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

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RT Models & Experiments – why do them?

- Predict short-term chemical signals from CO₂
 - Help design pilot project sampling program
 - Provide data useful to licensing and safety
 - Evaluate injectivity and reservoir effects
- Predict long-term CO₂, 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



CRUNCH simulation

• Calculate radial velocity field

Match breakthrough time (2.1d) to calculate cell thickness

 $\rightarrow T_{bt} = (\pi x^2 h \phi S_g \rho)/Q$

 \rightarrow In agreement with RST (reservoir saturation tool) = 1.2m

Essentially a 1D, "radially symmetric" calculation
 V(x) = Q/(2πxhφS_σρ)

→Calculated velocities range from 2.1x10⁵ to 4.4x10² m³/m²y

- Inject CO₂-charged water into 1.2m of "C" sand
 - Equivalent to 178 T/d CO₂ 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)
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- 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 NaAlCO₃(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...)
 - $\diamond O_2 = SO_4 / H_2 S$

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

mineral	log k	Ea	n	source
	(mol/m^2*s)	(kcal)		
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 Mineral dissolution/precipitation:
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) $\mathbf{P} = \mathbf{I} \cdot \mathbf{A} \cdot \mathbf{P} \cdot $
Chalcedony	-12.7	16.5	0	Rimstidt & Barnes (1980) - α -cristobalite $\Gamma_m = \kappa_m A_m \prod a_i \ \frac{1}{K} \ - 1 \ $
Clinochlore	-11.6	15.0	0	Malmstrom et al. (1996) $i=1$ $ \langle \mathbf{N} \rangle $
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) Temperature dependence:
Kaolinite	-13.0	15.0	0	Nagy (1995)
Magnesite	-4.36	4.54	1.0	Chou et al. (1989) $\begin{bmatrix} \mathbf{F} & \mathbf{F} \end{bmatrix}$
Magnesite	-9.35	15.0	0	Chou et al. (1989) $ -E_a 1 $
Muscovite	-11.7	5.26	.4	Knauss & Wolery (1989); Nagy (1995) $k_m = k_m T exp \frac{m}{D} \frac{m}{D} \frac{m}{D}$
Muscovite	-13.0	15.0	0	Knauss & Wolery (1989); Nagy (1995) $\mathbf{r} = \mathbf{r} \mathbf{r}$
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)



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

$$\mathbf{V}(\mathbf{x}) = \mathbf{Q}/(2\pi \mathbf{x}\mathbf{h}\boldsymbol{\phi}\mathbf{S}_{\mathbf{g}}\boldsymbol{\rho})$$

$$T_{bt} = (\pi x^2 h \phi S_g \rho)/Q$$





Frio simulation vs. field data





Frio simulation vs. field data





Frio simulation vs. field data





Frio simulation vs. no field data







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
 - \rightarrow 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





Reactive Transport Experiments







Frio (PFR15+) Experimental Design

Conditions

- $T = 56^{\circ}C$
- $P = 100b (f_{CO2} = 54.3b)$
- Flow rate = 151 g/d ⇒ 2058 m³/m²/y ⇒ 5144 m/y for PFR
 Frio pilot test = 30m/51h = 5156 m/y
- Time = 9 d (following 1d flow w/o CO₂)

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 & 2.2x10⁻³ m NaHCO₃ (simplified Frio brine)
 - **Equilibrated with CH**₄
 - Sampled throughout experiment
 - ◆ Measured: pH, CO₂, O₂, Na, K, Ca, Mg, Fe, Mn, Al & Si





Hd



















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 CO₂-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

	Carlo a		die	
Stan -			23	
4.19			5 1	W
1	1		- produce	1
		-5		
	200 μm			

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



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