MODELING OF REACTIVE GEOCHEMICAL TRANSPORT IN GEOLOGICAL MEDIA (TOUGHREACT):

Tianfu Xu
Tianfu_Xu@lbl.gov

Earth Sciences Division
Lawrence Berkeley National Laboratory
TOUGHREACT FLOW CHART

FLOW (TOUGH2)

TRANSPORT

Computational Approach
- Sequential Iterative (SIA)
- Sequential Non-Iterative (SNIA)

CHEMISTRY
CAPABILITIES OF TOUGHREACT (1)

Processes:
- Transport: advection and diffusion in both liquid and gas phases
- Chemical reactions:
  - Aqueous complexation
  - Acid-base
  - Redox
  - Mineral dissol./precip. (equilibrium and/or kinetics)
  - Gas dissol./exsol.
  - Cation exchange
  - Surface complexation
  - Linear Kd adsorption
  - Decay

Special Features:
- Changes in porosity and permeability, and unsaturated zone properties due to mineral dissol./precip. and clay swelling
- Gas phase and gaseous species are active in flow, transport, and reaction
- Pitzer and Debye-Hückel activity models
- General: Porous and fractured media; 5 φ-k models; rate laws; any number of chemical species
- Two types of thermodynamic database including EQ3/6 (Wolery, 2004)
- Wide range of conditions
- Widely used: in-house projects, 21 institutions, 22 J. papers
- http://esd.lbl.gov/TOUGHREACT/
Other Features:

- Sequential iteration
- Transport equations: component by component
- Reaction equations: grid block by grid block
- Newton-Raphson iteration
- Preconditioned conjugate gradient solvers
- Integral finite difference
- Implicit time weighting
- 1-D, 2-D, or 3-D
- Porous and fractured media
- Non-isothermal, multiphase
- Physical and chemical heterogeneity

Equations for fluid and heat flow, and chemical transport.

| General governing equations: | \( \frac{\partial M}{\partial t} = -VF + q_e \) |
| Water: \( M_w = \phi (S \rho_x X_{ai} + S \rho_y X_{ay}) \) | \( F_w = X_{ai} \rho_x u_i + X_{ay} \rho_y u_y \) |
| Air: \( M_i = \phi (S \rho_x X_{ai} + S \rho_y X_{ay}) \) | \( F_i = X_{ai} \rho_x u_i + X_{ay} \rho_y u_y \) |
| Heat: \( M_h = \phi (S \rho_{1i} U_j + S \rho_{2i} U_2) + (1 - \phi \rho_{1i} U_1) \) | \( F_h = \sum h_p \rho_p u_p - \lambda VT \) |

where \( u_p = -k \frac{k_d}{\mu_p} (VP - p_r g) \), \( \beta = 1, g \) (Darcy’s Law)

Chemical components in the liquid phase (\( j = 1, 2, ..., N_1 \)):
\( M_j = \phi S_j C_j \)
\( F_j = u_j C_j - D_j V C_j \)
\( q_j = q_{\beta j} + q_{\mu j} + q_{\gamma j} \)

Chemical components in the gas phase (\( k = 1, 2, ..., N_2 \)):
\( M_k = \phi S_k C_k \)
\( F_k = u_k C_k + D_k V C_k \)
\( q_k = -q_{\gamma k} \)

where \( C_k = f_k / RT \) (gas law)

Example of chemical reaction equations

General dissociation reactions
\( S_k = \sum_{j=1}^{N_c} S_j^p \)

(1) General mass action equations:
\( K_i a_{S_i}^r = \sum_{j=1}^{N_c} (a_{S_j}^p)^{y_{ji}} \)

Aqueous dissociation: \( \text{HCO}_3^- = \text{CO}_3^{2-} + \text{H}^+ \)
\( K_{\text{HCO}_3^-} \gamma_{\text{HCO}_3^-} c_{\text{CO}_3^{2-}} = \gamma_{\text{CO}_3^{2-}} c_{\text{CO}_3^{2-}} \gamma_{\text{H}^+} c_{\text{H}^+} \)

Mineral dissolution: \( \text{CaCO}_3(s) = \text{CO}_3^{2-} + \text{Ca}^{2+} \)
\( K_{\text{CaCO}_3(s)} = \gamma_{\text{CO}_3^{2-}} c_{\text{CO}_3^{2-}} \gamma_{\text{Ca}^{2+}} c_{\text{Ca}^{2+}} \)

