



Preliminary Reactive Geochemical Transport Modeling Study on Changes in Water Chemistry Induced by CO₂ Injection at Frio Pilot Test Site

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INTRODUCTION

- One promising means of reducing atmospheric CO₂ emissions is to store CO₂ in deep saline aquifers.
- Frio (located near Dayton, Texas) pilot test was conducted. A total of 1600 tons of CO₂ were injected into the Frio "C" sandstone layer at a depth of 1500 m over a period of 10 days.
- The test employed one injection well and one observation well, separated laterally by about 30 m.
- Following CO₂ breakthrough at the observation well, saw drops in pH (6.5 to 5.7), and pronounced increases in concentrations of HCO₃⁻ (100 to 3000 mg/L), Fe (30 to 1100 mg/L), and dissolved organic carbon.
- Numerical modeling was used to understand changes of aqueous HCO₃⁻ and Fe caused by CO₂ injection.
- Results from the numerical simulation are in reasonable agreement with field observations.

NUMERICAL MODEL

Simulations were carried out using the non-isothermal reactive geochemical transport code TOUGHREACT (Xu et al., 2006).

Processes

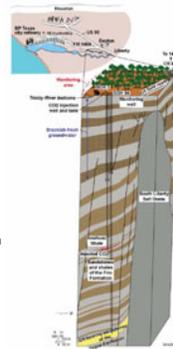
- 3D multi-phase fluid and heat flow through porous or fractured media: TOUGH2 V2 (Pruess, 1999).
- New fluid property module ECO2N with an accurate description of the thermophysical properties of mixtures of water, brine, and CO₂ at conditions of interest for CO₂ storage (Spycher and Pruess, 2005).
- Transport: advection and diffusion.
- Reactions: aqueous complexation, mineral dissolution and precipitation, gas dissolution and exsolution, and ion exchange.

Special Features

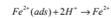
- CO₂ solubility dependence on P, T, and salinity.
- Changes in porosity and permeability due to mineral dissolution and precipitation; choice of 5 φ-k models.
- Gas phase and gaseous species are active in flow, transport, and reaction.
- Mineral reactions kinetically controlled using rate laws.
- Any number of chemical species present in liquid, gas and solid phases.
- Wide range of conditions of P, T, ionic strength, pH, and Eh.

PROBLEM SETUP

- A calibrated 1-D radial flow model was used (Christine Doughty). The residual liquid saturation S_r is set to an high number (s_r=0.75) to account for the fact that in the real formation, buoyancy flow and reservoir heterogeneity result in significant bypass of a large fraction of the formation. Assigning a large S_r allows the CO₂ to bypass brine and thereby arrive at the observation well at about the right time. A porosity of 0.34, a permeability of 2.664×10⁻¹² m, and an injection rate of about 2 kg/s were used.
- Mineral composition was taken from Xu et al. (2006). Dissolution and precipitation are kinetically-controlled. Parameters are given in the table below. Several scenarios were used to reproduce increases in Fe concentration including (1) dissolution of carbonate minerals, (2) dissolution of iron oxyhydroxides, (3) desorption of Fe.



De-sorption reaction:



Kinetic rate:

$$r = k_1 [Fe^{2+}(ads)] [H^+]^2 - k_2 [Fe^{2+}]$$

Initial at equilibrium, $r = 0 \rightarrow k_2 = \frac{[Fe^{2+}(ads)] [H^+]^2}{[Fe^{2+}]}$ k_1

Assume initially $[Fe^{2+}(ads)] = 2.6 \times 10^{-2}$ mol/l, we know $[Fe^{2+}] = 3.852 \times 10^{-4}$ mol/l and $[H^+] = 2.571 \times 10^{-7}$ mol/l

$\rightarrow k_1 = 4.4614 \times 10^{-12}$ k_2

Overall the Fe de-sorption rate can be expressed as

$$r = k_1 [Fe^{2+}(ads)] [H^+]^2 - 4.4614 \times 10^{-12} k_2 [Fe^{2+}]$$

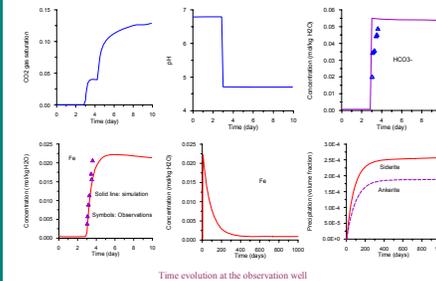
- A kinetic de-sorption model for sorbed Fe was developed

