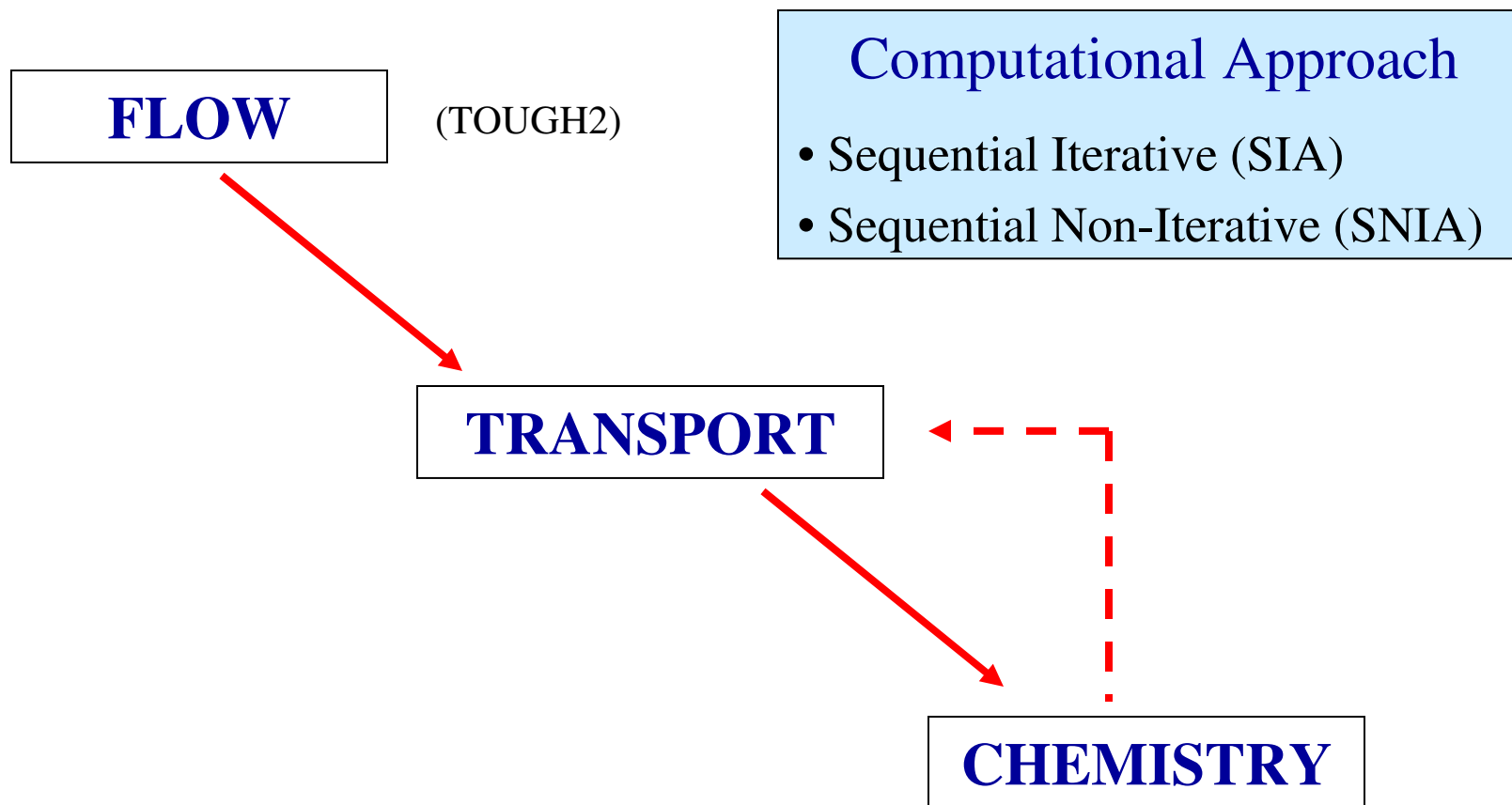# MODELING OF REACTIVE GEOCHEMICAL TRANSPORT IN GEOLOGICAL MEDIA (TOUGHREACT):