Gas dissolution: \( \text{CO}_2(g) = \text{CO}_2(aq) \)
\( K_{\text{CO}_2(g)} f_{\text{CO}_2(g)} c_{\text{CO}_2(aq)} = c_{\text{CO}_2(aq)} \gamma_{\text{CO}_2(aq)} \)

(2) Rate expressions:
\( R_m = \sigma_m k_m (1 - \Omega_m)^p \)

negative for precipitation

Calcite dissolution rate (first order):
\( r_{\text{CaCO}_3(s)} = k_{\text{CaCO}_3(s)} A \left( 1 - \frac{Q_{\text{CaCO}_3(s)}}{K_{\text{CaCO}_3(s)}} \right) \)
\( Q_{\text{CaCO}_3(s)} = \gamma_{\text{Ca}^{2+}} c_{\text{Ca}^{2+}} \gamma_{\text{CO}_2(aq)} c_{\text{CO}_2(aq)} = K_{\text{CaCO}_3(s)} \)
at equilibrium

(3) Conservation of chemical component in a closed chemical system:
Carbonate component \( \text{CO}_3^{2-} \):
\( T_{\text{CO}_3^{2-}} = c_{\text{CO}_3^{2-}} + \gamma_{\text{CaCO}_3(s)} c_{\text{CaCO}_3(s)} \)
where \( c_{\text{CO}_3^{2-}} = c_{\text{CO}_3^{2-}} + c_{\text{HCO}_3^-} + c_{\text{CO}_2(aq)} \)
(total dissolved, subject to transport)
Modeling Examples

- Overview of modeling capabilities
- Nuclear waste disposal
- CO$_2$ geological sequestration
- CO$_2$ co-injection with H$_2$S or SO$_2$
- Formation damage from waterflooding
- Geothermal well scaling
- Groundwater quality
- Biogeochemistry
- Ongoing and future developments
THC Coupled Processes (1)

- Reaction rates increase with temperature
- Evaporation concentrates aqueous species in remaining liquid phase
- pH affected by CO₂ degassing and mineral alterations
- Mineral dissolution and precipitation

Spycher et al., *JCH*, 2003
Sonnenthal et al., *Rock Mechanics*, 2005
THC Coupled Processes (2)

- TH validation
  - 250°C

- THC validation

Change in Matrix Saturation From Preheat Conditions

Dryout zone
Previous work

Long-term Simulations of Ambient Groundwater Chemistry at Horonobe URL Site, Hokkaido, Japan

Hajime Yamamoto\textsuperscript{a}, Takanori Kunimaru\textsuperscript{b}, Michito Shimo\textsuperscript{a}, Yasushi Fujiwara\textsuperscript{a}, Tianfu Xu\textsuperscript{c}, Marcus Laaksoharju\textsuperscript{d}

Current TMVOC-REACT degassing modeling

- **Two-phase/Degassing**
  - Water, Gas (CO\textsubscript{2}, CH\textsubscript{4})
  - Degass
  - Drift
  - Rock
  - Formation of UZ
  - Change in pH due to decline in CO\textsubscript{2} partial Pressure

- **Redox Reaction**
  - Dissolution of pyrite, siderite
  - Oxygen Diffusion
  - Change in pH and Eh

- **Mineral Precipitation**
  - Concrete Lining
  - High pH Water
  - Water/Rock reaction
  - Mineral precipitation such as gypsum and calcite
Canister Corrosion and H₂ Generation

- Nuclear waste
- Geological repository (right Fig
- Corrosion of steel canisters leads to H₂ gas generation
  \[3 \text{Fe} + 4\text{H}_2\text{O} \leftrightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2\]
- Pressure buildup affects long-term repository safety
- Previous used a constant H₂ generation rate
- H₂ generation rate depends on factors such as water chemistry, water availability, and water contact area
- We developed a chemistry model related to iron corrosion, coupled with two-phase flow

Land Surface

Schematic representation of a nuclear waste repository with single waste canister, bentonite backfill, and opalinus clay host rock (NAGRA, 2002).