Mineral	Vol % of solid	A (cm ³ /g)	Parameters for kinetic rate law						
			K _d (mol ² /s)	E _a (KJ/mol)	Ac ₁	E _a (kJ/mol)	Ac ₂	E _a (kJ/mol)	
Primary:									
Quartz	57.888	9.8	1.403e-10	87.7					
Calcite	2.815	110.6	6.918e-10	222	4.206e-10	45.9	0.779	6.913e-10	117.9
Clayite	1.529				No mineral precipitation				
Illite	0.954	151.6	1.266e-10	35	1.047e-10	23.0	0.34	1.026e-10	58.9
Opal-CT	19.789	9.8	1.455e-10	69.8	2.138e-10	65	0.829		
K-feldspar	8.179	9.8	1.309e-10	39	8.710e-10	57.1	0.5	6.310e-10	94.1
Na-saponite	1.897	151.6	1.266e-10	35	1.047e-10	23.0	0.34	1.026e-10	58.9
Chlorite	4.556	9.8	1.025e-10	58	1.762e-10	38	0.5		
Humate	0.497	12.9	2.312e-10	66.2	4.054e-10	66.2	1		
Secondary:									
Muscovite	9.8	4.251e-10	23.5	4.109e-10	14.3	1			
Dolomite	9.8	2.951e-10	52.2	6.455e-10	36.1	0.5			
Low-millie	9.8	2.254e-10	69.7	6.918e-10	36	0.495	2.512e-10	71	
Siderite	9.8	1.266e-10	62.76	6.455e-10	36.1	0.5			
Ankerite	9.8	1.266e-10	62.76	6.455e-10	36.1	0.5			
Dolomite	9.8	1.266e-10	62.76	6.455e-10	36.1	0.5			
Ca-saponite	151.6	1.266e-10	35	1.047e-10	23.0	0.34	1.026e-10	58.9	
Pyrite	12.9								

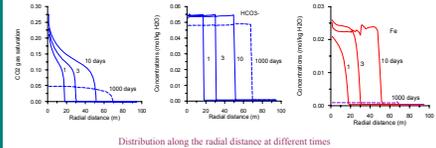
MODEL RESULTS AND DISCUSSION

At the observation well:

- CO₂ breakthrough occurs about 3 days after injection began.
- pH drops to 4.8, which is different from the surface observation (5.7), but above initial calculated subsurface (3.0) condition (Kharaka et al., 2006). Differences between simulated and observed pH are mainly because the degassing from samples occurred before the surface measurement. Other reasons can also cause the differences, including sampling over a number of layers within the reservoir, discrepancies associated with using a 1-D model instead of a multi-layered model or, other due to real difference in mineralogy and fluid composition.
- Simulated HCO₃⁻ has a step change because of CO₂ gas dissolution equilibrium model, and overall capture the observations.
- Simulations with dissolution of the carbonate minerals siderite and ankerite or/and dissolution of the iron oxyhydroxide hematite produced much smaller Fe concentrations than the observations.
- The kinetic de-sorption model with a calibrated initial adsorbed Fe concentration can reproduce the increases in Fe concentration that were observed following the CO₂ breakthrough.
- Later, simulated Fe concentrations decrease due to carbonate mineral siderite and ankerite precipitation, which is consistent with observation (Fe decreases to 0.0046 mol/L, 250 ppm after 180 days)



- Close to the injection well, water is completely displaced by CO₂ (S_r = 1).
- Fe drops significantly after 400 days depending on the reaction kinetics.



SUMMARY AND CONCLUSIONS

- Increases in HCO₃⁻ concentration were well reproduced by an initial simulation.
- Increases in Fe concentration can not be explained by dissolution of carbonate minerals, or/and dissolution of iron oxyhydroxides.
- A simple model of kinetic de-sorption from sorbed Fe can reproduce the increases in concentration following the CO₂ breakthrough.
- Later, simulated Fe concentrations decrease due to carbonate mineral siderite and ankerite precipitation.
- pH drops to 4.8, which is below the observed pH (5.7). This is mainly because the degassing from samples occurred before the surface measurement.
- Further lab work is needed to obtain detailed Fe and Mn mineralogical composition on the surface coating and to confirm carbonate mineral precipitation for late Fe concentration decreases.
- Additional lab, field, and modeling investigations are proposed to better understand changes in dissolved organic carbon and isotope composition.

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