Preliminary Reactive Transport Modeling and Laboratory Experiments Conducted in Support of the Frio Pilot Test

GCCC Digital Publication Series #05-04m

K. G. Knauss
J. W. Johnson
Y. K. Kharaka

Keywords:
Reactive Transport (RT), CRUNCH Simulation, PFR15+ Simulation, Plug Flow Reactor

Cited as:
Knauss, K.G., Johnson, J.W., and Kharaka, Y.K., Preliminary reactive transport modeling and laboratory experiments conducted in support of the Frio Pilot test: presented at the National Energy Technology Laboratory Fourth Annual Conference on Carbon Capture and Sequestration, Alexandria, Virginia, May 2-5, 2005. GCCC Digital Publication Series #05-04m, pp. 1-26.

Preliminary Reactive Transport Modeling and Laboratory Experiments Conducted in Support of the Frio Pilot Test

Kevin G. Knauss[1], James W. Johnson[1] and Yousif K. Kharaka[2]

Lawrence Livermore National Laboratory[1]
U.S. Geological Survey[2]

RT Models & Experiments – why do them?

- **Predict short-term chemical signals from CO_2**
  - **Help design pilot project sampling program**
  - **Provide data useful to licensing and safety**
  - **Evaluate injectivity and reservoir effects**
- **Predict long-term CO_2, fluid & mineral geochemical interactions**
  - **Various sequestration processes => capacity assessment needed for credits**
  - **Chemical integrity of seals**
    - **Cap rock (Anahuac Shale)**
    - **Cements and other borehole seals**
- **RT simulators require reactive transport experiments for validation**

Requirements For RT Modeling

- **Hydrologic model physical characteristics**
  - **Based on field measurements and TOUGH2 (Pruess) models from Chris Doughty (LBL)**
- **Baseline geochemical samples**
  - **Reservoir fluids, injection fluids, reservoir rock**
    - **Compositions and estimate of heterogeneity**
- **Time series geochemical samples during field or lab experiment for simulator validation**
  - **Reservoir fluids and gases & post-test solids**
    - **Major inorganic and organic ions (& rock forming elements)**
    - **pH, TIC, TOC, isotopes, tracers**
    - **T & P**
- **A RT code**
  - **CRUNCH (Steefel) for preliminary modeling**
  - **NUFT (Nitao) for more fully coupled modeling**

Frio Fm. injection scenario

- **CRUNCH simulation**
  - **Calculate radial velocity field**
    - **Match breakthrough time (2.1d) to calculate cell thickness**
      - → $T_{bt} = (\pi x^2 h \varphi S_g \rho)/Q$
      - → **In agreement with RST (reservoir saturation tool) = 1.2m**
    - **Essentially a 1D, "radially symmetric" calculation**
      - → $V(x) = Q/(2\pi x h \varphi S_g \rho)$
      - → **Calculated velocities range from 2.1×10^5 to 4.4×10^2 m^3/m^2y**
  - **Inject CO_2-charged water into 1.2m of "C" sand**
    - **Equivalent to 178 T/d CO_2 for 9 days**
      - → **Single phase approximation for fluid chemistry**
    - **P_{CO2} = 152b at T = 56°C => f_{CO2} = 78.3b**
    - **Look for chemistry changes in fluid as front passes well**
  - **Reservoir fluid (initial) is sample 04FCO2-218**
  - **Reservoir rock (initial) is BEG Pilot No. 1 at 5065.55'**

Frio Fm. Problem Definition

- Mineralogy (Frio "C" sand)
  - Quartz 71.0%
  - K-feldspar 9.0%
  - Labradorite 13.0%
  - Illite/muscovite 4.9%
  - Calcite 0.4%
  - Kaolinite 0.3%
  - Dolomite 1.0%
  - Pyrite 0.4%
- Porosity 35.0%
- Thermo & kinetics data
  - Calculated data for An60
  - 2 rate equations/mineral
    - Acid catalyzed
    - Neutral pH
- Potential secondary minerals
  - Siderite
  - Magnesite
  - Dawsonite - $NaAlCO_3(OH)_2$
  - Chalcedony
  - Barite
  - Anhydrite
  - Strontianite
- Water chemistry for Frio "C" sand
  - Measured: Na, K, Ca, Mg, Ba, Sr, Si, Cl, S, C, pH (04FCO2-218)
  - Mineral/gas equilibria assumed:
    - Al = muscovite
    - Fe = pyrite (measured, but…)
    - $O_2 = SO_4/H_2S$

Reference State (25°C, 1b) Kinetic Parameters

mineral	log k (mol/m^2*s)	E_a (kcal)	n	source
Albite	-9.69	14.3	.5	Blum & Stillings (1995)
Albite	-12.0	16.2	0	Blum & Stillings (1995)
Anhydrite	-2.76	7.65	.11	Barton & Wilde (1971); Dove & Czank (1995)
Labradorite	-8.86	15.9	.5	Blum & Stillings (1995)
Labradorite	-12.0	16.2	0	Assume similar to albite
Barite	-7.19	7.65	.11	Dove & Czank (1995)
Calcite	-1.16	4.54	1.0	Alkattan et al. (1998)
Calcite	-6.19	15.0	1.0	Chou et al. (1989)
Chalcedony	-12.7	16.5	0	Rimstidt & Barnes (1980) - α-cristobalite
Clinochlore	-11.6	15.0	0	Malmstrom et al. (1996)
Dawsonite	-7.00	15.0	0	Assume between calcite and magnesite
K-feldspar	-9.45	12.4	.4	Blum & Stillings (1995)
K-feldspar	-12.0	13.8	0	Blum & Stillings (1995)
Kaolinite	-11.6	15.0	.17	Nagy (1995)
Kaolinite	-13.0	15.0	0	Nagy (1995)
Magnesite	-4.36	4.54	1.0	Chou et al. (1989)
Magnesite	-9.35	15.0	0	Chou et al. (1989)
Muscovite	-11.7	5.26	.4	Knauss & Wolery (1989); Nagy (1995)
Muscovite	-13.0	15.0	0	Knauss & Wolery (1989); Nagy (1995)
Pyrite	-8.00	15.0	0	Steefel (2001)
Quartz	-13.9	20.9	0	Testor et al. (1994)
Siderite	-3.01	5.00	.9	Gautelier et al. (1999) - dolomite
Siderite	-8.90	15.0	0	Steefel (2001)
Strontianite	-3.03	10.0	1	Sonderegger (1976)
Strontianite	-7.35	10.0	0	Sonderegger (1976)

Mineral dissolution/precipitation:

