CO_2 Injection at the Frio-I Brine Pilot: the Uncertainties Associated with the Reactive Transport Modeling

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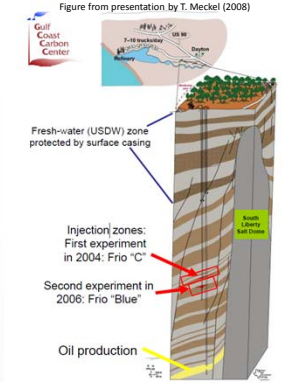
Project Goals

- Identify a set of chemical reactions in response to CO_2 injection, using Frio test site as a case study.
- Construct a reactive flow model of the processes taking place in response to CO_2 injection, and evaluate how choice of modeling parameters (particularly, rate constants for the key reactions and mineral surface areas) affect the model prediction, and what is the model's uncertainty.
- Identify critical processes for up-scaling and construct a continuum scale binary phase reactive flow model, using Frio test site as a case study.

Frio Brine Pilot Field Site

Figure from presentation by T. Meckel (2008)



Water chemistry

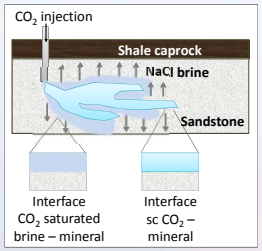
Component	Concentration (mol/kg H_2O)
Ca^{2+}	6.6×10^{-2}
Mg^{2+}	2.2×10^{-2}
Na^{+}	1.35
K^{+}	4.53×10^{-3}
Iron	4.63×10^{-4}
$SiO_2(aq)$	2.50×10^{-4}
Carbon	5.04×10^{-2}
Sulfur	4.20×10^{-5}
Al^{3+}	1.56×10^{-8}
Cl^{-}	1.49
$O_2(aq)$	4.88×10^{-68}
pH	6.7
Temperature	59 °C

Minerals

Quartz	Oligoclase	Illite
Kaolinite	K-feldspar	Na-smectite
Calcite	Chlorite	Hematite

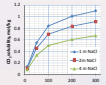
- Setting: salt dome flank, Frio sandstone, 5,000 ft deep;
- 1600 tons at 3 kg/s, 10 day injection ~1545 m deep well in **2004**;
- ~40 water samples collected for 4 days using 1530m deep monitoring well.

Geochemical Modeling



CO_2 injection creates two new distinct geochemical interfaces:
1. Supercritical CO_2 – mineral interface: **H_2O activity is decreasing**
2. CO_2 saturated brine – mineral interface: **CO_2(aq) is increasing**

Boundary condition 1: Solubility of CO_2 in brine



- Estimated CO_2 solubility at 333.15 K, 150 bar, 1.65 M NaCl = **0.8143 M**

Boundary condition 2: amount of H_2O removed due to dehydration by CO_2

- Assumed maximum **90 wt.** % of H_2O is removed due to "drying" by CO_2

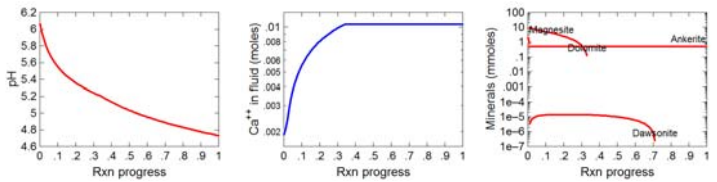
Geochemists Work Bench (GWB)

Updated thermodynamic database: Modified EQ3/6 v. 8.0
Pitzer activity correction method.
20 elements: O, **Al**, B, Br, C, Ca, Cd, Cl, F, Fe, H, K, Li, Mg, Mn, **N**, Na, **P**, S, **Si**.
Updated carbonate solubility: dolomite (Holland and Powell, 1998); magnesite (Holland and Powell, 1998), hydromagnesite (Robie and Hemingway, 1995), dawsonite (Benezeth et al. 2007), siderite (Benezeth et al. 2009), added ankerite (Holland and Powell, 1998), ΔG and ΔH values for HCO_3^- species from (Robie and Hemingway, 1995).

