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Reactivity of Iron Bearing Minerals and CO_2 Sequestration: A Multi-Disciplinary and Experimental Approach

Dr. Martin A Schoonen
Professor of Geochemistry
Department of Geosciences
Stony Brook University

Abstract

The reactivity of sandstones was studied under conditions relevant to the injection of supercritical carbon dioxide in the context of carbon geosequestration. The emphasis of the study was on the reactivity of iron-bearing minerals when exposed to supercritical CO_2 (scCO2) and scCO2 with commingled aqueous solutions containing H_2S and/or SO_2. Flow through and batch experiments were conducted. Results indicate that sandstones, irrespective of their mineralogy, are not reactive when exposed to pure scCO2 or scCO2 with commingled aqueous solutions containing H_2S and/or SO_2 under conditions simulating the environment near the injection point (flow through experiments). However, sandstones are reactive under conditions simulating the edge of the injected CO_2 plume or ahead of the plume (batch experiments). Sandstones containing hematite (red sandstone) are particularly reactive. The composition of the reaction products is strongly dependent on the composition of the aqueous phase. The presence of dissolved sulfide leads to the conversion of hematite into pyrite and siderite. The relative amount of the pyrite and siderite is influenced by the ionic strength of the solution. Little reactivity is observed when sulfite is present in the aqueous phase. Sandstones without hematite (grey sandstones) show little reactivity regardless of the solution composition.

Rationale

Carbon sequestration through capture and storage in the subsurface by injection into deep saline aquifers is part of an array of possible strategies for managing carbon in the future. Experiments were conducted to evaluate the reactivity of various sandstones toward supercritical CO_2 (scCO_2) and scCO_2 with commingled aqueous solutions containing H_2S and/or SO_2. The rationale for the study was that the injected waste streams will likely include water and depending on the point source also SO_2 or H_2S. The focus of the experiments was on the reactivity of iron-containing minerals contained in sandstone. These minerals were hypothesized to be the most reactive component under conditions expected to exist near the injection point (near field conditions dominated by injected fluid) at the leading edged of the injection and beyond the edge in the deep saline aquifer. Several types of sandstones, representing a range of iron mineralogies and abundance, and fluid compositions, representing variations in injectate composition and ionic strength of deep saline aquifer fluid were tested.

Experimental Strategy

Two types of experiments were conducted: flow-through experiments and static batch experiments. Flow-through experiments with scCO_2 pumped through crushed sandstone with or without added sulfite or sulfide solution were conducted to evaluate the reactivity of the sandstone around the point of injection, where the conditions are governed by the composition of the injectate and the pore space is completely filled with injectate (sometimes referred to as near-field conditions). The experimental setup for the flow through experiments is shown in Fig. 1. Batch experiments with scCO_2 in contact with a separate aqueous phase overlaying crushed sandstone were conducted to simulate conditions near the edge of the plume where injectate is in contact with the aqueous fluid in the deep aquifer.
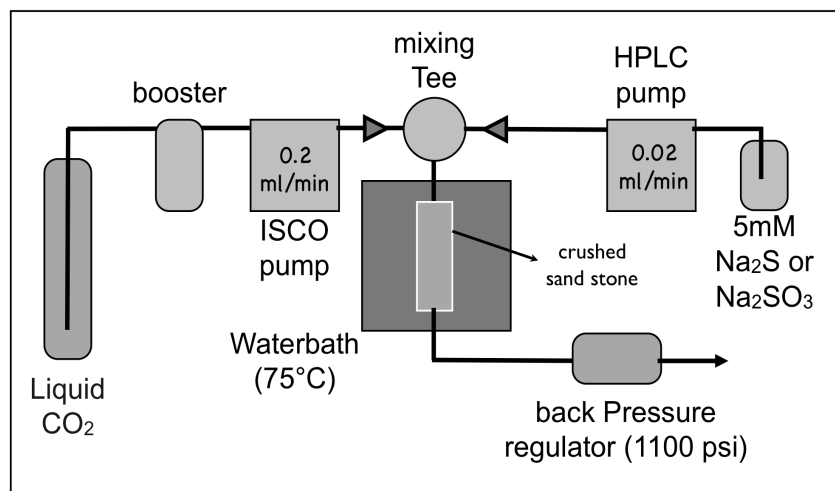

Figure 1. Experimental setup flow through experiments.

