Ferric Iron Minerals as Geologic Traps for CO_2 Sequestration: Iron Reduction Using Sulfur-Bearing Waste Gas

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I. Introduction

Studies of in situ mineral trapping of CO_2 (e.g Gunter et al., 1997; Gunter et al., 2000; Johnson et al., 2001; Pruess et al., 2001) consider the use of Ca-bearing arkosic or Fe-bearing glauconitic sediments, to trap CO_2 in calcite, magnesite siderite, or ankerite. Glauconitic beds, which contain the desired ferrous iron, are generally of limited thickness and geographical occurrence. However, ferric iron-bearing sediments, including redbeds, have the advantages of widespread geographic distribution, and generally greater thickness, and higher porosity and permeability.

One study (Pruess et al., 2001) makes passing reference to ferric iron, and refers to organic matter or H_2S as possible agents for the reduction of iron. In the case of H_2S, the authors point out that even relatively low partial pressures favor the precipitation of ferrous iron in pyrite. Given that flue gas from fossil fuel-fired power plants may contain small amounts of SO_2, can SO_2 (or added H_2S) be used to reduce ferric iron to ferrous, while maintaining fugacities of H_2S and CO_2 so that precipitation of iron carbonate is favored over iron sulfides?

This question is explored with a few simple calculations.

II. Methods

Equilibrium simulations herein are computed using CHILLER (M.H. Reed, U-Oregon); time-dependent simulations are computed using GAMSPATH (E.H. Perkins, Alberta Research Council). Both computer codes calculate the distribution of chemical components among minerals, gases and species in the aqueous phase.

Initial fluid conditions in all simulations:
- T = 100°C
- P = 120 bar
- 1.0 kg. of 1.0 molal NaCl
- Initial pH = 5.1 adjusted. with HCl

All simulations use 10.0 kg. of rock.
All simulations except in section V. use rock composed of 99.75 wt % quartz and 0.25 wt % hematite - a synthetic redbed.
A small amount of hematite is used because the amount of ferric iron in sediments is generally small, and to complete as much of the reaction as possible before gas saturation, since the properties of SO_2/CO_2 mixtures are not well known.

IIIa. Iron-Sulfur-Water Chemistry: Basics

It has been shown in studies of volcanic systems that SO_2 gas, when mixed with water, disproportionates into sulfate and sulfide (Getahun et al., 1996; Symonds et al., 2001):

$$4SO_2 + 4H_2O = H_2S + 3H_2SO_4 \quad (1)$$

It has been shown (Palandri, 2000) that the reaction of H_2S with ferrous iron in hematite that yields high concentrations of Fe^{2+}:

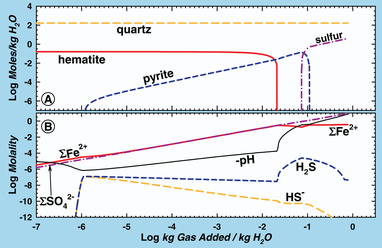
$$8Fe^{3+} + HS + 4H_2O = 8Fe^{2+} + SO_4^{2-} + 9H^+ \quad (2)$$

The remaining Fe^{2+} resides in iron sulfide minerals:

$$4Fe^{2+} + SO_4^{2-} + 7HS + H^+ = 4FeS_2\ (\text{pyrite}) + 4H_2O \quad (3)$$

$$Fe^{2+} + HS = FeS\ (\text{amorphous}) + H^+ \quad (4)$$

IIIb. Iron-Sulfur-Water Chemistry: Reaction of Pure SO_2 With Hematite



- The rock and fluid are equilibrated before adding gas.
- This has negligible affect on the mineral assemblage

RESULTS:
- Hematite dissolves completely before the aqueous sulfide concentration begins to increase again
- A similar result is obtained (not shown) using H_2S, in an amount one quarter that of SO_2 (mole frac.), and producing one quarter the amount of sulfate.
- **After the pyrite maximum, ~55% of the iron is in the aqueous phase, almost all in the ferrous state**
- **Dissolved sulfide and iron increase, and pyrite precipitates early, because there is no other sink to remove ferrous iron.**
- ***That sink can be CO_2***