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TOUGHREACT FLOW CHART

FLOW (TOUGH2)

Computational Approach

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

TRANSPORT

CHEMISTRY

CAPABILITIES OF TOUGHREACT (1)

Processes:

- Multiphase fluid and heat flow: TOUGH2 V2 (Pruess, et al., 1999)
- 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./preci. 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/

CAPABILITIES OF TOUGHREACT (2)

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: $\dfrac{\partial M_\kappa}{\partial t} = -\nabla F_\kappa + q_\kappa$

Water: $M_w = \phi(S_l\rho_l X_{wl} + S_g\rho_g X_{wg})$ $\qquad F_w = X_{wl}\rho_l\mathbf{u}_l + X_{wg}\rho_g\mathbf{u}_g$ $\qquad q_w = q_{wl} + q_{wg}$

Air: $M_a = \phi(S_l\rho_l X_{al} + S_g\rho_g X_{ag})$ $\qquad F_a = X_{al}\rho_l\mathbf{u}_l + X_{ag}\rho_g\mathbf{u}_g$ $\qquad q_a = q_{al} + q_{ag}$

Heat: $M_h = \phi(S_l\rho_l U_l + S_g\rho_g U_g) + (1-\phi)\rho_s U_s$ $\quad F_h = \sum\limits_{\beta=l,g} h_\beta\rho_\beta\mathbf{u}_\beta - \lambda\nabla T$ $\quad q_h$

where $\qquad \mathbf{u}_\beta = -k\dfrac{k_{r\beta}}{\mu_\beta}(\nabla P_\beta - \rho_\beta\mathbf{g})$ $\qquad \beta = l, g$ $\qquad$ (Darcy's Law)

Chemical components in the liquid phase ($j = 1,2,...,N_l$):

$M_j = \phi S_l C_{jl}$ $\qquad F_j = \mathbf{u}_l C_{jl} - D_l\nabla C_{jl}$ $\qquad q_j = q_{jl} + q_{js} + q_{jg}$

Chemical components in the gas phase ($k = 1,2,...,N_g$):

$M_k = \phi S_l C_{kl}$ $\qquad F_k = \mathbf{u}_{gl} C_{kg} - D_g\nabla C_{kg}$ $\qquad q_k = -q_{jg}$

where $\qquad C_{kg} = f_{kg}/RT$ (gas law)

Example of chemical reaction equations

General dissociation reactions $\qquad S_i^s = \sum\limits_{j=1}^{N_C}\nu_{ij}S_j^p$

(1) General mass action equations: $\qquad K_i a_{S_i^s} = \sum\limits_j^{N_C}(a_{S_j^p})^{\nu_{ij}}$

Aqueous dissociation: $HCO_3^- = CO_3^{2-} + H^+$ $\quad K_{HCO_3^-}\gamma_{HCO_3^-}c_{HCO_3^-} = \gamma_{CO_3^{2-}}c_{CO_3^{2-}}\gamma_{H^+}c_{H^+}$

Mineral dissolution: $CaCO_3(s) = CO_3^{2-} + Ca^{2+}$ $\quad K_{CaCO_3(s)} = \gamma_{Ca^{2+}}c_{Ca^{2+}}\gamma_{CO_3^{2-}}c_{CO_3^{2-}}$

Gas dissolution: $CO_2(g) = CO_2(aq)$ $\qquad K_{CO_2(g)}f_{CO_2(g)} = \gamma_{CO_2(aq)}c_{CO_2(aq)}$

(2) Rate expressions: $\qquad R_m = \sigma_m k_m(1-\Omega_m^n)^p$ $\qquad$ negative for precipitation

Calcite dissolution rate (first order): $\qquad r_{CaCO_3(s)} = k_{CaCO_3(s)}A\left(1 - \dfrac{Q_{CaCO_3(s)}}{K_{CaCO_3(s)}}\right)$