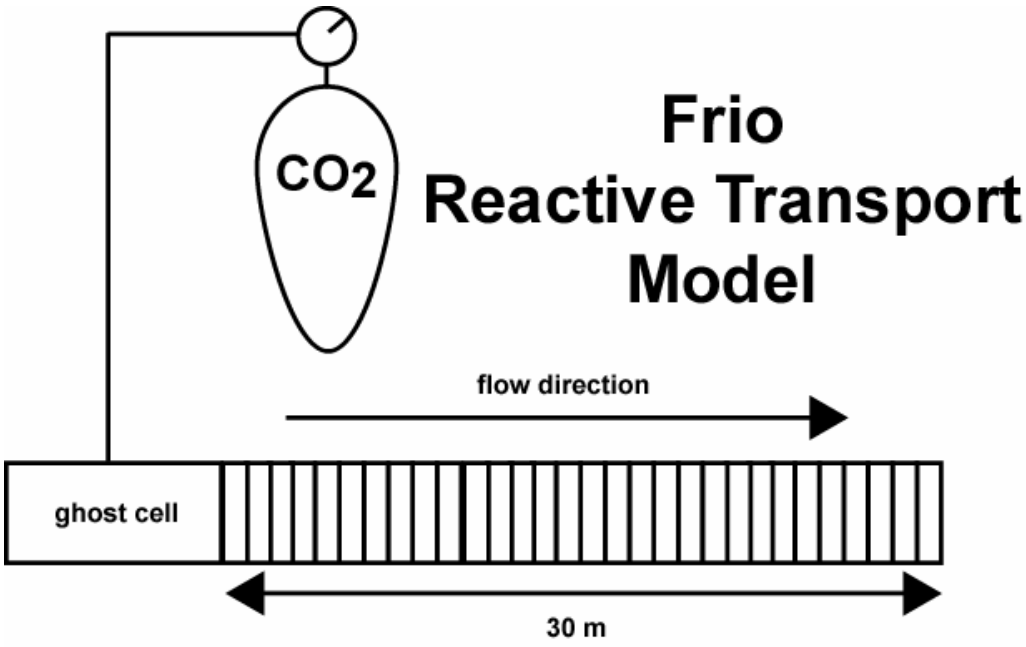
$$r_m = k_m A_m \prod_{i=1}^{N} a_i^n \left| \left(\frac{Q}{K} \right) - 1 \right|$$

Temperature dependence:

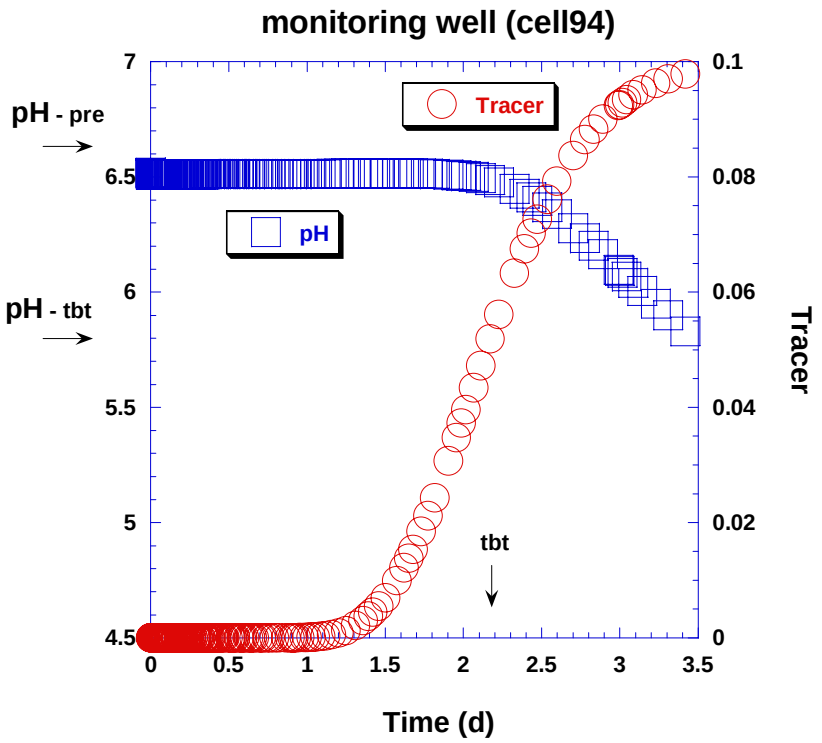
$$k_m = k_{m,T_r} \exp\left[\frac{-E_a}{R} \left(\frac{1}{T} - \frac{1}{T_r} \right) \right]$$

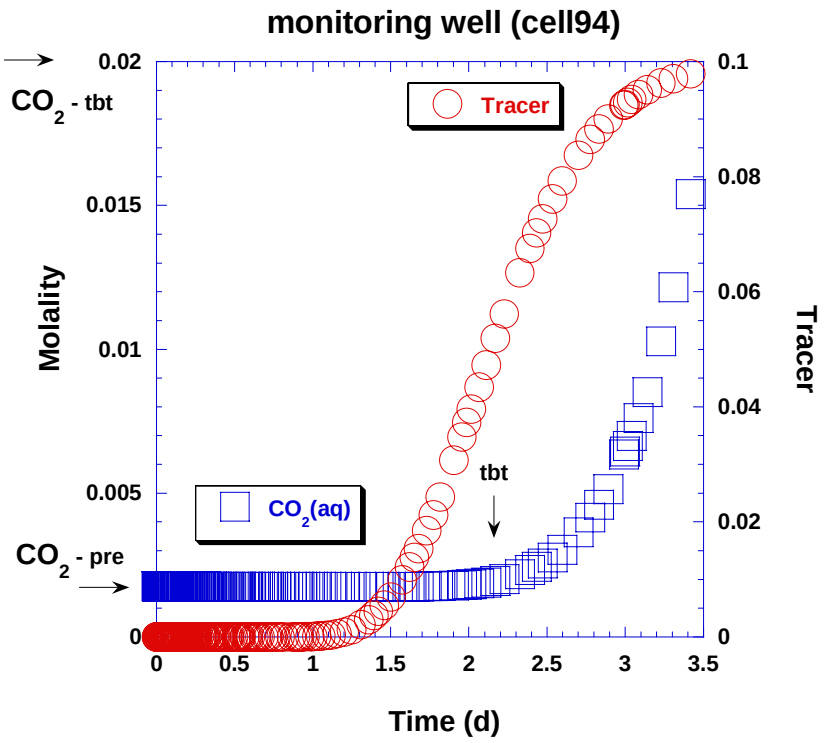
1D Reactive Transport Modeling – Frio

- CRUNCH
  - Carl Steefel (LBL)
  - Full chemistry reactive transport simulator
  - Fictive tracer to track front
  - Simplified flow model – chem not coupled to flow, only 1 mobile phase
  - Use to help define chem for coupled RT simulator
  - 1D approximates a single streamline
  - Radial or Cartesian coordinates
  - Radial front velocity model
    - $V(x) = Q/(2\pi x h \varphi S_g \rho)$
    - $T_{bt} = (\pi x^2 h \varphi S_g \rho)/Q$