The study was focused on the reactivity of iron-containing minerals in the system under study. An array of standard techniques (XRF, XRD, FTIR, Raman, VNIR) were used to study changes in the composition of the sandstones before and and after the experiments, but Mössbauer Spectroscopy was most useful in determining changes in mineralogy.

We studied the reactivity of a red sandstone and several grey sandstones. The red sandstone was a very well-characterized sample of Moenkopi sandstone, Arizona, with 0.87 wt % Fe(III) present as hematite. Other work has shown that hematite in this rock occurs as coatings (possibly nano-scale crystallites precipitated on quartz) and coarser hematite. Grey sandstones, including material from the Timbalier formation in the Gulf Coast, contain iron, but it is mostly in the form of iron associated with clays.

Summary of Results

In flow through experiments, neither the red sandstone or the grey sandstones showed any changes in mineralogy after advecting $scCO_2$ with or without a aqueous sulfite or sulfide solution. This is illustrated with the lack of change in the Mössbauer spectra shown in Figure 2 (top panel).
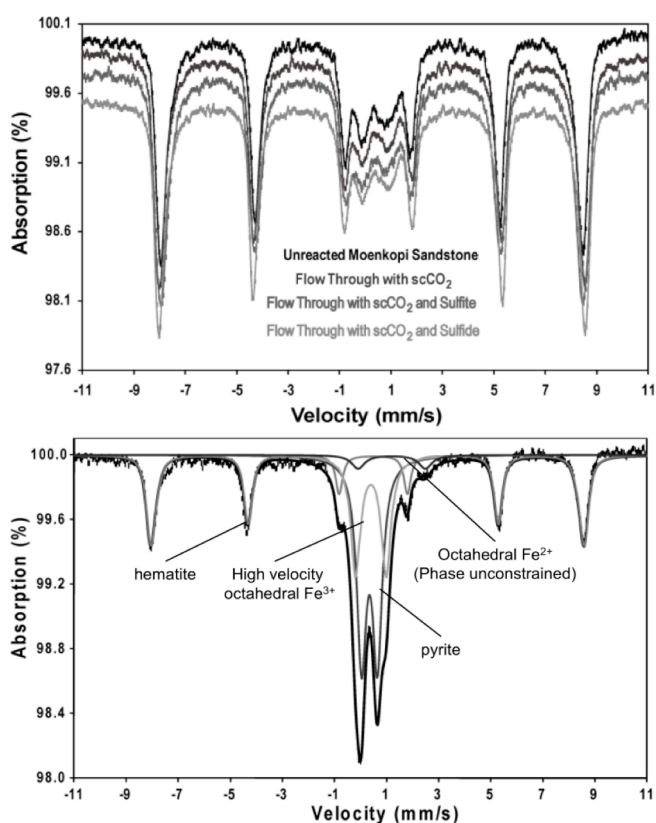

Figure 2: Mossbauer spectra of reacted Moenkopi sandstone. Top panel: sandstone retrieved from flow-through experiments as well as unreacted sandstone for comparison. Bottom panel: Moenkopi sandstone retrieved from batch experiment with $scCO_2$ and sodium sulfide solution.

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While the flow-through experiments did not show a change in iron mineralogy, we did observe changes in mineralogy when the red sandstone was exposed to sulfide solutions and mixed sulfide/sulfite solutions equilibrated with scCO$_2$. Pyrite was formed in batch experiments with scCO$_2$ and aqueous sulfide solutions (Figure 2, bottom panel), while siderite formed in batch experiments with scCO$_2$ and an aqueous solution containing both sulfide and sulfite. The composition of the reaction products in batch experiments with both sulfite and sulfide present and red sandstones showed a dependence on ionic strength (Figure 3). Less conversion of hematite was seen with higher ionic strength. The results of all batch experiments are summarized in Figure 4.