$Q_{CaCO_3(s)} = \gamma_{Ca^{2+}}c_{Ca^{2+}}\gamma_{CO_3^{2-}}c_{CO_3^{2-}} = K_{CaCO_3(s)}$ $\quad$ at equilibrium

(3) Conservation of chemical component in a closed chemical system:

Carbonate component CO_3^{2-}: $\qquad T_{CO_3^{2-}} = C_{CO_3^{2-}} + c_{CO_2(g)} + c_{CaCO_3(s)}$

where $\qquad C_{CO_3^{2-}} = c_{CO_3^{2-}} + c_{HCO_3^-} + c_{CO_2(aq)}$ $\quad$ (total dissolved, subject to transport)

Modeling Examples

- Overview of modeling capabilities

- Nuclear waste disposal

- CO_2 geological sequestration

- CO_2 co-injection with H_2S or SO_2

- Formation damage from waterflooding

- Geothermal well scaling

- Groundwater quality

- Biogeochemistry

- Ongoing and future developments
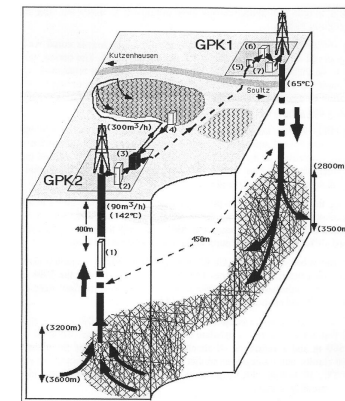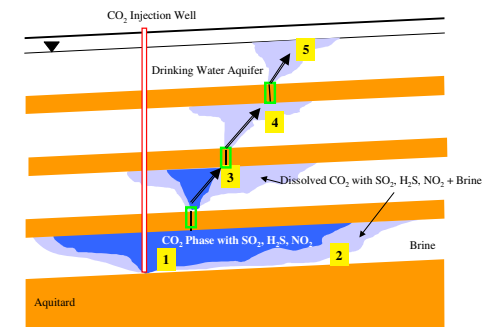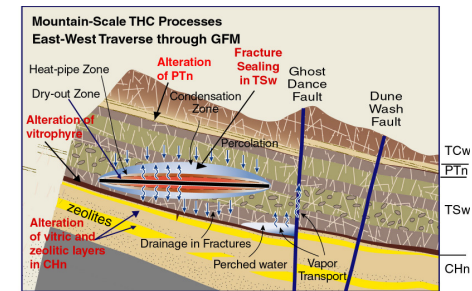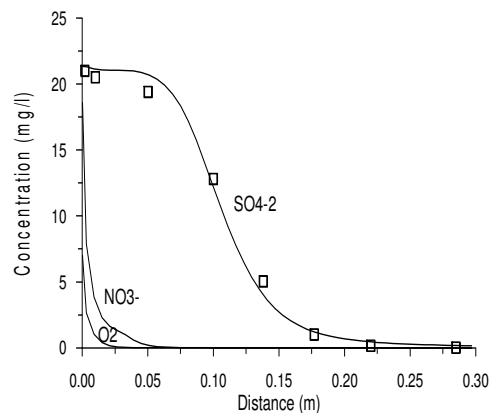
THC Coupled Processes (1)