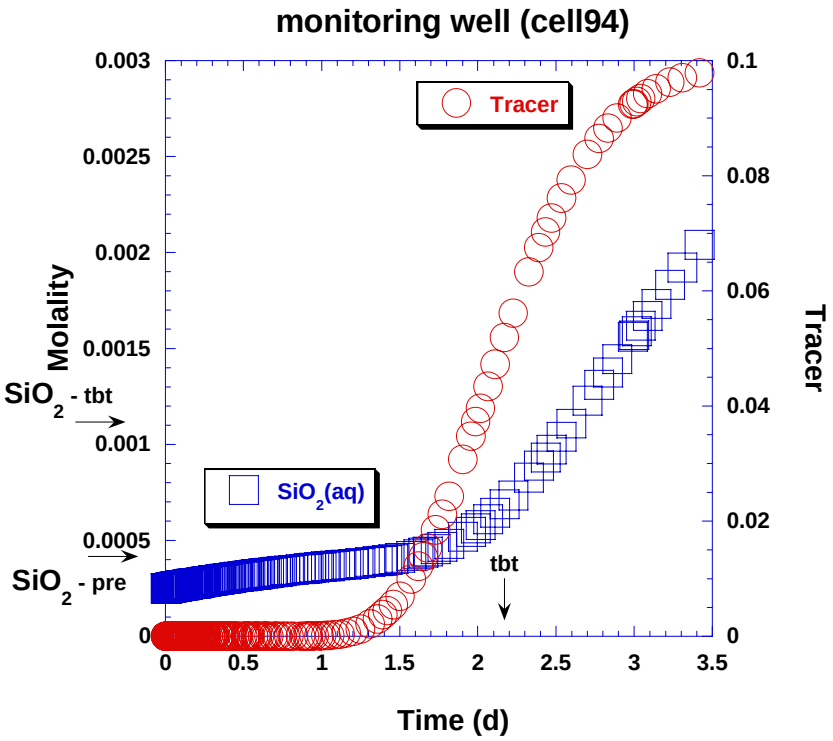


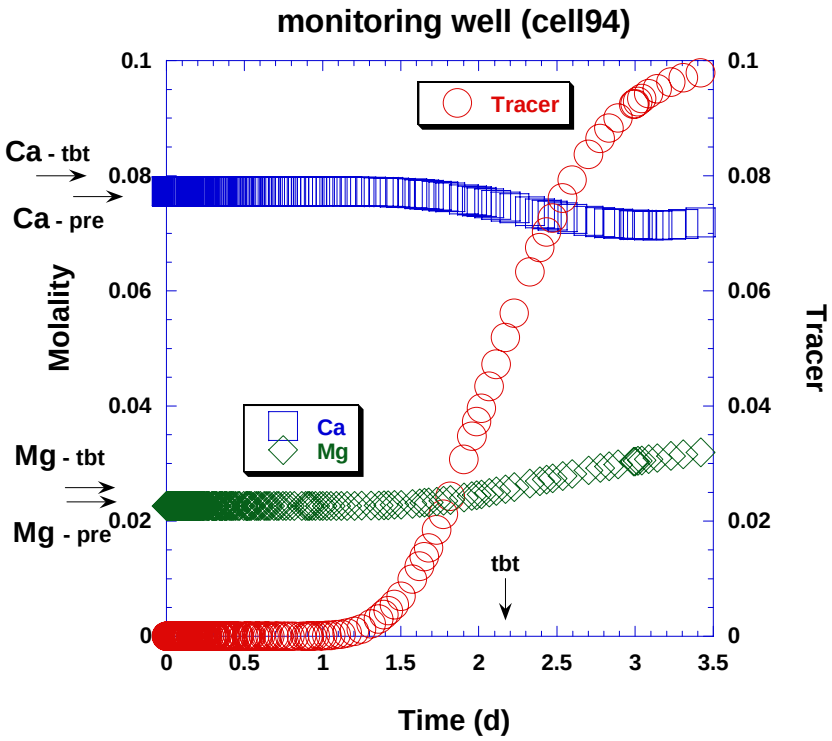
Frio simulation vs. field data



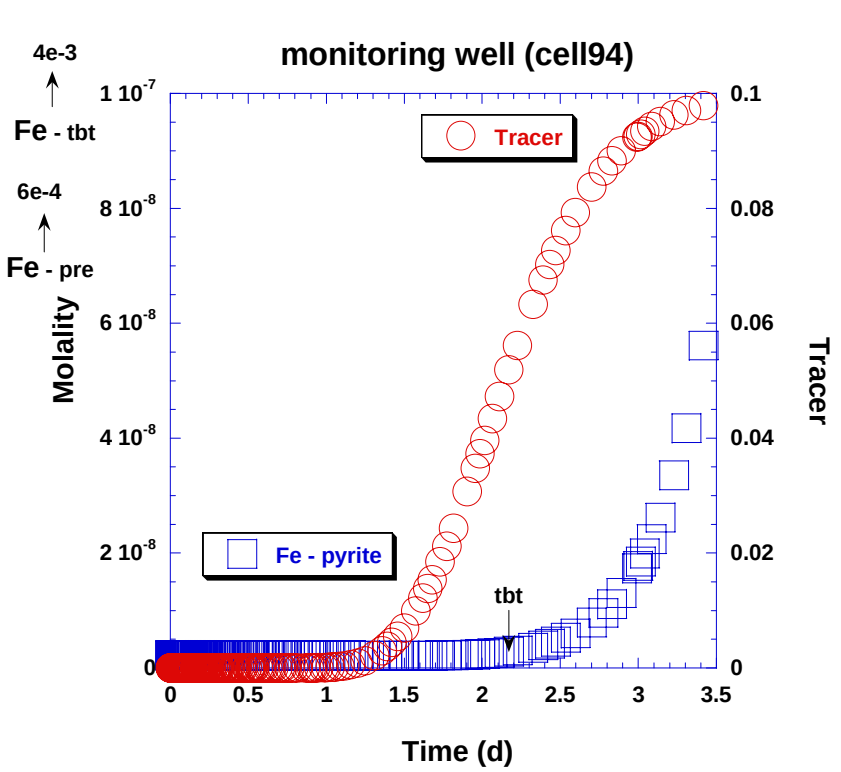


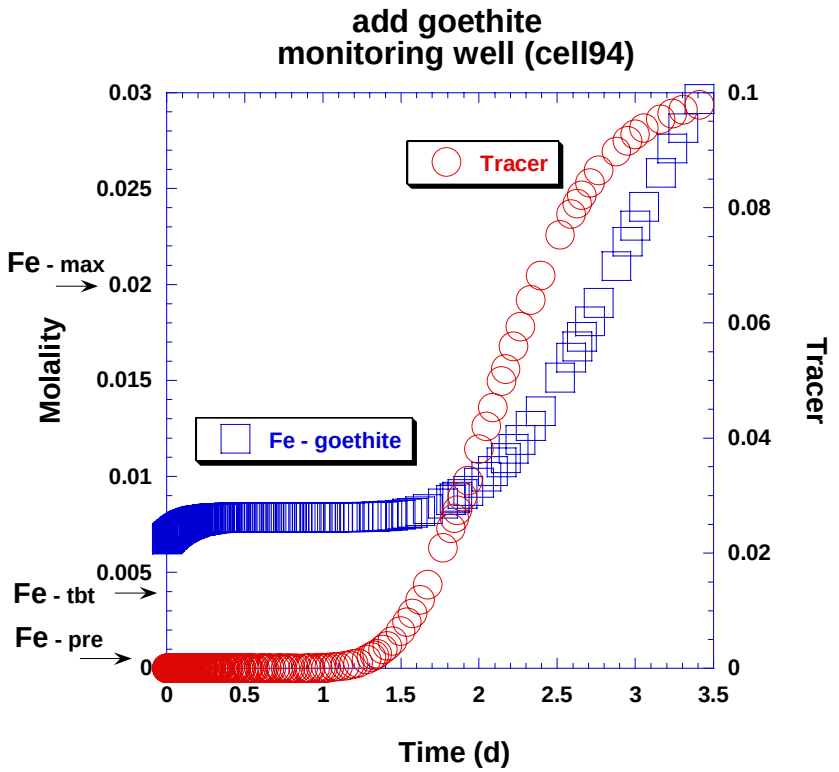
Frio simulation vs. field data



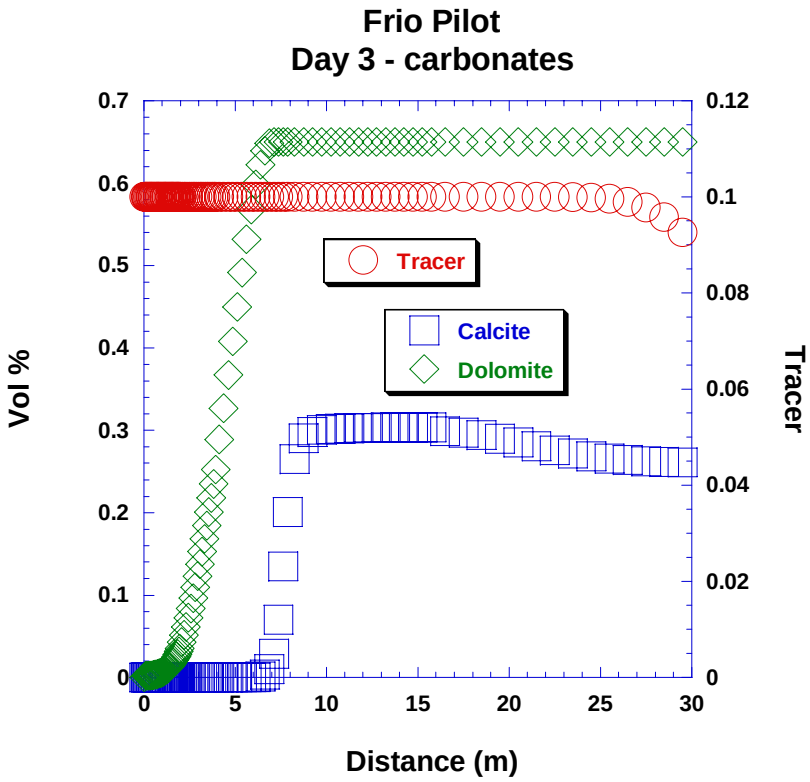


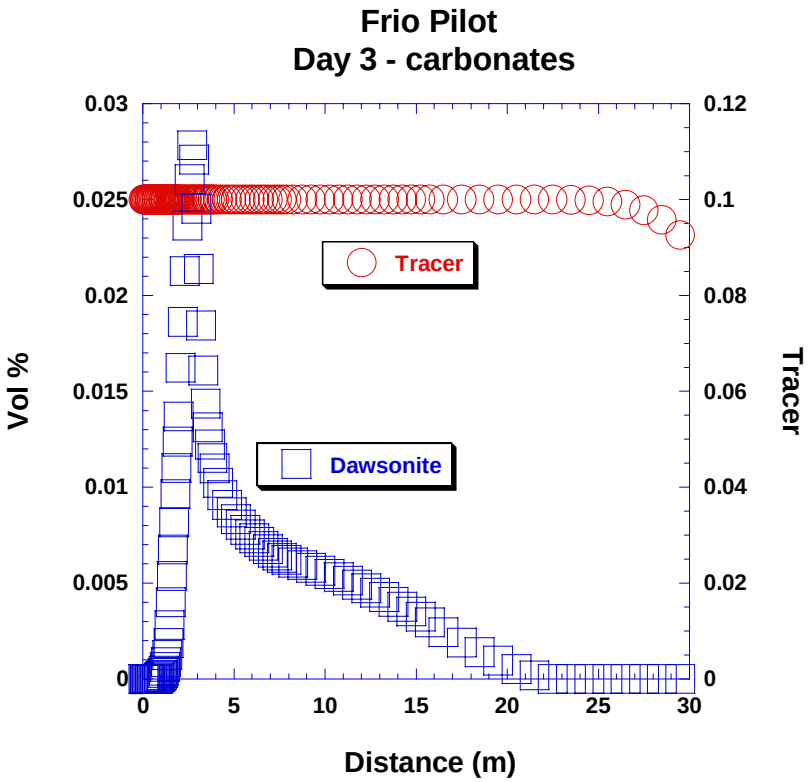
Frio simulation vs. field data





Frio simulation vs. no field data





Frio simulation vs. field data

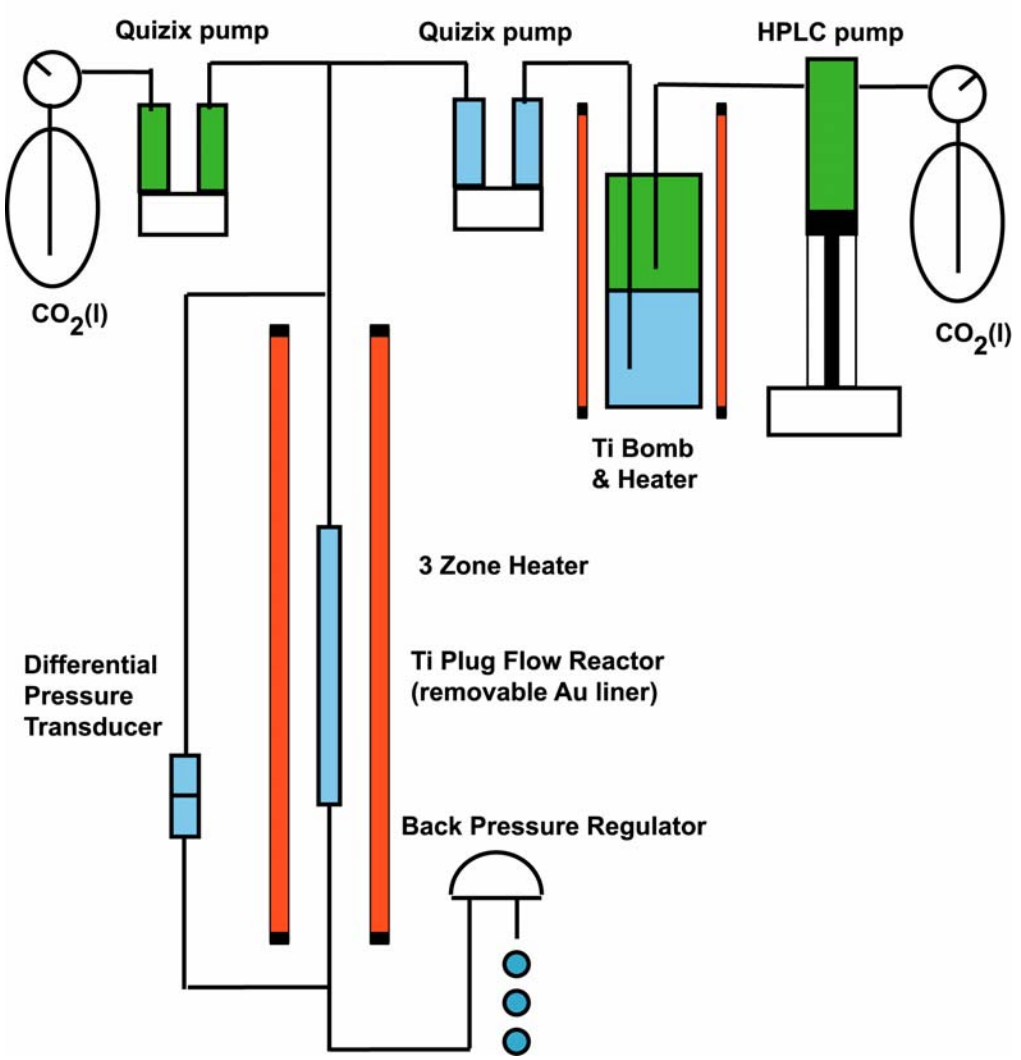
- How'd we do?
  - Trends OK, thermo/kinetic data may be OK – see next
  - Absolute concentrations off, need fully coupled 2-phase RT simulations
- What can we do to improve?
  - Modeling
    - Include ion exchange to help improve very short term agreement
    - Include "grain coating" minerals – tweedle thermo & kinetic data, as needed, using RT lab experiments – see next
    - Use a more fully coupled RT model – NUFT, etc.
  - Field data
    - Measure missing components – Al, redox couples, etc.
    - Better characterize composition & mineralogy of reservoir rock