Working in progressing, Supported by Switzerland NAGRA
CO2 SEQUESTRATION

- Sequestration:
  - Geological
  - Ocean
  - Terrestrial
- Geological Sequestration:
  - Deep saline aquifers
  - Depleted oil and gas reservoirs (EOR, EGR)
  - Unminable coal beds
- Processes:
  - Capture
  - Sequestration/Storage
  - Monitoring and verification

CO₂ Storage in Saline Aquifers: Issues to be Addressed by Numerical Modeling

- What is the long-term fate of injected CO₂?
- What fraction of CO₂ is stored as a free phase (mobile or trapped), dissolved in the aqueous phase, or sequestered in solid minerals?
- How do the relative proportions of CO₂ in these different storage modes change over time?
- Can CO₂ leaks self-seal or self-enhance?
- How fast can the CO₂ be injected?
- What fraction of subsurface volume can be accessed?
- What is the storage capacity of a given site?
- Leakage of stored CO₂: Will it leak? How much? How?
- Where does all the brine go that is displaced by CO₂?
- Ancillary benefits? (EOR, EGR, EGS with CO₂)
- Identify and characterize potential storage sites.
- Design and analyze tests.
- Design monitoring systems. (Doughty and Pruess, 2004)
- What is the role of chemical, mechanical, and thermal effects in CO₂ leakage?
Modelling of CO$_2$ injection in a saline aquifer at the Sleipner

Gas from Sleipner West

Sleipner East Field

Utsira Formation

Sleipner T

Sleipner A

Nordland Shale Caprock

CO$_2$-injection well

1 M tons/yr

700-1000 m

Audigane et al., 2007; AJS
CO$_2$ injection at the Sleipner (2)

Representation of the Utsira formation by a 2D mult-layered mesh with cylindrical symmetry. The CO2 is injected in a cell at 160 m from the top of the formation. The porous media consist of highly permeable sands, separated by four semi-permeable shale layers. b) Vertical section and planar views of the seismic images three years after CO2 injection (SACS, 2002; Arts et al., 2004).
CO₂ injection at the Sleipner (3)
**CO₂ injection at the Sleipner (4)**

**Calcite**

**Dawsonite**

**Mineral trapping**

**Porosity Change**
Comparison of CO2 inventories in the different phases for three different cases: Case 1 with the original mesh and a residual saturation of 0.20, Case 2 with the same mesh and a reduced residual gas saturation of 0.05, and Case 3 with a residual gas saturation of 0.20 and a mesh that is more refined near the injection point.
Cap Rock Alteration due to CO$_2$ Storage

Self sealing

Fracture enhanced dissolution

(F. Gherardi, T. Xu and K. Pruess, 2007; *Chem. Geol.*)
The deadlock between Kazakhstan and its main source of foreign investment, ChevronTexaco, appears to have tightened after a court in the oil-rich Atyrau region ordered the Chevron-led Tengizchevroil (TCO) joint venture to pay a fine of $71 million for failing to clear huge piles of sulfur stacked up outside the supergiant Tengiz field.

ASTANA, Kazakhstan -- Kazakhstan's Ecology Ministry said Wednesday that it had dropped claims against the Chevron-led firms operating a large oil field after the group pledged $300 million per year for environmental protection.

At least five international energy companies submitted bids on Sunday for a giant sour gas project in the United Arab Emirates that could be have a price tag as high as $10 billion.
Sequestering less-pure flue gas (CO₂) containing H₂S and/or SO₂ requires less energy to separate.

pH conditions are important for well corrosion.

Here we present simulation results on sequestration of CO₂, H₂S and SO₂ in a Gulf Coast Frio formation.

Use conditions and parameters encountered in brine aquifers at a depth of order 2 km.

*Xu et al., 2007; Chem Geol.*
Co-injection of SO₂ → stronger acidic zone close to the well. Corrosion and well abandonment are issues.
- The CO₂ mineral trapping capability can reach 60 kg/m³ medium.
- Increase in porosity close to the well.
- Decrease at distances.
Geothermal Injectivity at Tiwi Field (1)

- Injectivity loss from scale formation at well Nag-67
- Suspected precipitation of amorphous silica (kinetically controlled)
- Workover: scale drillout, acidizing
- Performed modeling study using TOUGHREACT, in cooperation with Unocal Corp.
- Porosity-Permeability (Verma and Pruess, 1988)

\[
\frac{k}{k_0} = \left( \frac{\phi - \phi_c}{\phi_0 - \phi_c} \right)^n
\]
Geothermal Injectivity at Tiwi Field (2)

Injectivity loss

Injectivity recovery due to acid

\[ \frac{k}{k_0} = \left( \frac{\phi}{\phi_0} \right)^3 \left( \frac{1-\phi_0}{1-\phi} \right)^2 \]

\[ \frac{k}{k_0} = \left( \frac{\phi - \phi_c}{\phi_0 - \phi_c} \right)^n \]

Xu et al., *Geothermics*, 2004
Formation Damage from Waterflooding

- Understand physical, chemical, and biological processes that may cause plugging of the injection interval.
- Design a treatment procedure for produced water for its injection into the reservoir.