THC Processes

Spycher et al., *JCH*, 2003
Sonnenthal et al., *Rock Mechanics*, 2005
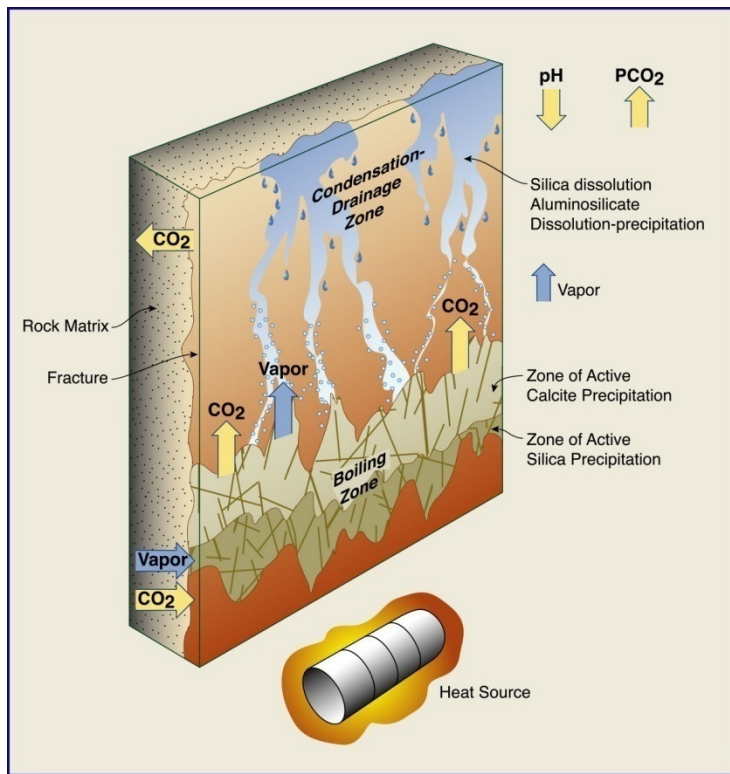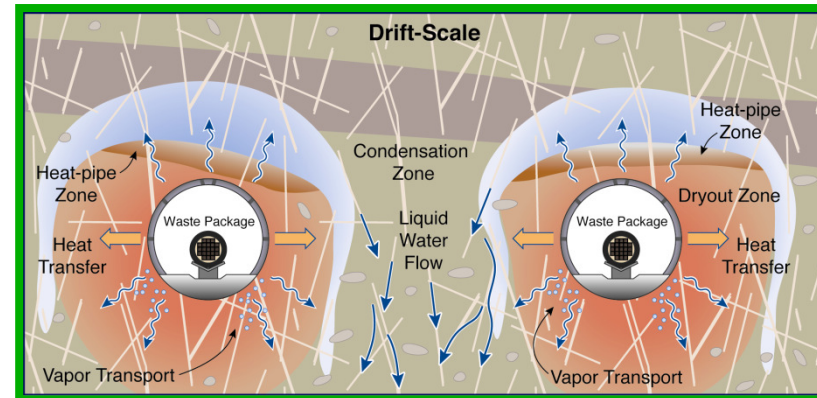
- Reaction rates increase with temperature

- Evaporation concentrates aqueous species in remaining liquid phase

- pH affected by CO_2 degassing and mineral alterations

- Mineral dissolution and precipitation

THC Coupled Processes (2)