The grey sandstones showed essentially no changes in iron mineralogy in batch experiments. An example of a set with batch experiments with a grey sandstone from the Caspian Sea is shown in Figure 5 and a summary of all experiments is presented in Figure 6.
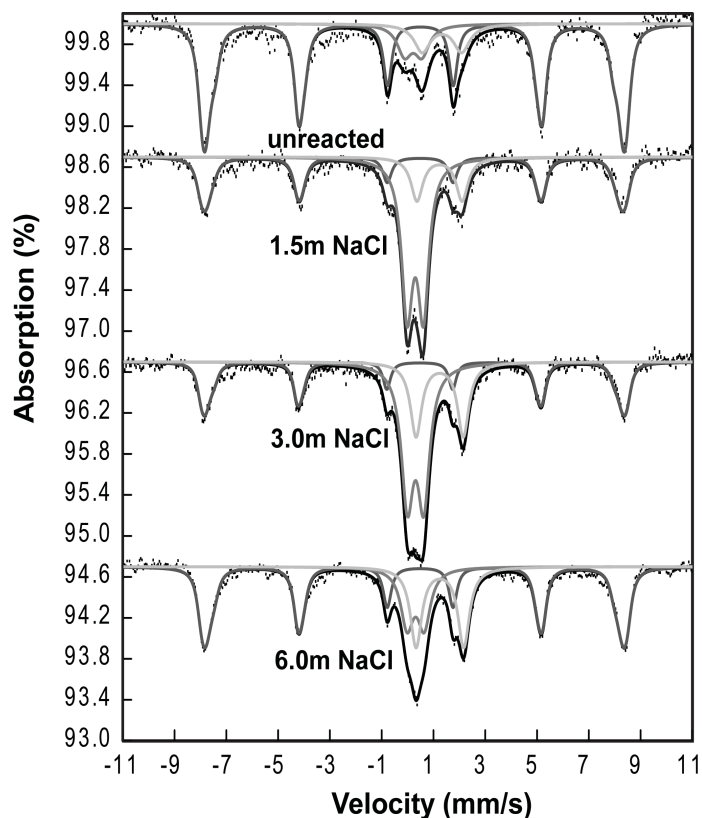

Figure 3. Mossbauer spectra of red sandstone recovered from batch experiment with both sulfite and sulfide in aqueous fluid.
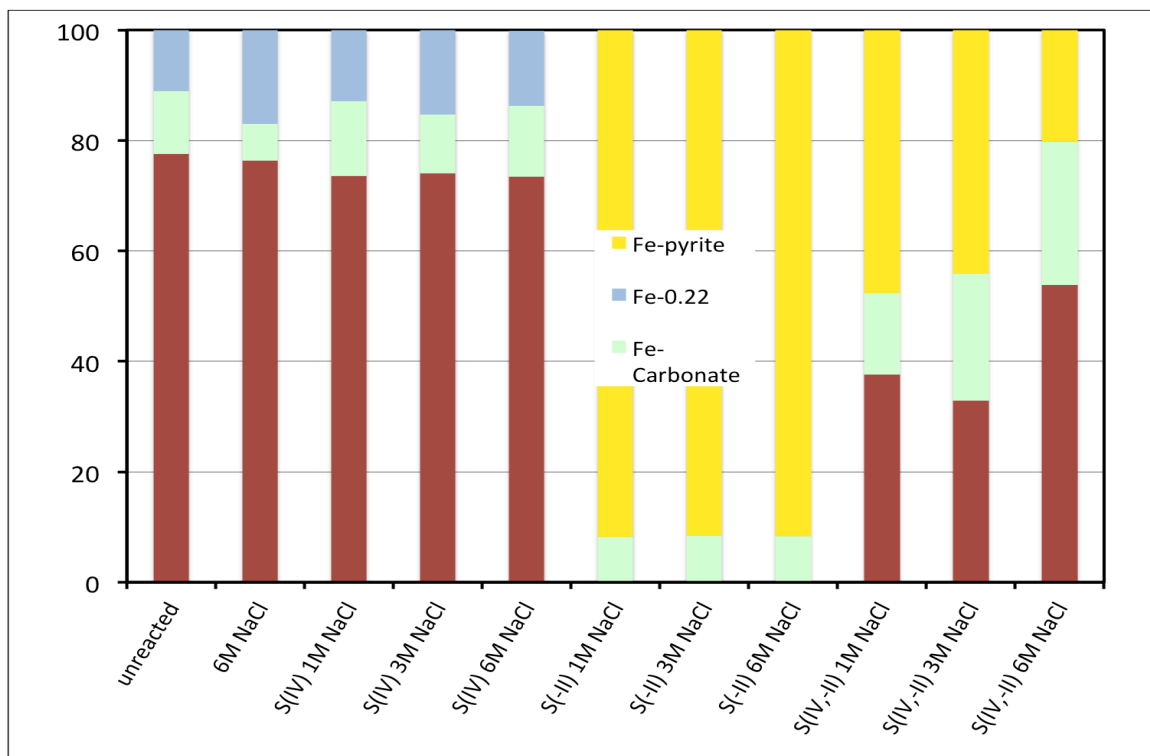
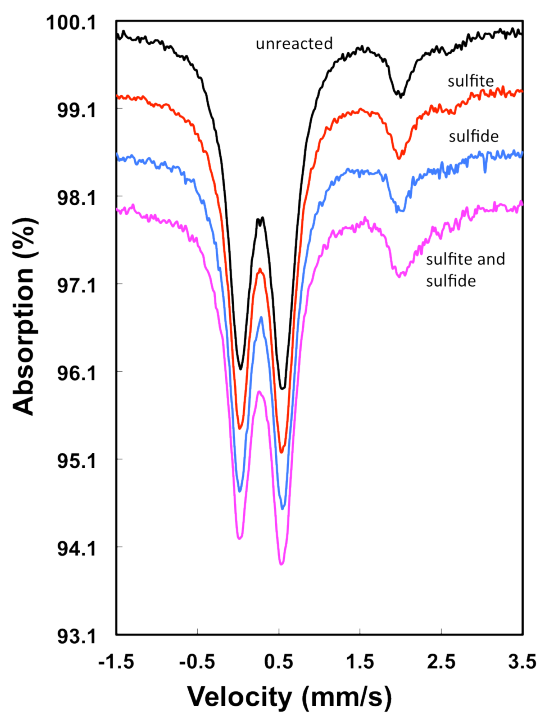**Figure 4. Summary of results batch experiments with red sandstones.**