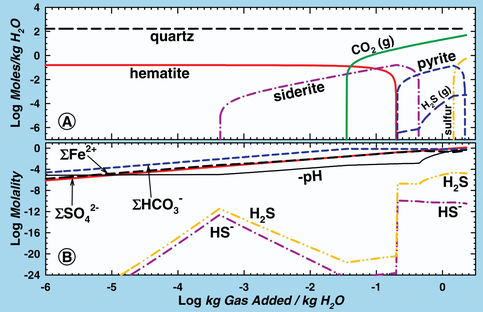
IVa. Iron-Sulfur-Water-CO_2 Chemistry: CO_2 Trapping in Siderite

The overall relevant reaction:

$$Fe_2O_3\ (\text{hematite}) + 2\,CO_2\ (g) + SO_2\ (g) + H_2O = 2\,FeCO_3\ (\text{siderite}) + H_2SO_4 \quad (5)$$

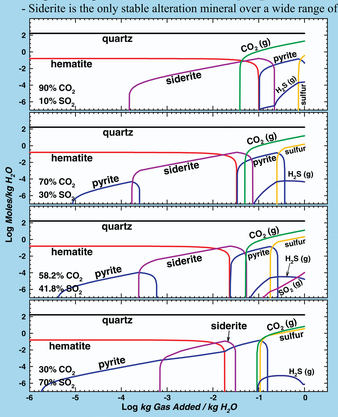
The required gas composition contains two moles of CO_2 per mole SO_2.
We use a gas composition with much less SO_2: 95 wt. % CO_2, 5 wt. % SO_2
This composition is representative of flue gas from burning high-sulfur fossil fuel

RESULTS:
- Siderite is stable over a wide range of total gas added
- Aqueous sulfide initially increases, but decreases between siderite-in and CO_2 gas-in, because siderite provides a sink for aqueous Fe^{2+}, allowing further dissolution of hematite, reduction of Fe^{3+}, and oxidation of sulfide
- Hematite dissolves out before the sulfide concentration increases again and pyrite precipitates
- Porosity decreases from 21% initially to 20.9% at the siderite maximum
- Approximately 1.4 g. of CO_2 is sequestered per kg of rock, or about 2.9 kg per m^3 of rock



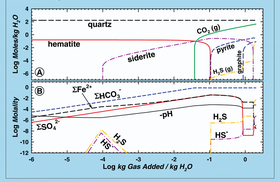
IVb. Iron-Sulfur-Water-CO_2 Chemistry: Variation in the Injected Gas Composition

- At gas ratios greater than ~20/80 (wt. % SO_2/CO_2), a small amount of pyrite precipitates before siderite.
- Siderite is the only stable alteration mineral over a wide range of gas added, at ratios up to approximately 50/50.



Reaction With H_2S

Approximately the same result as in IVa. is obtained using H_2S instead of SO_2, one quarter as much on a molar basis (see eqn. 1). The primary difference is a much lower sulfate concentration for the same total mass of gas added.



IVc. Iron-Sulfur-Water-CO_2 Chemistry: Reaction Kinetics

- Rate parameters are for dissolution; precipitation rates computed by dividing the dissolution rate by the equilibrium constant
- Concentration gradients at mineral surfaces, leading to diffusion controlled reactions, are not considered. Reaction kinetics are strictly surface controlled, and therefore, the software simulates an infinitely well-stirred batch reactor, and the simulation provides an estimate of the minimum time for equilibration
- Rate parameters:

Quartz: 0.10 mm spheres; $k_{25°C,\ pH=0}$ = -13.34 log mol $m^{-2}s^{-1}$; Ea = 90.1 kJ mol^{-1}
Hematite: 0.01 mm spheres; $k_{25°C,\ pH=0}$ = -9.39 log mol $m^{-2}s^{-1}$; Ea = 66.2 kJ mol^{-1}; order = 0.23 w.r.t a_{HCO3}, order = -1.00 w.r.t a_{H+}, 1.0 (arbitrary)
Pyrite: 0.10 mm spheres; $k_{25°C,\ pH=0}$ = -7.52 log mol $m^{-2}s^{-1}$; Ea = 56.9 kJ mol^{-1}; order = -0.50 w.r.t a_{H+}, 0.50 wrt a_{Fe+++}
Siderite: 0.10 mm spheres; $k_{25°C,\ pH=0}$ = -0.30 log mol $m^{-2}s^{-1}$; Ea = 14.4 kJ mol^{-1}; order = -1.00 w.r.t a_{H+}, 0.50 wrt a_{HCO3-}
Sulfur: No data (yet), rate set arbitrarily fast at 1.0 mol $m^{-2}s^{-1}$

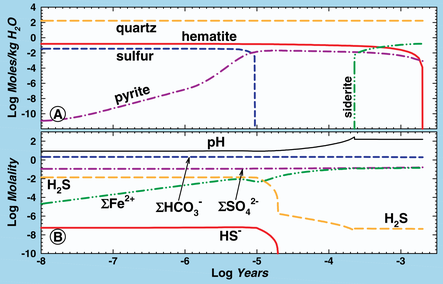
Quartz - Tester et al. 1994; hematite - Bruno et al. 1992, Ruan & Gilkes 1995; pyrite - McKibben & Barnes, 1986; siderite(calcite) - Talman et al. 1990.

- Rock and gas compositions as in IVa
- Because of software limitations, the fluid must be charged with gas before adding rock. Charging the fluid with SO_2 leads to precipitation of sulfur:

$$0.75HS + 1.25H^+ + 0.25SO_4^{2-} = S(\text{native}) + H_2O \quad (6)$$

The sulfur re-dissolves as the reaction with hematite in the rock proceeds. In the absence of data for the rate of sulfur dissolution, we have set the rate arbitrarily fast at 1.0 mol m^{-2} s^{-1}. In the context of flue gas injection, occurrence of sulfur in the alteration assemblage may be irrelevant, as sulfur in the gas may be oxidized before sulfur saturation is reached. Quartz has the slowest rates, but does not participate in the reactions of interest. Hematite is the next slowest, and controls the time to equilibrate.

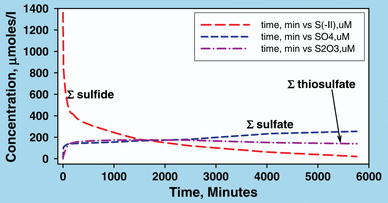
The time to siderite precipitation is ~2 hours.
The time to complete equilibration where hematite dissolves out is ~18 hours.



Kinetics Experiments - H_2S Sequestration with Ferric Iron in Sediments

In studies of disposal of H_2S from natural gas, the general conclusion of rapid reaction rates are confirmed by experimental data (Y. Xu and M. Schoonen, SUNY Stonybrook, unpublished data).
Fluid: 0.80 L 1500 µM Na_2S, 100 mM Boric acid, 100°C
Rock: "Arizona Redbed" ~1.0 wt. % Fe_2O_3

- Over 50 percent of the H_2S is consumed after 30 minutes
- Over 98 percent of the H_2S is consumed after 96 hours
- Approximately 20% of the H_2S is converted to metastable thiosulfate at 96 hours
- Similar results were obtained in many experiments ranging in temperature from 82° to 160°C with rocks containing various amount of Fe_2O_3, i.e. near-complete equilibration in times from hour to days



V. Calcium-Bearing Systems

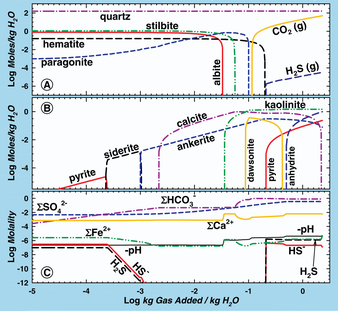
What are the implications for sediments containing both iron and calcium?
In particular, will the calcium reside in carbonate minerals, or anhydrite/gypsum?