➢ TH validation

➢ THC validation

250°C

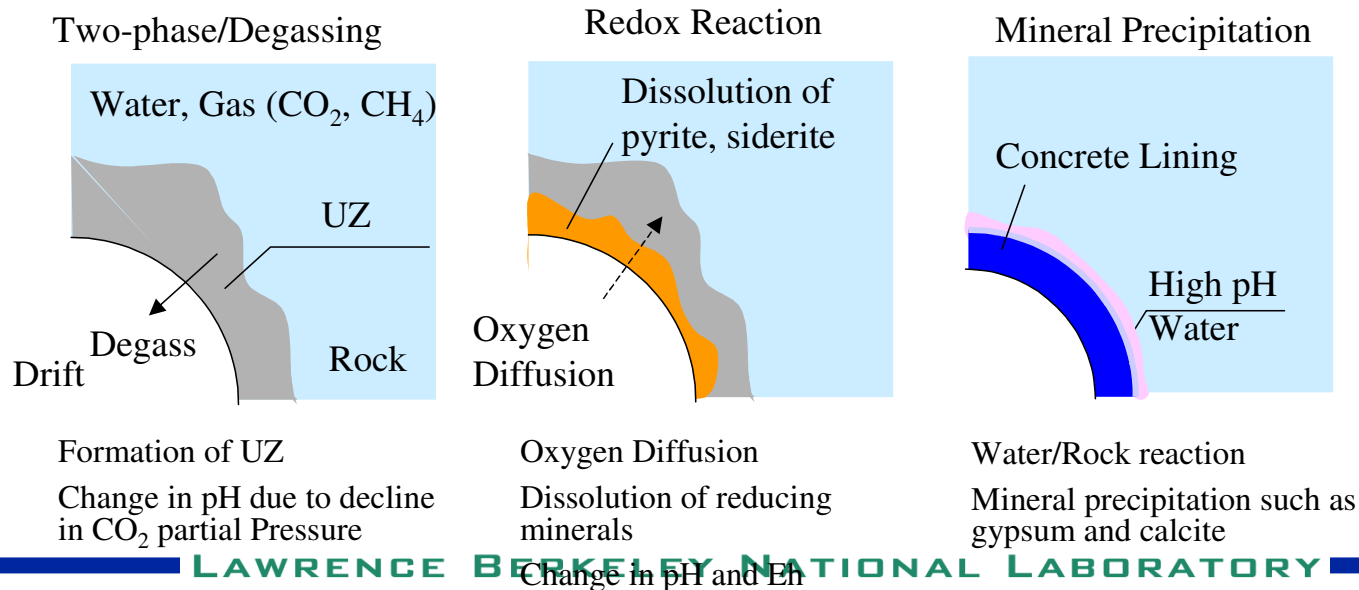**Dryout zone**
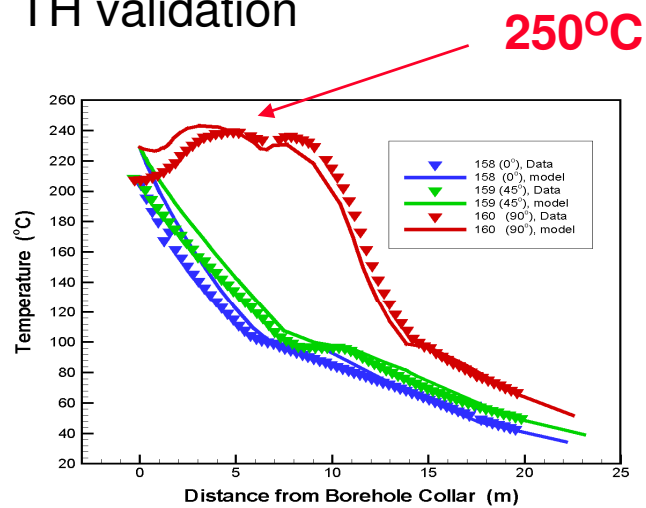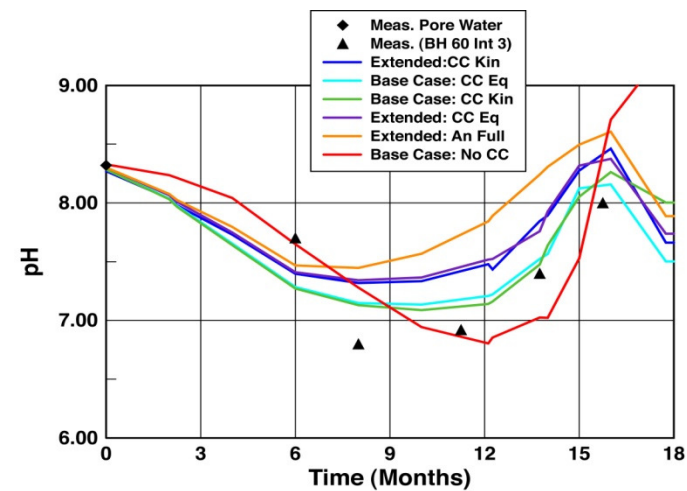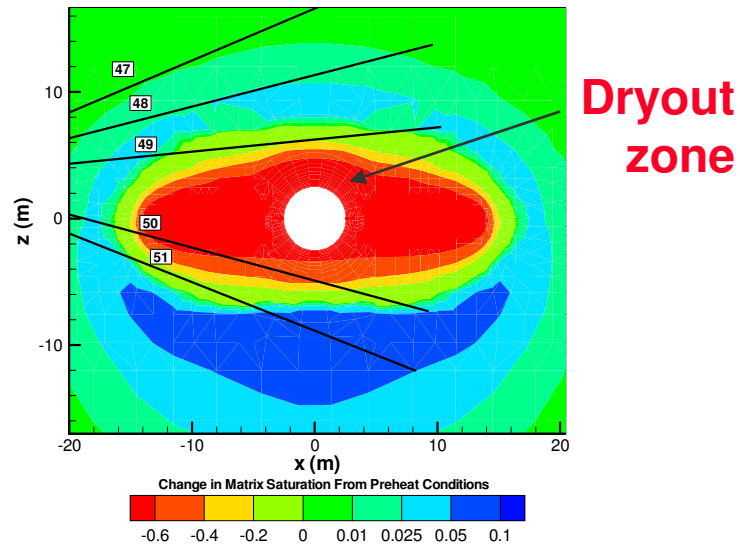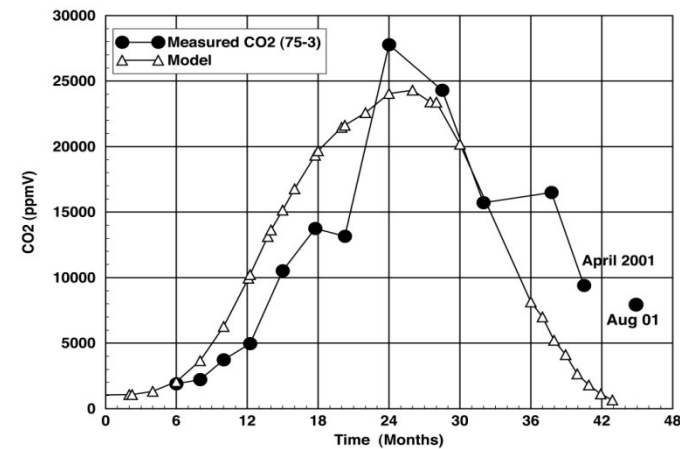
Japan Horonobe URL Site