Reactive Transport Experiments

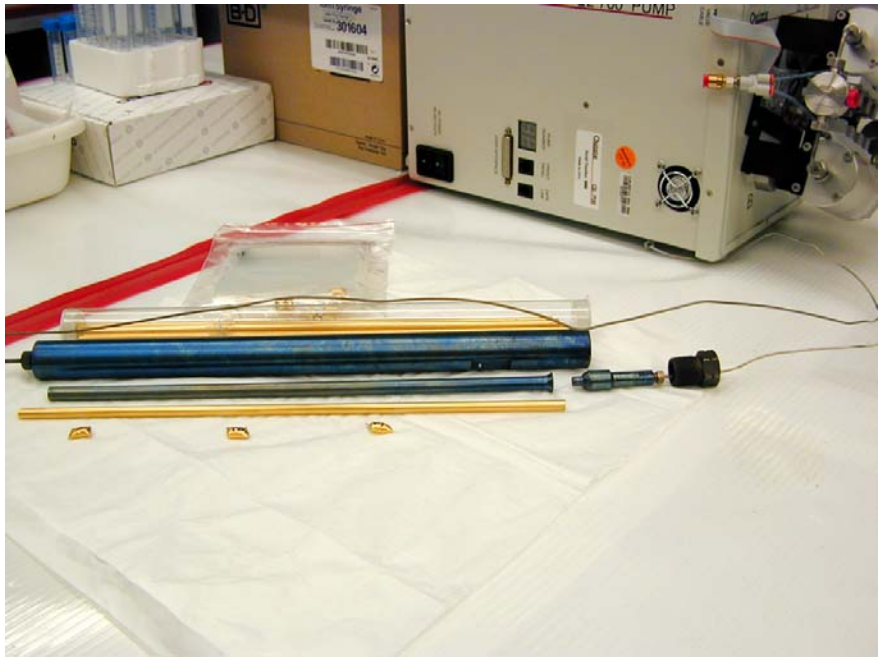
- **Why do them?**
  - **Short term issues**
    - **Validate short term model predictions**
    - **Identify dominant mineral-water reactions**
      - → **Dominated by dissolution processes in short term**
    - **Optimize thermodynamic, kinetic and surface area model parameters**
  - **Long term issues**
    - **Determine appropriate growth kinetics parameters**
      - → **Existing growth kinetics data very sparse**
    - **May require "over-driving" the system to obtain results**
      - → **Use temperature as accelerator, being careful about stability fields and relative growth kinetics (E_a) – keep it relevant**
    - **Needed for RT simulator validation**

Reactive Transport Experiments

- **Plug Flow Reactor**
  - Ideal 1D Physical Model
  - Quantitative validation
    - Models (processes)
    - Codes
      - Flow and Transport
      - Geochemical
    - Data
      - Thermodynamic & Kinetic
      - Physical & Hydrological
    - Post-mortem on solids
  - Wide parameter space
    - 20-300 °C (isothermal or gradient)
    - 1-345 b
    - 0.0001-10 mL/min
    - Supercritical CO_2, 0-5 m NaCl, etc.
    - Darcy Law permeability on the fly