Rock (synthetic redbed):
- 94.75 wt. % Quartz
- 5.0 wt. % Labradorite
- 0.25 wt. % Hematite

Gas:
- 90 wt. % CO_2
- 10 wt. % SO_2

The given rock composition is equilibrated with the fluid before adding gas, thereby altering it to an assemblage of quartz, stilbite, albite, hematite, and paragonite. Porosity decreases from 20.9% to 18.4%, due mostly to hydration of labradorite to stilbite.

RESULTS:
- As in part IV, iron-bearing carbonates are stable over a wide range of total gas added
- Ankerite replaces siderite, as calcium is released from dissolving stilbite
- The pH is buffered until albite dissolve out, by the assemblage albite+paragonite+quartz
- Porosity increases from 18.8% to 20.6% where dawsonite precipitates, but the rock is already hydrated
- Approximately 5.6 g. of CO_2 is sequestered per kg of rock, or about 14.8 kg. of CO_2 per m^3 of rock where stilbite dissolves out
- Anhydrite replaces calcite and ankerite only at the highest gas-rock ratios, and only far after the initial reactants are consumed. The replacement is driven by increasing sulfate concentration



Mineral Formulae

Albite	$NaAlSi_3O_8$
Anhydrite	$CaSO_4$
Ankerite	$CaFe(CO_3)_2$
Calcite	$CaCO_3$
Dawsonite	$NaAl(CO_3)(OH)_2$
Hematite	Fe_2O_3
Kaolinite	$Al_2Si_2O_5(OH)_4$
Paragonite	$NaAl_3(Si_3Al)O_{10}(OH)_2$
Pyrite	FeS_2
Siderite	$FeCO_3$
Stilbite	$CaAl_2(SiO_3)_6(OH)_{10}.3H_2O$

VI. Conclusions

Ferric iron in sediments can be used to trap CO_2 in ferrous iron-bearing carbonate minerals, by including SO_2 or H_2S in the injected waste gas stream to reduce the iron. The iron can be made to reside almost entirely in carbonate minerals, and sulfur mostly dissolved as sulfate. In rocks containing only ferric iron as a potential CO_2 trap , the required gas composition is two moles of CO_2 to one mole of SO_2. Given that the waste gas from fossil fuel-fired power plants has a higher ratio of CO_2 to SO_2, targeted sediments must contain other divalent metals such as Ca or Mg_2 or additional sulfur-bearing gas must be added to the waste gas stream, to trap all of the CO_2 in siderite. Conversely, sediments need to contain only a small amount of ferric iron to convert sulfur into dissolved sulfate, for the quantities of sulfur typical in waste gas from combustion of fossil fuel. Once dried and scrubbed of nitrous oxides, the CO_2 and SO_2 remaining in the waste gas can be injected together. In rocks also containing calcium, anhydrite and gypsum are less stable than calcite or ankerite except at very high sulfate concentrations, and calcium sulfate precipitation that might plug the formation should not occur. For quartz arenite containing 1% hematite, approximately 5.5 g of CO_2 is sequestered per kg of rock, or about 12 kg per m^3 of rock

All of these conclusions are based on idealized computer simulations. Although the thermodynamic part of the calculations are built upon a solid framework, there exist considerable uncertainties in the kinetics of mineral precipitation and dissolution, and of aqueous speciation. The reaction of H_2S with hematite has been verified experimentally, and is expected to occur on time scales of hours to days. However, rigorous experiments with detailed mineral and solution chemistry should be conducted in the future, to determine whether reduced iron will reside in carbonate or sulfide minerals, and to determine the rates of sulfur precipitation and dissolution.

The use of iron-rich sediments, e.g. redbeds, introduces a CO_2 mineral trap commonly with high porosity and permeability, with widespread geographic distribution and great thickness, and therefore potentially great capacity. The benefits are twofold – not only can ferric iron be used as a trap for CO_2, but SO_2 gas that may already be part of the flue gas can be injected with the CO_2.

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