➢ Previous work

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

Hajime Yamamoto [a], Takanori Kunimaru[b], Michito Shimo[a],

Yasushi Fujiwara[a], Tianfu Xu[c], Marcus Laaksoharju[d]

➢ Current TMVOC-REACT degassing modeling

Two-phase/Degassing

Water, Gas (CO_2, CH_4)

UZ

Degass

Drift

Rock

Formation of UZ

Change in pH due to decline in CO_2 partial Pressure

Redox Reaction

Dissolution of pyrite, siderite

Oxygen Diffusion

Oxygen Diffusion

Dissolution of reducing minerals

Change in pH and Eh

Mineral Precipitation

Concrete Lining

High pH Water

Water/Rock reaction

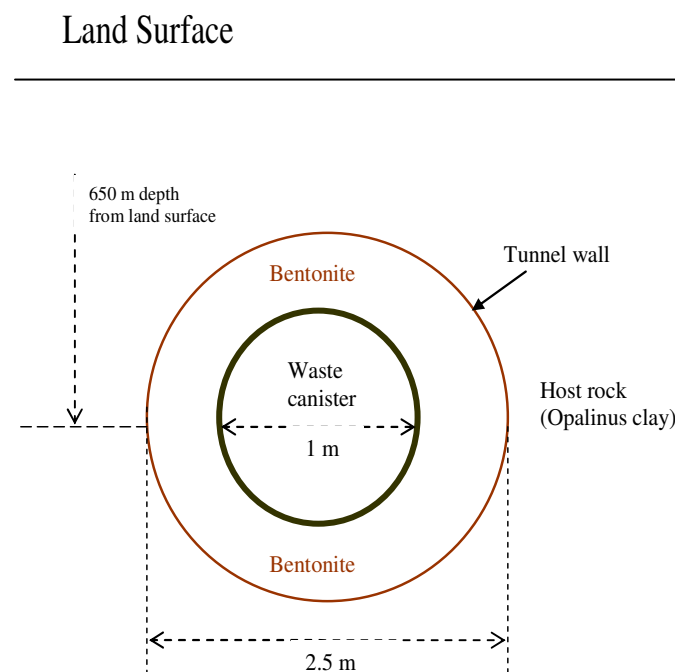Mineral precipitation such as gypsum and calcite