Figure 5. Result of batch experiments with grey sandstone from Caspian Sea.

Discussion

The lack of reactivity in the flow-through experiments, simulating the environment around a CO_2 injection well, is probably due to the preferential wetting of mineral surfaces by the $scCO_2$ phase. In essence, the $scCO_2$ dries the surface under these conditions and prevents the reaction of aqueous sulfite or sulfide. In the batch experiments, simulating conditions at the edge of the CO_2 plume, the mineral surfaces are in contact with the aqueous phase, which allows dissolved sulfur species to react with the minerals.

The results indicate that hematite-containing sandstones are reactive when exposed to aqueous solutions in equilibrium with $scCO_2$ commingled with H_2S or a mixture of SO_2/H_2S. Increased ionic strength suppresses the amount of pyrite formed and promotes the amount of siderite formed, but the mechanism for this shift in outcome is not clear.

Grey sandstones, with iron contained in clays, are essentially unreactive under both flow through and batch conditions.
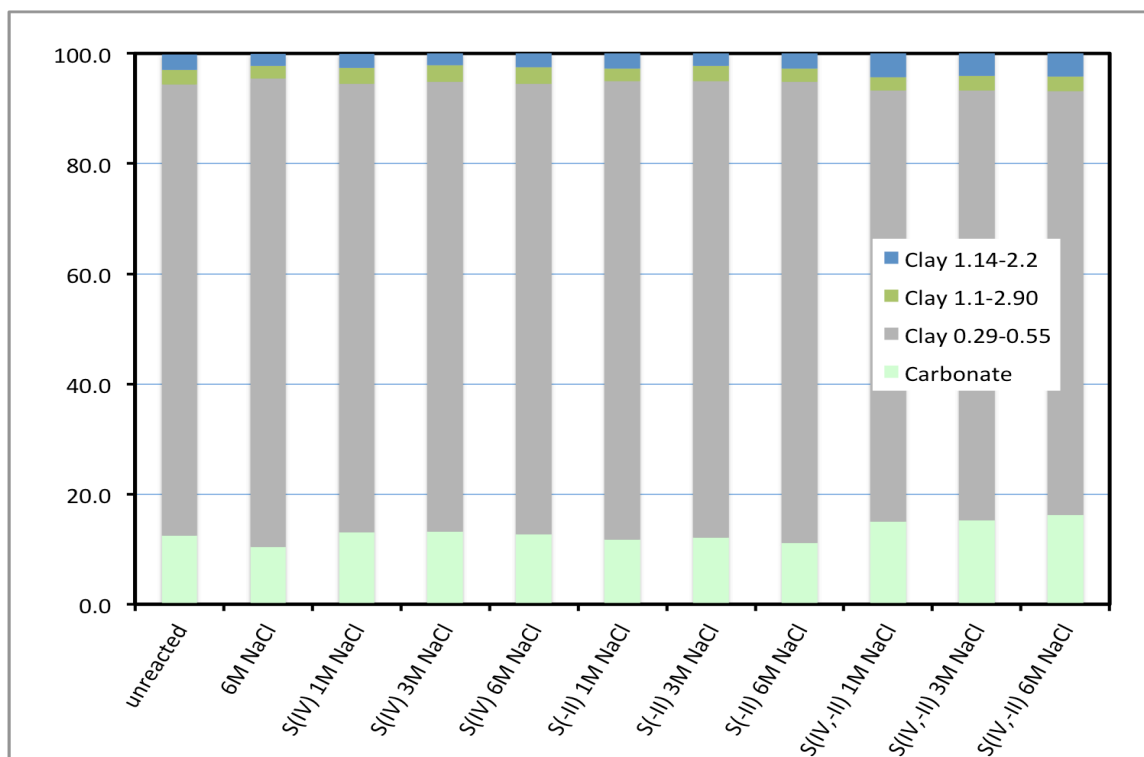