GWB Path of Reaction Modeling Results

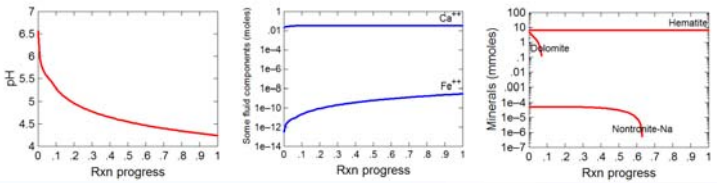
- Oversaturated minerals are allowed to precipitate before reaction path calculation – initial brine is slightly oversaturated with respect to dolomite, ankerite, magnesite, and dawsonite.

Input: Aqueous species + Calcite; Single reactant 0.8143 moles of CO_2(g)



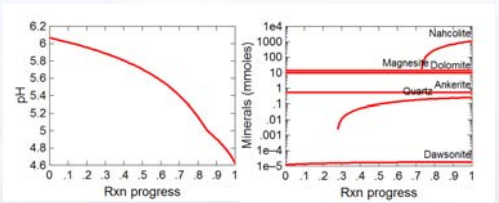
•**Prediction**: pH decreases to 4.7, predicted dissolution of calcite, dolomite, dawsonite, and magnesite.

Input: Aqueous species + Calcite+Hematite; Single reactant 0.8143 moles of CO_2(g)



Prediction: pH decreases to 4.2, predicted release of Ca^{2+} and Fe^{2+}
$[Fe^{2+}]$ is limited by Fe^{3+} solubility/redox reactions.

Input: Aqueous species + Calcite; $[HCO_3^-]$ is fixed at 0.3 M; 900 g of H_2O is removed



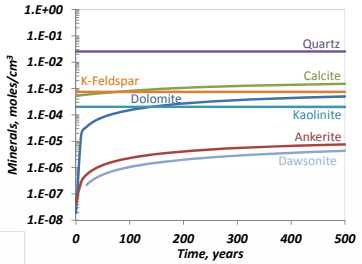
Prediction: pH decreases to 4.6, nahcolite, dolomite, magnesite, quartz, ankerite, and dawsonite precipitate.

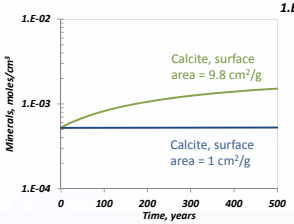
GWB Reactive Flow Modeling Results

- 1-D Reactive Flow Model;
- 1 m block, 34 % porosity;
- Initial brine composition of Frio reservoir;
- Temperature 59 °C;
- Time 500 years;
- Reacting fluid – Frio brine saturated with CO_2(g): 0.8167M HCO_3^-, pH = 3.3;
- Over the course of the simulation pH is allowed to rise back to 6.7.

Mineral	Specific surface area cm^2/g	Kinetic rate constant mol/cm^2 sec
Calcite	9.8	$5.012\cdot10^{-10}$
Quartz	9.8	$1.023\cdot10^{-18}$
Kaolinite	151.6	$6.918\cdot10^{-18}$
K-feldspar	9.8	$3.89\cdot10^{-17}$
Albite	9.8	$1.445\cdot10^{-16}$

Values adapted from Xu et al., 2010, values for albite are assumed equal to oligoclase.





- Conditions – same as above;
- Surface area for calcite = 1 cm^2/g, for kaolinite = 15 cm^2/g.

Conclusions

- Injection of CO_2 in a geologic formation creates two distinct geochemical interfaces: (1) mineral surfaces/CO_2-saturated brine, and (2) mineral surfaces/supercritical CO_2. The predominant trends in carbonate mineral precipitation and dissolution are opposite at these interfaces, mineral dissolution is predicted as a result of pH decrease with increasing dissolved CO_2 in brine. Due to dehydration of the reservoir by supercritical CO_2, mineral precipitation is predicted.
- Reactive flow models suggest that as CO_2 is dispersed, carbonate precipitation is predicted for time scale of >100 years. The uncertainty of these models arises from uncertain reactive surface areas of the minerals, as well as kinetics parameters.

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