to use, and system blank runs included the dialysis membrane to check for any potential ions liberated to solution from either the reactor or dialysis tubing. Siderite–ankerite mineral samples in the dialysis tubing were contained in a PEEK basket holder to keep them immersed in the water phase. Boiled deoxygenated MQ water was added to the reactor at the sample loading stage with a water:rock mass ratio of 20:1.

Residual air in the headspace of the vessel was purged with a low pressure CO_2 flush with an injection pump. Either pure food grade CO_2 or 0.16% SO_2 in a balance of CO_2 gas (Coregas) was pumped into the vessels with an injection pump to a pressure of 200 ± 5 bar.

Each experiment was run for a total of 192 h, with water samples collected periodically to determine changes in pH, conductivity, cation, and anion concentrations resulting from supercritical CO_2–(SO_2)–fluid–water–rock interactions. When the experiments were terminated, the residual solids were collected for analysis, rinsed and oven dried. Generally pressure was maintained during experimental runs, but in the case of minor pressure drops during sampling, additional food grade CO_2 was added to maintain the vessel pressure.

Approximately 0.5–1 ml of fluid was sampled (0.45 μm filtered), then diluted 10 times and acidified to 2% HNO_3 for analysis by ICP-OES (Perkin Elmer Optima 3300 DV ICP-OES with a 3σ detection limit of 0.001 mg l^{-1}, error 5%). Conductivity and pH were measured ex situ immediately after sampling the SO_2–CO_2–water experiment with a TPS WP81 meter and probes (error of ±0.01). Although CO_2 degassing from solution generally results in ex situ measurements representing a maximum pH, solution pH was not observed to increase significantly over time after sampling indicating control by sulphuric rather than carbonic acid.

Selected unacidified solution aliquots were analysed for carbonate and bicarbonate alkalinity (as $CaCO_3$) by pulsating sensor-based conductometric titration (±1 mg/kg), and chloride concentration by automated ferricyanide discrete analysis (CAS no. 16887-00-6) (±1 mg/kg) (ALS Environmental Division, Brisbane). Sulphate concentration was determined by precipitation with BaCl and Turbidimetric Analysis by UV–VIS Spectrophotometry (CAS no. 14808-79-8) (±1 mg/kg), and Ion Chromatography (ALS Environmental Division, Brisbane).

Blank reactor system tests were conducted in the absence of sample rock material, to determine the extent of fluid contamination from corrosion of the reaction vessel to either pure CO_2–water or SO_2–CO_2–water. Prior to experiments the system was cleaned and conditioned with $scCO_2$ and water mixtures. All vessel liners and samplers were cleaned prior to and post-reaction with a nitric acid bath and MQ water, and the reactor itself also subject to a cleaning and conditioning cycle between experimental runs with a supercritical CO_2–water mixture at experimental pressure and temperature.

Additional siderite–ankerite samples were subject to a water–rock soak (MQ water) at similar conditions but without CO_2 under ~1 bar of Ar (to reduce the presence of oxygen) to check for mineral dissolution or ion exchange induced by pure water. Also a dilute sulphuric acid leach at similar conditions but without CO_2 present and a starting pH of 1.42 was performed for 192 h under ~1 bar of Ar.

Pre- and post-reaction, mineral grain surfaces (on carbon tabs) were analysed by Scanning Electron Microscopy with an Energy Dispersive Detector (SEM-EDS) (low-vacuum JEOL 6460LA environmental SEM with an EDS detector) to detect corrosion effects and the potential formation of new precipitates. High-resolution images were taken of the relative electron densities using a backscatter detector (BSE), to allow interpretation of areas of differing elemental compositions within an image. Semi-quantitative spectra were obtained using the JEOL Analysis

Table 1
Kinetic geochemical modelling parameters.

Mineral	$K_{25(acid)}$ mol/cm²/s	$E_{a(acid)}$ kJ/mol	n	$K_{25(neut)}$ mol/cm²/s	$E_{a(neut)}$ kJ/mol	A_s[a] cm²/g	$K_{(precip)}$ mol/cm²/s	Γ
Quartz				1.70E−17	68.70	10	$K_{(diss)}$	2E+10
Ankerite	1.59E−08	45.0	0.900	1.26E−13	62.76	10	$K_{(diss)}$/1e5	3E+10
Siderite	1.59E−08	45.0	0.900	1.26E−13	62.76	10	$K_{(diss)}$	2E+10
Hematite	4.07E−14	66.2	1.000	2.51E−19	66.20	70	$K_{(diss)}$	1E+10
Gypsum/anhydrite				6.46E−08	14.30	10	$K_{(diss)}$	1E+10

[a] Initial.