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Experimental and simulation studies of iron oxides for geochemical fixation of CO_2-SO_2 gas mixtures

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Abstract

Iron-bearing minerals are reactive phases of the subsurface environment and could potentially trap CO_2-SO_2 gas mixtures derived from fossil fuel combustion processes by their conversion to siderite ($FeCO_3$) and dissolved sulfate. Changes in fluid and mineral compositions resulting from reactions, involving the co-injection of SO_2 with CO_2 were observed both theoretically and experimentally. Experiments were conducted with a natural hematite (α-Fe_2O_3) sample. A high pressure-high temperature apparatus was used to simulate conditions in geologic formations deeper than 800 m, where CO_2 is in the supercritical state. Solid samples were allowed to react with a NaCl-NaOH brine and SO_2-bearing CO_2-dominated gas mixtures. The predicted equilibrium mineral assemblage at 100°C and 250bar became hematite, dawsonite ($NaAl(OH)_2CO_3$), siderite ($FeCO_3$) and quartz (SiO_2). Experimentally, siderite and dawsonite, derived from the presence of kaolinite ($Al_2Si_2O_5(OH)_4$) in the parent material, were present in residual solids at longer reaction time intervals, which agreed well with results from the modelling work.

Keywords: saline aquifers; CO_2-SO_2 gas mixtures; CO_2 storage.

1. Introduction

Successful geological sequestration of carbon in deep saline aquifers as a technological strategy to reduce CO_2 emissions and combat climate change requires accurate predictive models of rock-brine-CO_2 interactions. Laboratory experiments are needed to validate and refine these models. The trapping of CO_2 underground in mineral phases is comparatively slow (hundreds to thousands of years) but is considered the safest and most permanent sequestration strategy because CO_2 is converted to stable carbonate minerals [1-5]. To date, studies have focused on

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Ca-, Mg- and Fe^{II}-bearing sediments to precipitate aqueous CO_2 as calcite ($CaCO_3$), magnesite ($MgCO_3$), siderite ($FeCO_3$) or ankerite ($CaFe(CO_3)_2$) [6-13]. Recent studies have considered the injection into Fe^{III}-bearing sediments, provided that a reducing agent is available to convert Fe^{III} to Fe^{II}, and precipitate CO_2 as siderite ($FeCO_3$). Sulfur dioxide (SO_2) gas is a potential reductant since it is a component of the flue gas and could be co-injected with CO_2 instead of separated from the gas stream at great expense [14,15].

Experimental studies of mineral trapping with CO_2-SO_2 gas mixtures are generally lacking [15-17] and only one has targeted ferric iron-bearing sediments as potential host repositories for underground CO_2 storage [15]. There is a need, therefore, for extensive laboratory studies directed at the sequestration of CO_2 in iron oxides-brine-CO_2-SO_2 systems. Red beds and sedimentary iron ores are groups of iron-containing sediments where hematite (α-Fe_2O_3) and goethite (α-FeOOH) are the main iron-bearing minerals. Hematite is abundant in ancient red beds whereas goethite is abundant in younger yellow-brown coloured deposits [18]. Furthermore, Fe^{III}–bearing sediments, including red beds, are thick and highly porous and have high permeability. They are widespread geographically [15], making them potential sites for underground CO_2 sequestration in carbonate form. Hence, this research aims to identify the altered mineralogy of a geological setting when the SO_2 present in a flue-gas stream is injected with CO_2 into subsurface iron oxide formations.

2. Experimental solids and methods

Experimental solids

A natural iron oxide solid sample, hematite (α-Fe_2O_3), was utilised in this research project. The hematite sample is from South Africa and was crushed, ground and sieved to segregate different particle size fractions (<38, 38-150 and 150-300 µm). XRD spectra confirmed the presence of hematite (82.6%) but also of a quite high percentage (17.4%) of kaolinite ($Al_2Si_2O_5(OH)_4$) in the parent material.

Modelling methods

Thermodynamic models were computed to predict equilibrium for systems consisting of 1.0m NaCl and 0.5m NaOH brine, CO_2 and SO_2 gases, and either hematite or hematite+kaolinite. Computer program CHILLER [19] was used to calculate equilibria in these systems. For a given temperature, pressure and chemical composition, CHILLER computes multi-component heterogeneous chemical equilibria among solids, gases and an aqueous phase. Variables in a reaction path may include temperature, pressure and relative masses of aqueous phase, gases and minerals and /or oxides [19]. The software does not predict the effects of mineral grain size and reaction time of the mineral carbonation reaction because it does not account for reaction kinetics.

For the simulations presented herein temperature and pressure were kept constant (100°C and 250bar respectively), the volume of brine was 400ml and the minerals were either 10g of hematite or 10g of hematite/kaolinite (82.6/17.4%). The models were constructed by 1) equilibrating the brine and mineral, 2) equilibrating the brine and mineral with 165g of CO_2, 3) incrementally adding SO_2 where CHILLER recalculates equilibrium at each step. Only step 3) is presented in the results. The simulation with a 100% pure hematite sample was constructed to be further compared with the computed one for a hematite/kaolinite (82.6/17.4%) rock sample, which would predict equilibrium for experimental runs.