Figure 6. Summary of results batch experiments with grey sandstones.

Conclusions and Implications

 The main conclusions of this work are:
- ❖ **The hematite in the red sandstone studied here is not reactive under conditions simulating the environment around the point of scCO$_2$ injection.**
- ❖ **Hematite is not reactive in water or brine containing only sulfite and saturated with scCO$_2$.**
- ❖ **Hematite is completely converted to pyrite in scCO$_2$-saturated water or brine containing sulfide, regardless of NaCl content.**
- ❖ **Some hematite is converted to pyrite and siderite in scCO$_2$-saturated water or brine containing sulfide and sulfite. Reactivity of hematite decreases and siderite formation is favored with increasing NaCl content.**
- ❖ **Grey sandstones are essentially unreactive over a wide range of conditions.**
- ❖ <u>**Grey sandstones would be preferred targets if the scCO$_2$ stream contains any H$_2$S or H$_2$S+SO$_2$ as loss of permeability as a result of conversion of iron mineralogy will be minimal.**</u>

Other Synergistic Activity Supported by Award

   The Schoonen laboratory also conducted XRD and TGA analysis in support of work spearheaded by collaborators in the Strongin laboratory as well as geochemical modeling to assist in the interpretation of experimental results on related experiments studying the carbonization of pure iron-containing hydroxides.   While we were building the flow-through setup for the experiment described above, Schoonen and graduate student Andrea Harrington finalized a study on the role of hydrogen peroxide and hydroxyl radical in the reaction mechanism of pyrite oxidation by molecular oxygen.   This work wrapped up some outstanding issues of work we conducted over the last decade on pyrite oxidation with DOE-BES support.

Publications Supported by Award

Schoonen, M.A.A., Sklute, E.C., Dyar, M.D., Strongin, D.R., 2012. Reactivity of sandstones under conditions relevant to geosequestration: 1. Hematite-bearing sandstone exposed to supercritical carbon dioxide commingled with aqueous sulfite or sulfide solutions. Chemical Geology 296, 96-102.

Murphy, R., Lammers, K., Smirnov, A., Schoonen, M.A.A., Strongin, D.R., 2011. Hematite reactivity with supercritical CO(2) and aqueous sulfide. Chemical Geology 283, 210-217.

Lammers, K., Murphy, R., Riendeau, A., Smirnov, A., Schoonen, M.A.A., Strongin, D.R., 2011. CO$_2$ sequestration through mineral carbonation of iron oxyhydroxides. Environmental Science & Technology 45, 10422–10428.

Schoonen, M.A.A., Harrington, A.D., Laffers, R., Strongin, D.R., 2010. Role of hydrogen peroxide and hydroxyl radical in pyrite oxidation by molecular oxygen. Geochimica

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Sklute, E.C., 2014. On the Subject of Analyzing Iron and Sulfur Bearing Minerals from Three Extreme Environments: Geological Carbon Sequestration, Acid Mine Drainage, and Mars. Ph.D. Thesis Geosciences. Stony Brook University, Stony Brook, NY, p. 292.

Papers in Review:

Sklute, E.C., Schoonen, M.A., Dyar, M.D., Strongin, D., 2014. Reactivity Of Sandstones Under Conditions Relevant To Geosequestration: 2. Hematite-Bearing Sandstone Exposed To Supercritical Carbon Dioxide Commingled with Saline Sulfite and/or Sulfide Solutions. . Chemical Geology in review.

Sklute, E.C., Schoonen, M.A., Dyar, M.D., Strongin, D.R., 2014. Reactivity Of Sandstones Under Conditions Relevant To Geosequestration: 3. Gray Sandstones Exposed To Supercritical Carbon Dioxide Commingled with Sulfite and/or Sulfide Solutions. Chemical Geology in review.