Canister Corrosion and H$_2$ Generation

- Nuclear waste
- Geological repository (right Fig)
- Corrosion of steel canisters leads to H$_2$ gas generation

$$3\,Fe + 4H_2O \leftrightarrow Fe_3O_4 + 4\,H_2$$
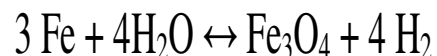
- Pressure buildup affects long-term repository safety
- Previous used a constant H$_2$ generation rate
- H$_2$ generation rate depends on factors such as water chemistry, water availability, and water contact area
- We developed a chemistry model related to iron corrosion, coupled with two-phase flow

Land Surface

650 m depth from land surface

Tunnel wall

Bentonite

Waste canister

Host rock (Opalinus clay)

1 m

Bentonite

2.5 m

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
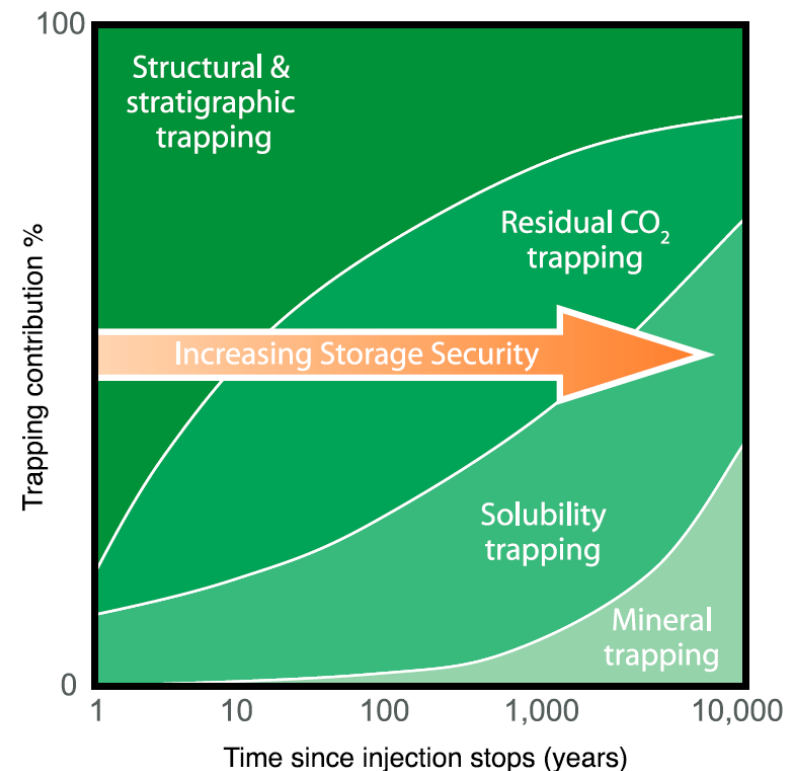
(Adapted from: *2005 IPCC Special Report on Carbon Dioxide Capture and Storage;* http://www.ipcc.ch/activity/srccs/index.htm)

CO$_2$ Storage in Saline Aquifers: Issues to be Addressed by Numerical Modeling

> **What is the long-term fate of injected CO$_2$?**

> **What fraction of CO$_2$ 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 CO$_2$ in these different storage modes change over time?**

> **Can CO$_2$ leaks self-seal or self-enhance?**

> How fast can the CO$_2$ be injected?

> What fraction of subsurface volume can be accessed

> What is the storage capacity of a given site?

> Leakage of stored CO$_2$: Will it leak? How much? How

> Where does all the brine go that is displaced by CO$_2$?

> Ancillary benefits? (EOR, EGR, EGS with CO$_2$)

> Identify and characterize potential storage sites.

> Design and analyze tests.

> Design monitoring systems.