Experimental methods

A number of short-term (24-264h) experiments at different temperature (75, 100, 125 and 150°C), pressure (120, 180, 250 and 320 bar), varying amounts of SO_2 in the gas phase (0.4, 0.9 and 1.2 %v/v), particle size of solid material (< 38, 38-150 and 150-300 µm), solids concentration (10, 25, 50 and 100 g/L) , brine composition (i.e. buffering effect) and reaction time (24, 62, 163 and 264 h) were conducted for hematite in a high pressure-high temperature 600ml reactor (Parr). The reaction vessel was composed of Hastelloy C276, a nickel chromium-molybdenum alloy that exhibits good corrosion resistance. This system is fitted with a high torque sealed magnetic

stirrer drive unit and variable speed electric motor. Two digital flow mass controllers accurately measure the amount of gas transferred into the reactor. Pressure is applied to the system with a CO_2 gas cylinder and a compressed air-driven gas booster. The stirring rate was set to a high constant value (750 rpm), so reaction rates are determined by reaction control rather than by processes in the boundary layer, i.e. diffusion, at either the solid/liquid or gas/liquid interface.

At the completion of each test, the pH of the slurry is measured and recorded, at ambient temperature, and the solution is vacuum-filtered to separate the solids from the aqueous solution. Iron in solution is measured immediately by molecular absorption spectroscopy. Filters are dried overnight in an oven at 110°C, and then the solid residues are collected, weighed and saved for X-ray diffraction (XRD), thermal analysis (TGA) and X-ray photoelectron analysis (XPS).

3. Results and discussion

In the simulation constructed with 10g of hematite, computed equilibrium mineral/gas phase assemblage (Figure 1a) for increasing amounts of SO_2 gas added indicate siderite is the stable phase over a wide range of SO_2 gas added, from -5.40 (off-scale left) to 1.21 log g (SO_2 from 4 µg to 16.4 g). Further addition of SO_2 will yield dissolution of siderite. After all of the hematite has dissolved, pyrite precipitates. Eventually in a very acidic environment, native sulfur replaces pyrite. Most added SO_2 dissolves in a disproportionation reaction yielding sulfide and sulfate.
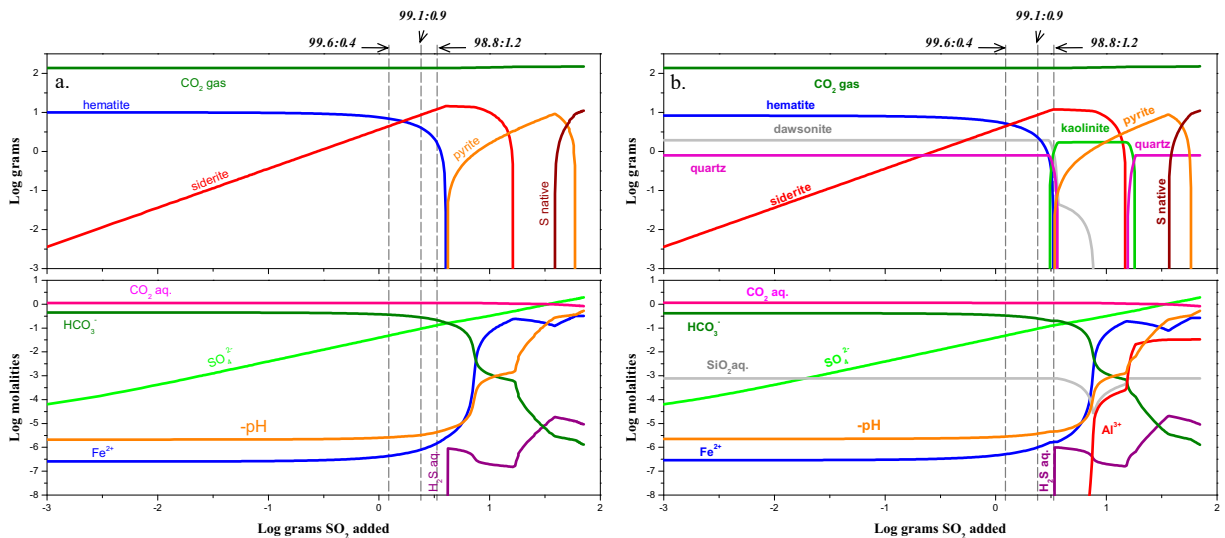

Figure 1. Results from the simulation at 100°C and 250 bar of the CO_2-SO_2 reaction with 10 g of hematite (a) or 10 g of rock (b), 82.6% of hematite and 17.4% of kaolinite, in 400mL of 1.0mNaCl, 0.5mNaOH brine using 165g (excess) CO_2 and showing mineral/gas phase assemblage (top) and fluid composition (bottom) for varying amounts of SO_2 in the gas added. Vertical lines denote the different CO_2:SO_2 gas compositions (%v/v) used in experimental runs.