*Inject produced water without treatment*

Calcite precipitation

Permeability

Birkle (IE, Mexico), …, Xu, 2006; SPE paper
Water Quality in the Aquia Aquifer (Maryland)

- Validation
- NaHCO₃ type waters in the coastal aquifers of the eastern US are related to freshening of the aquifer (Chapelle and Knobel, 1983).

- Processes:
  - Cation exchange
  - Calcite diss./prec.

![Graphs showing changes in pH, Na+, Mg²⁺, Ca²⁺ concentrations along the flowpath.](image)
CONCLUSIONS

- A comprehensive general-purpose reactive chemical transport simulation tool TOUGHREACT has been developed, driven by various programmatic needs.
- The tool has been successfully applied to
  - Nuclear waste disposal
  - CO₂ geological sequestration
  - Geothermal energy development
  - Environmental problems
  - Natural groundwater quality
  - ....
- Our simulation capabilities continue to be improved to meet program needs, and to contribute to the community.
- TOUGHREACT is available to the public from DOE’s Energy Science and Technology Software Center (ESTSC; http://www.osti.gov/estsc/)
ACKNOWLEDGEMENTS

- Our modeling activities in reactive fluid and chemical transport were jointly funded by (1) LDRD; (2) the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Geothermal Technologies (Geothermal); (3) by the Director, Office of Civilian Radioactive Waste Management (Nuclear Waste); (4) by the Director, Office of Science, Office of Basic Energy Sciences (BES); (5) by the Director, Office of Science, Environmental Management Science Program (EMSP); of the U.S. Department of Energy, under Contract No. DE-AC02-05CH11231.

- Thanks to our industrial and academic collaborators

- Thanks to all EDS colleagues contributing to these activities, especially Karsten Pruess, Eric Sonnenthal, Nicolas Spycher, John Apps, and Guoxiang Zhang.

Supported by the U.S. Department of Energy (DOE)
Ongoing Development and Future Directions

**Ongoing**
- Testing Pitzer ion-interaction model and related parameters
- Testing intra-aqueous kinetics and biodegradation
- Testing surface complexation models
- Coupling H2 generation due to iron corrosion to two-phase flow
- Fortran 90 code upgrading

**Future**
- THCM
- Inverse
- Colloid
- Isotope
- Others?

**TOUGHREACT V2**
- V1.2 +
- Aqueous kinetics
- Biodegradation
- Multi-site exchange
- Surface complexation
- V2/Pitzer ion-interaction model

Will be released from LBNL
A Multi-Region Model for Biogeochemistry

Chem-Region: quartz calcite gypsum goethite

Hydro-Region: \( \text{Na}^+, \text{Ca}^{2+}, \text{O}_2(\text{aq}), \text{DOC}, \text{NO}_3^-, \text{SO}_4^{2-} \)

Bio-Region: denitrifier, sulfate reducing bacteria,

Xu, Vadose Zone Journal 2008
Biogeochemistry: Denitrification and Sulfate Reduction

Rate law

\[
r_b^{O_2} = k_b^{O_2} X_b \left( \frac{C_{DOC}}{K_{DOC}^{O_2} + C_{DOC}} \right) \left( \frac{C_{O_2}}{K_{O_2}^{O_2} + C_{O_2}} \right)
\]

\[
r_b^{NO_3} = k_b^{NO_3} X_b \left( \frac{C_{DOC}}{K_{DOC}^{NO_3} + C_{DOC}} \right) \left( \frac{C_{NO_3}}{K_{NO_3}^{NO_3} + C_{NO_3}} \right) \left( \frac{l_{O_2 \rightarrow NO_3}}{l_{O_2 \rightarrow NO_3} + C_{O_2}} \right)
\]

\[
r_b^{SO_4} = k_b^{SO_4} X_b \left( \frac{C_{DOC}}{K_{DOC}^{SO_4} + C_{DOC}} \right) \left( \frac{C_{SO_4}}{K_{SO_4}^{SO_4} + C_{SO_4}} \right) \left( \frac{l_{O_2 \rightarrow SO_4}}{l_{O_2 \rightarrow SO_4} + C_{O_2}} \right) \left( \frac{l_{NO_3 \rightarrow SO_4}}{l_{NO_3 \rightarrow SO_4} + C_{NO_3}} \right)
\]

\[
r_b = r_b^{O_2} + r_b^{NO_3} + r_b^{SO_4} - bX_b
\]

Xu, Vadose Zone Journal 2008