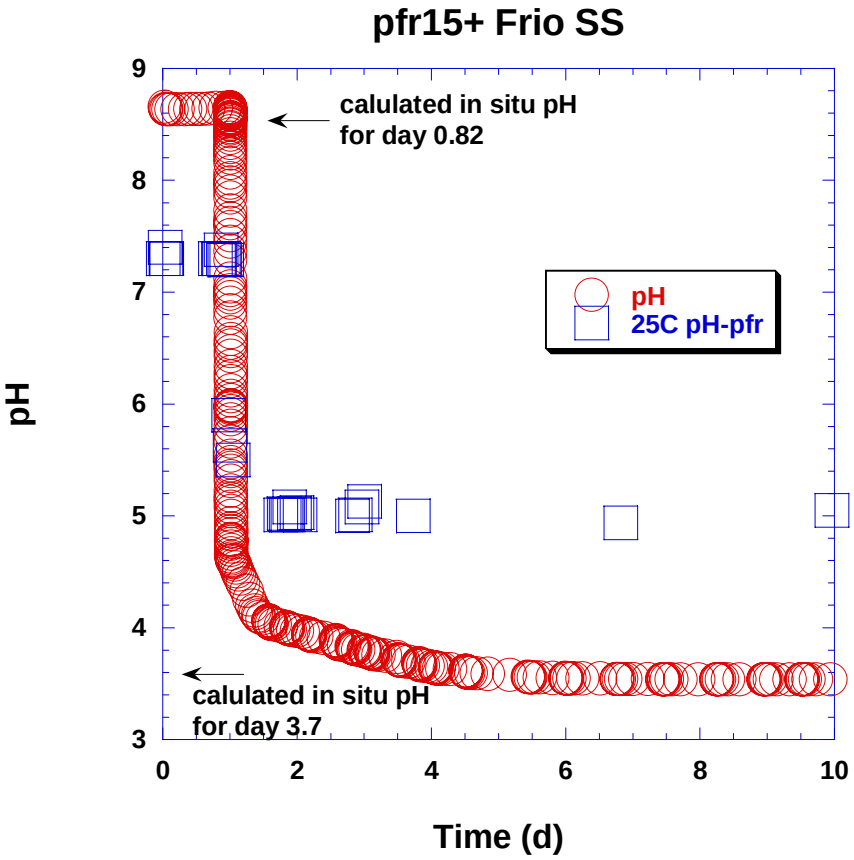
Reactive Transport Experiments

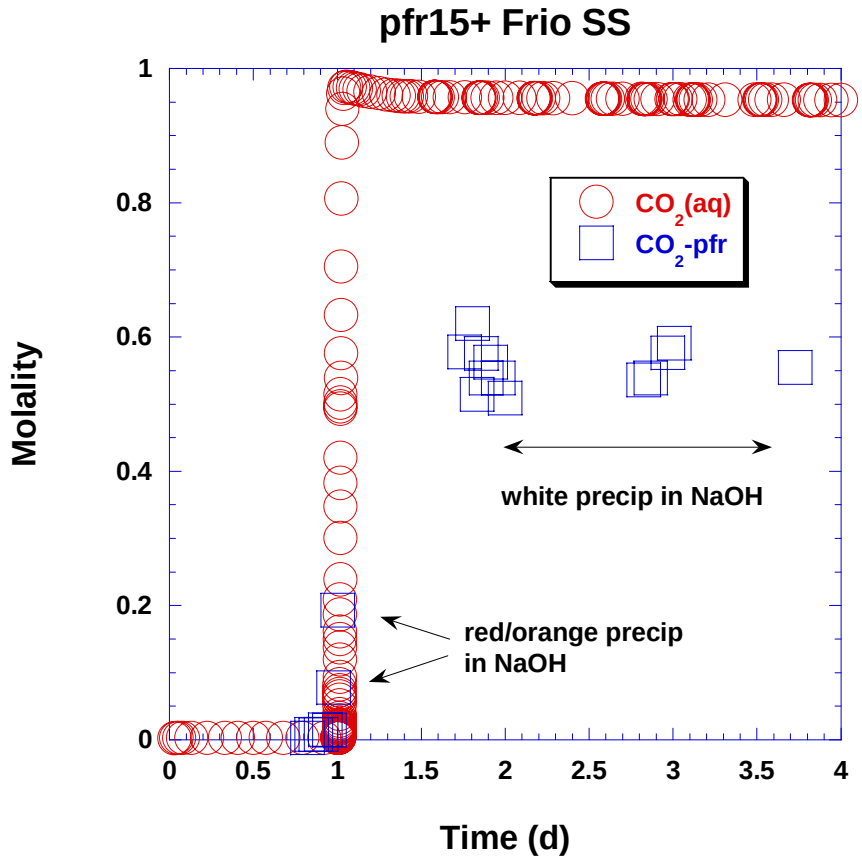


Frio (PFR15+) Experimental Design

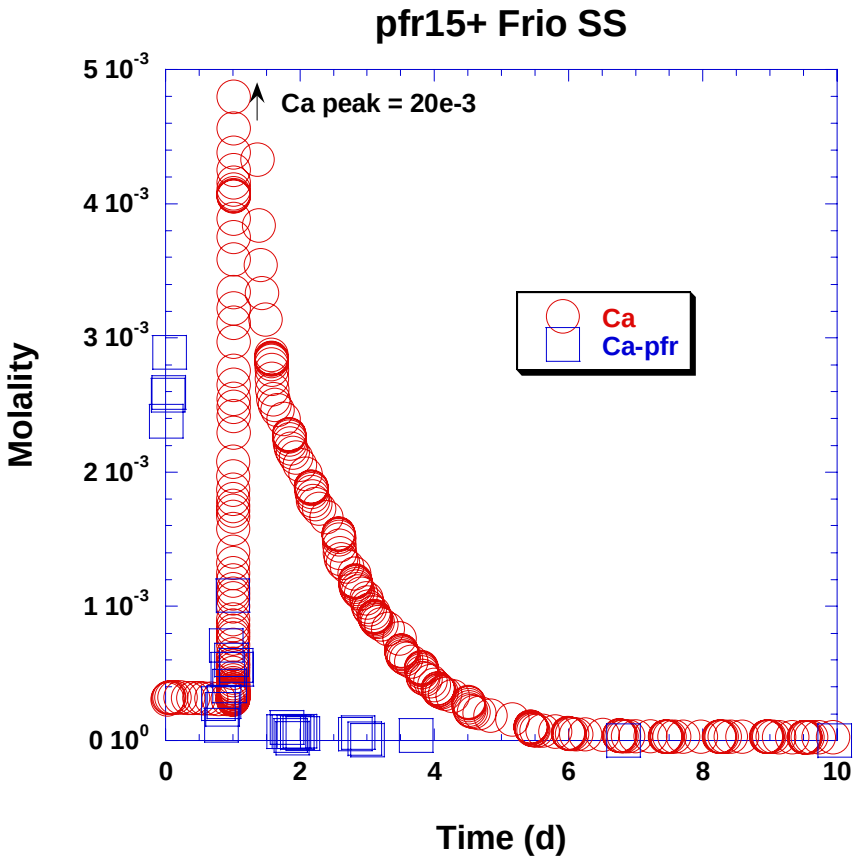
- **Conditions**
  - T = 56°C
  - P = 100b (f_{CO2} = 54.3b)
  - Flow rate = 151 g/d ⇒ 2058 $m^3/m^2/y$ ⇒ 5144 m/y for PFR
    - Frio pilot test = 30m/51h = 5156 m/y
  - Time = 9 d (following 1d flow w/o CO_2)
- **Solid**
  - Frio "C" sand from BEG Pilot No. 1 at 5065.55'
    - Recovered at end of experiment and subsampled along core
- **Aqueous phase**
  - 1.5 m NaCl & 2.2×10^{-3} m $NaHCO_3$ (simplified Frio brine)
    - Equilibrated with CH_4
    - Sampled throughout experiment
    - Measured: pH, CO_2, O_2, Na, K, Ca, Mg, Fe, Mn, Al & Si