Experimentally, the extent of reaction was dependent on reaction time. Siderite was identified by XRD as a reaction product after 264 h (Figure 2), which is in good agreement with results from modelling studies. XPS analysis also indicated the presence of another carbonate, possibly dawsonite ($NaAl(OH)_2CO_3$), whose decomposition temperature at ca. 300°C agrees well with results from thermal analysis (Figure 3). The influence of aluminium (i.e. kaolinite) in the modelling work with hematite (Figure 1b), has a dramatic effect on the composition of the altered mineral assemblage. It is substantially different from the simulation results with pure hematite; the

predicted equilibrium mineral assemblage becomes hematite, dawsonite, siderite and quartz. Hence, dawsonite precipitation, derived from the presence of kaolinite in the parent material, agrees well with results from the modelling work. The reaction product contains 3.6% dawsonite at 264h reaction time; residual sodium chloride (NaCl) and iron sulfate ($FeSO_4$) were detected only on the surface of the sample by XPS analyses and had not been predicted by the simulations.
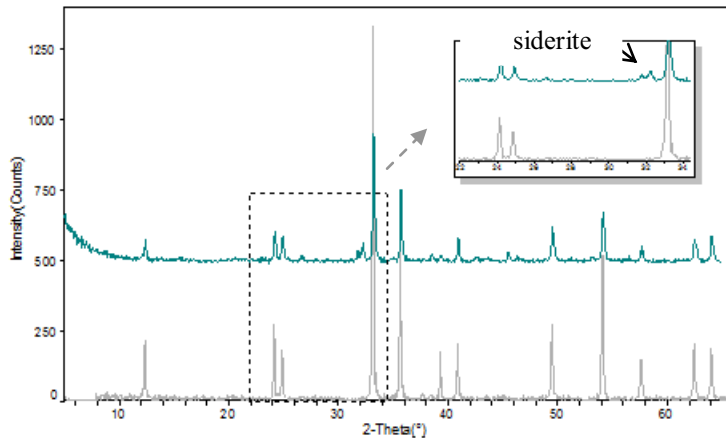

Figure 2. XRD diffractogramas of unreacted (grey line) and reacted (green line) hematite sample (264h).
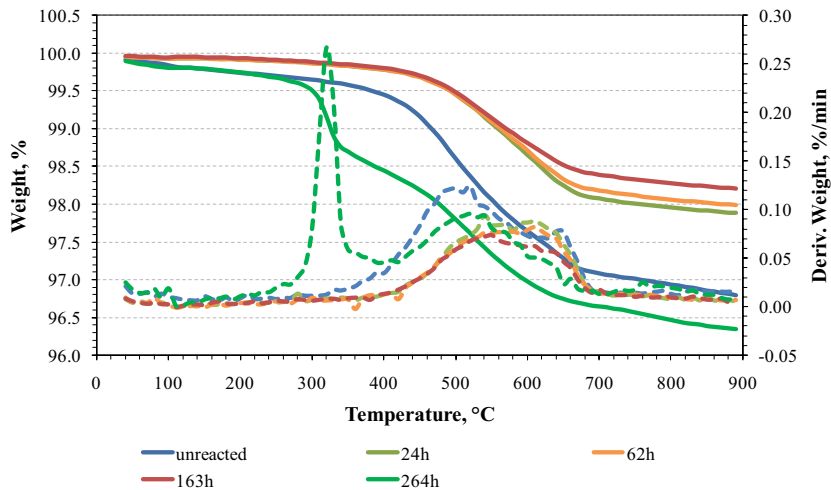

Figure 3. TGA curves of unreacted and reacted hematite samples collected at different reaction times. Dashed lines correspond to derivative weight curves.

Although increasing reaction times favoured the supersaturation and precipitation of secondary minerals (siderite and dawsonite), decreasing particle size of the solids, decreasing values of solids-to-liquid ratio and increasing reaction temperatures up to 100°C also increased precipitation of secondary minerals. Reaction pressure has a major effect on availability of dissolved SO_2 and CO_2 for further reaction with hematite and those cations in solution prone to be carbonated. Experimental 24 h tests with increasing SO_2 contents in the gas stream indicated potential

precipitation of S-bearing phases (pyrite, Fe-S amorphous and S native) when compared to experiments with lower SO_2 contents. Such experiments would be more representative of the initial reservoir conditions close to the well near the gas injection.

4. Conclusions

Short-term (ranging between 24 and 264 h) experiments conducted with hematite provide very valuable and novel information on changes in the mineralogy of the system under different reaction conditions. The kaolinite content of the parent sample seemed to be more altered than the iron oxide itself. Dawsonite precipitated with increasing reaction times and siderite could be only confirmed in the sample reacted for 264h. Precipitation of dawsonite over siderite in the experiments was favoured due to dawsonite's increasing stability at high CO_2 fugacities. This would be representative of near injection well conditions and immediately following injection. In a reality, however, with time, CO_2 fugacity will decrease with increasing distances from the injection site and, over longer periods of time after injection, due to CO_2 dispersion, migration and/or leakage. Under these latter conditions siderite becomes the only stable phase, taking up some of the released CO_2 from dawsonite dissolution.

5. Acknowledgements

6. References

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