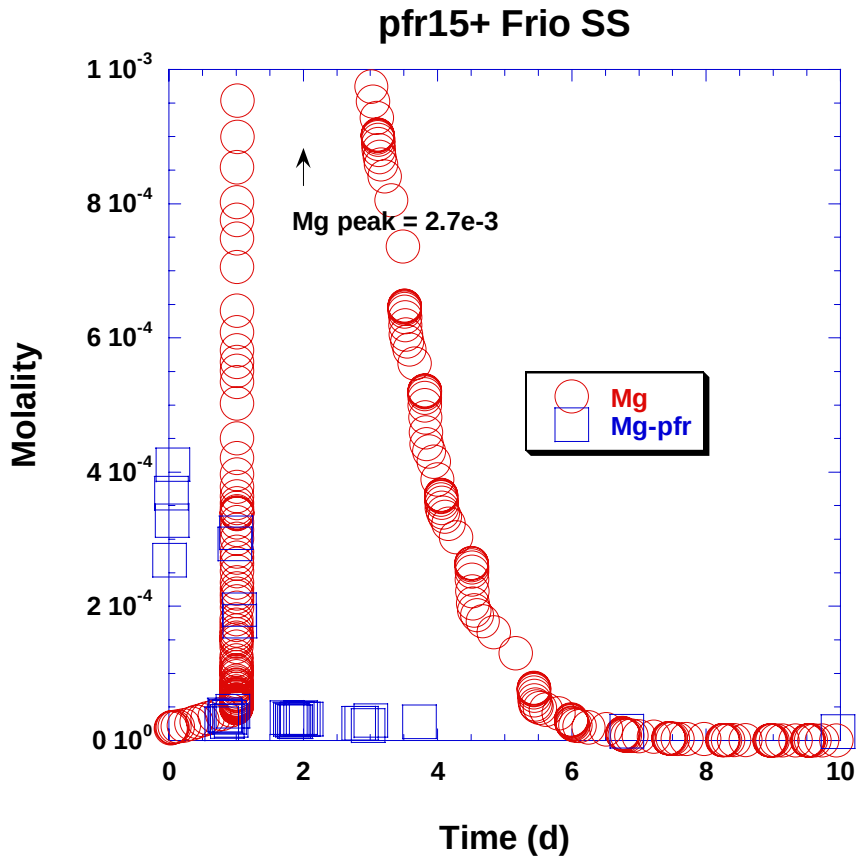
PFR15+ simulation vs. lab data



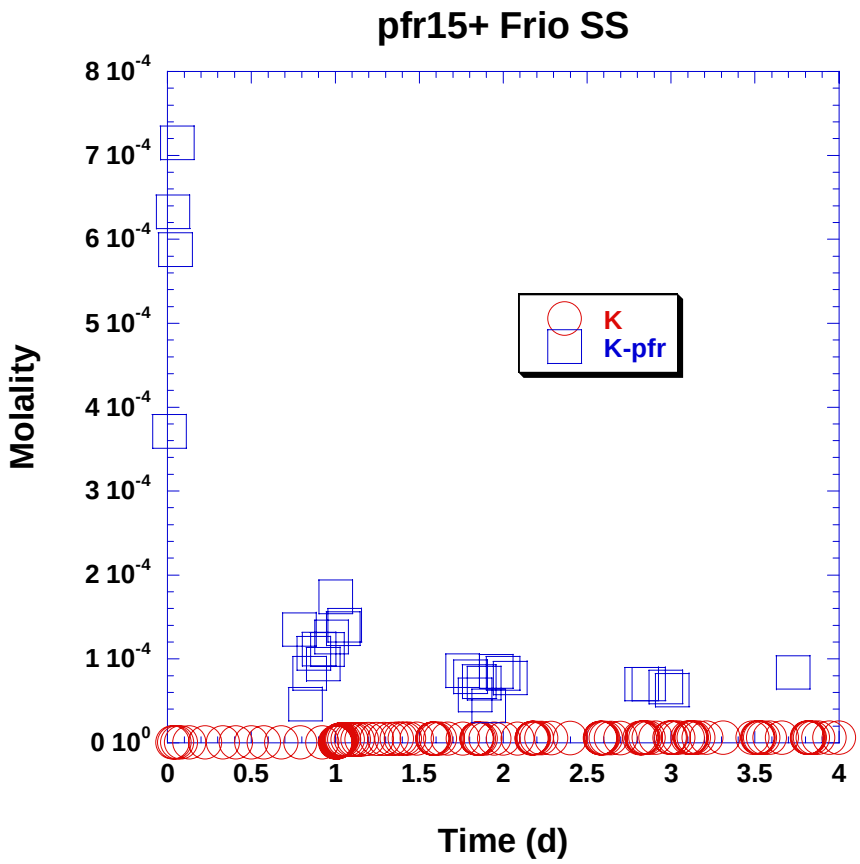


PFR15+ simulation vs. lab data

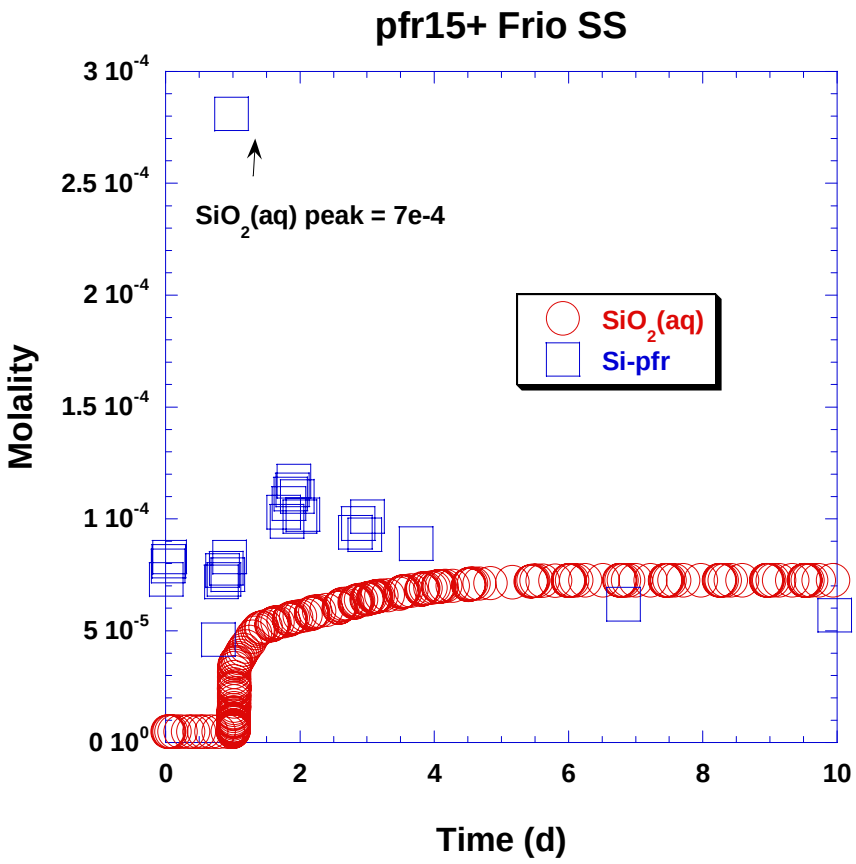


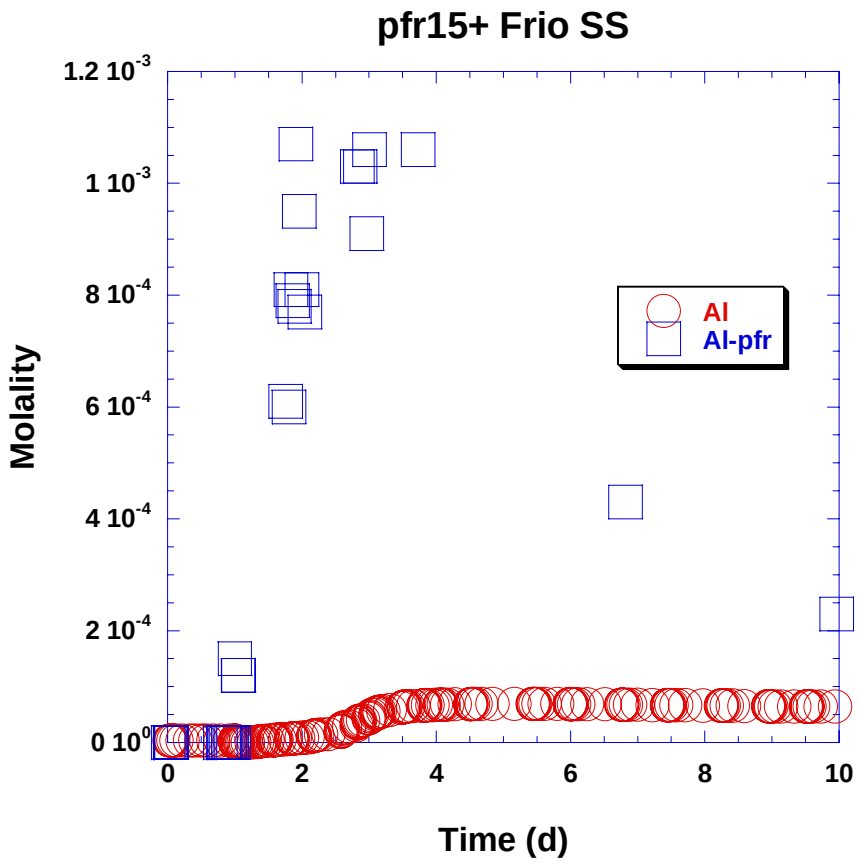


PFR15+ simulation vs. lab data

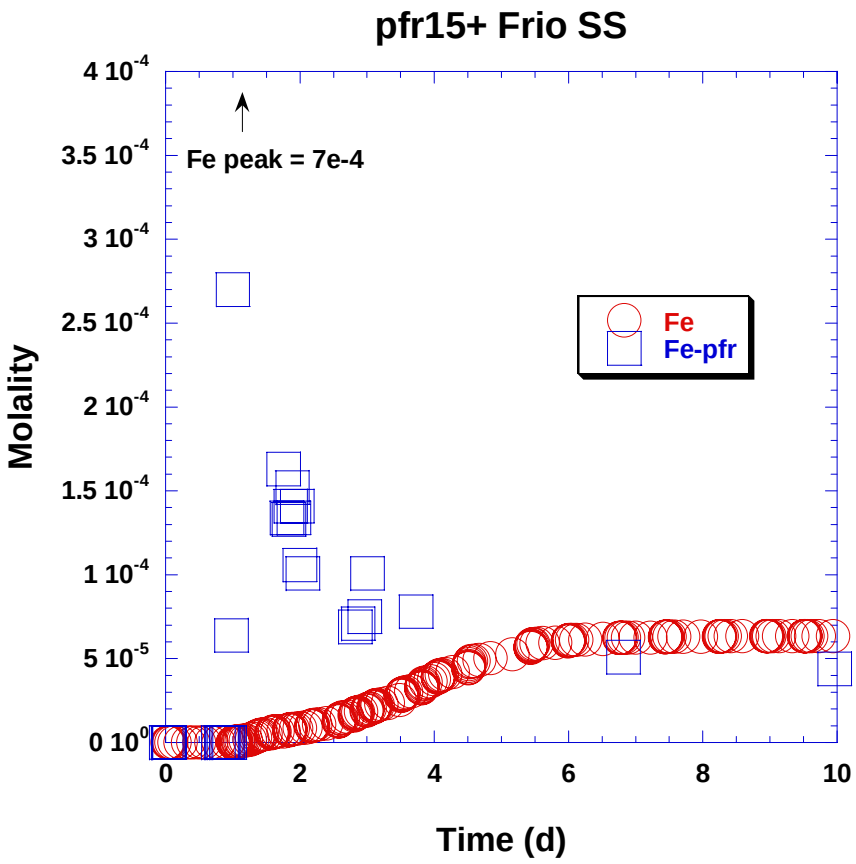


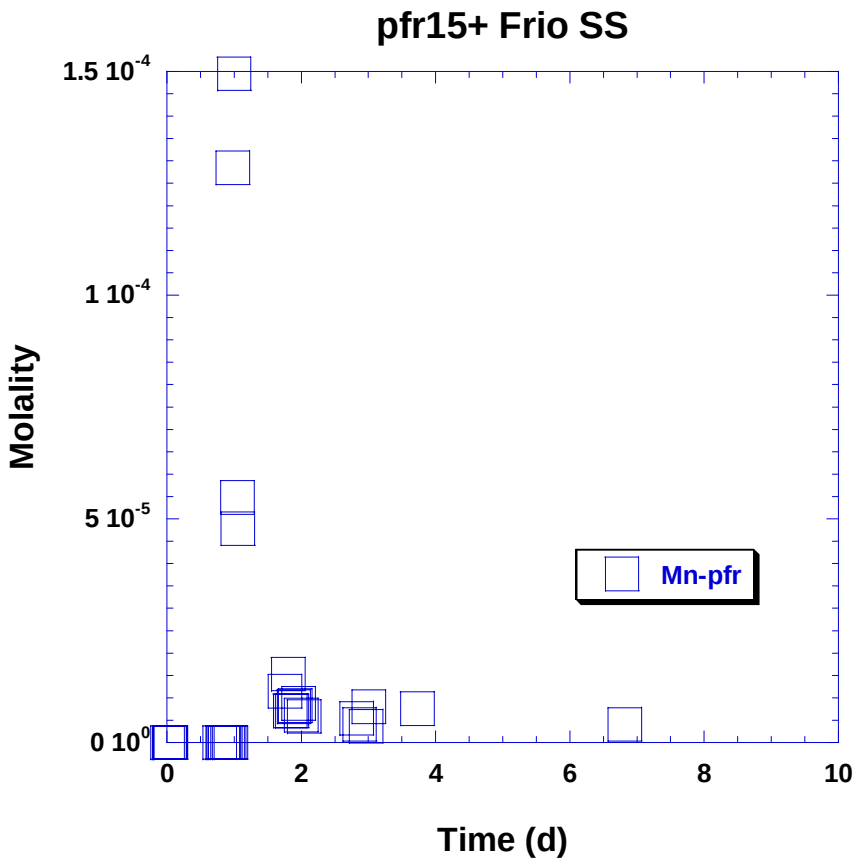
PFR15+ simulation vs. lab data





PFR15+ simulation vs. lab data





PFR15+ simulation vs. lab data

- How'd we do?
  - Steady-state concentrations are very close – this is good!
  - Missed some transient spikes
    - The lab spikes match those seen in field – this is good!
- What can we do to improve?
  - Modeling
    - Fe, Mn & Al spikes will require inclusion of less stable grain coating phases that quickly dissolve in early time
  - Lab data
    - Ca and Mg spike can be captured correctly by switching almost immediately to CO_2-charged fluid
      - → No need to run overnight

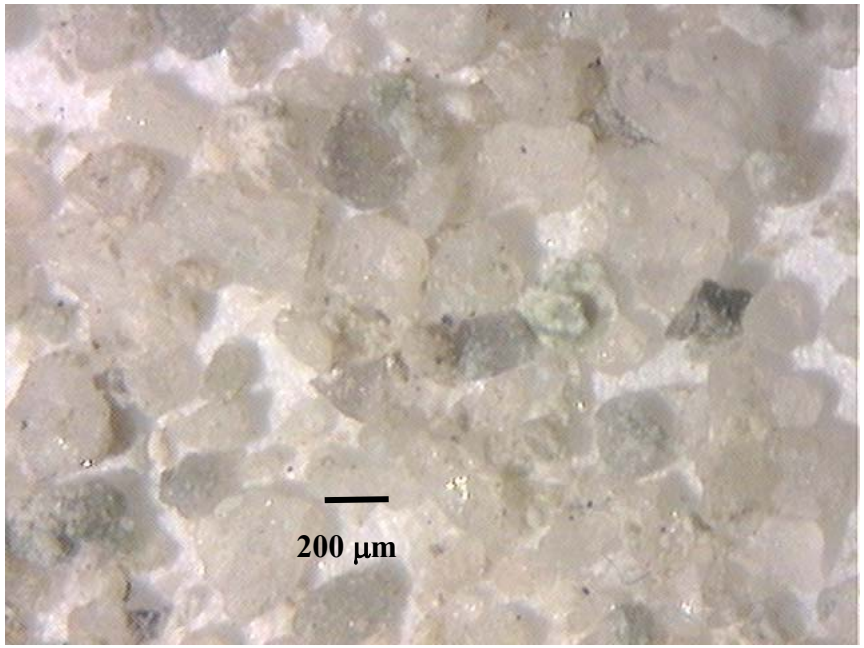
Conclusions

- RT simulations are required to make long-term capacity/performance assessment and assure safety
- Reactive transport experiments are required to provide the model parameters needed and to validate use of reactive transport simulators
  - They complement and quantify field experiments
- More fully coupled simulations are planned next for Frio data
  - More experiments are being done to validate the simulators

Slides behind here are backup

Mineral Specific Surface Areas

- Geometric approximation
  - Corrected to BET
  - 200 μm spheres
  - Mineral molar volumes
  - Primary minerals only
  - Secondary minerals have small initial area



Mineral	SSA (m^2/g)
Quartz	0.0566
K-feldspar	0.0939
Illite/muscovite	0.5299
Calcite	0.0533
Kaolinite	0.5782
Labradorite	0.0869
Pyrite	0.0299
Dolomite	0.0524

CO2 fugacity and pH at 56C