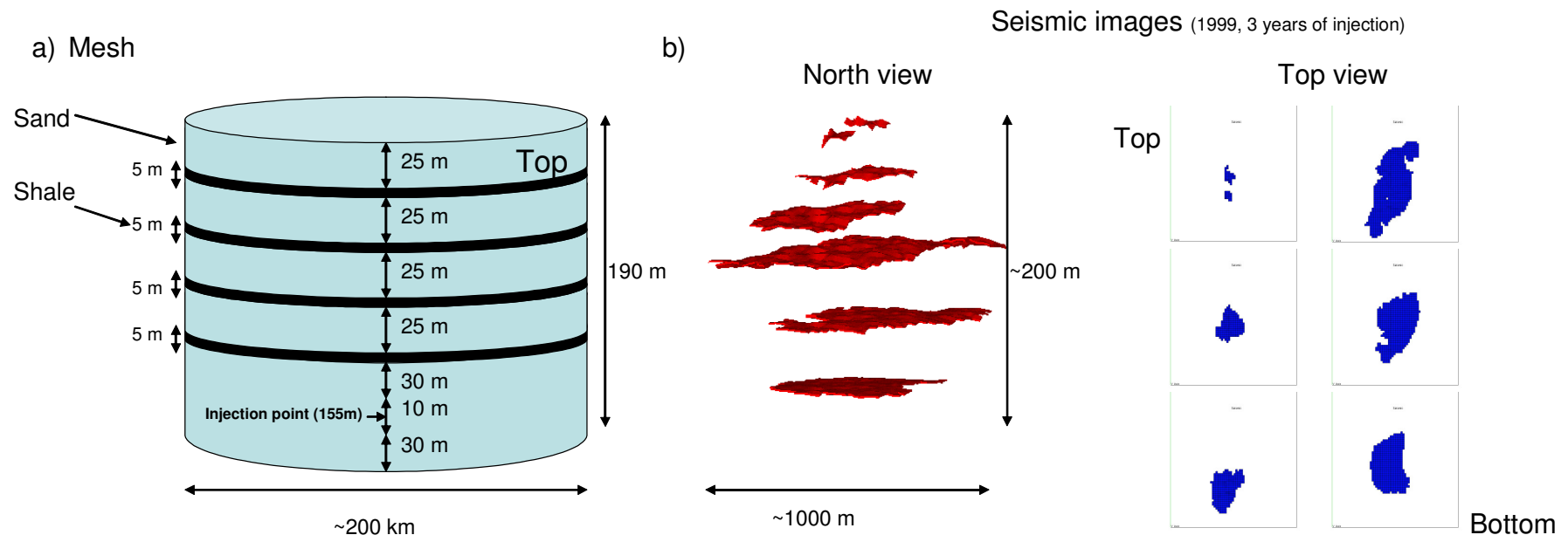> What is the role of chemical, mechanical, and thermal effects in CO$_2$ leakage?
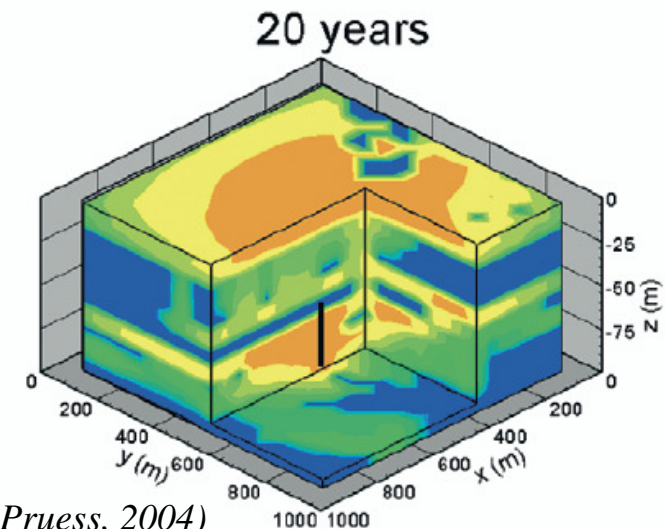
(Doughty and Pruess, 2004)

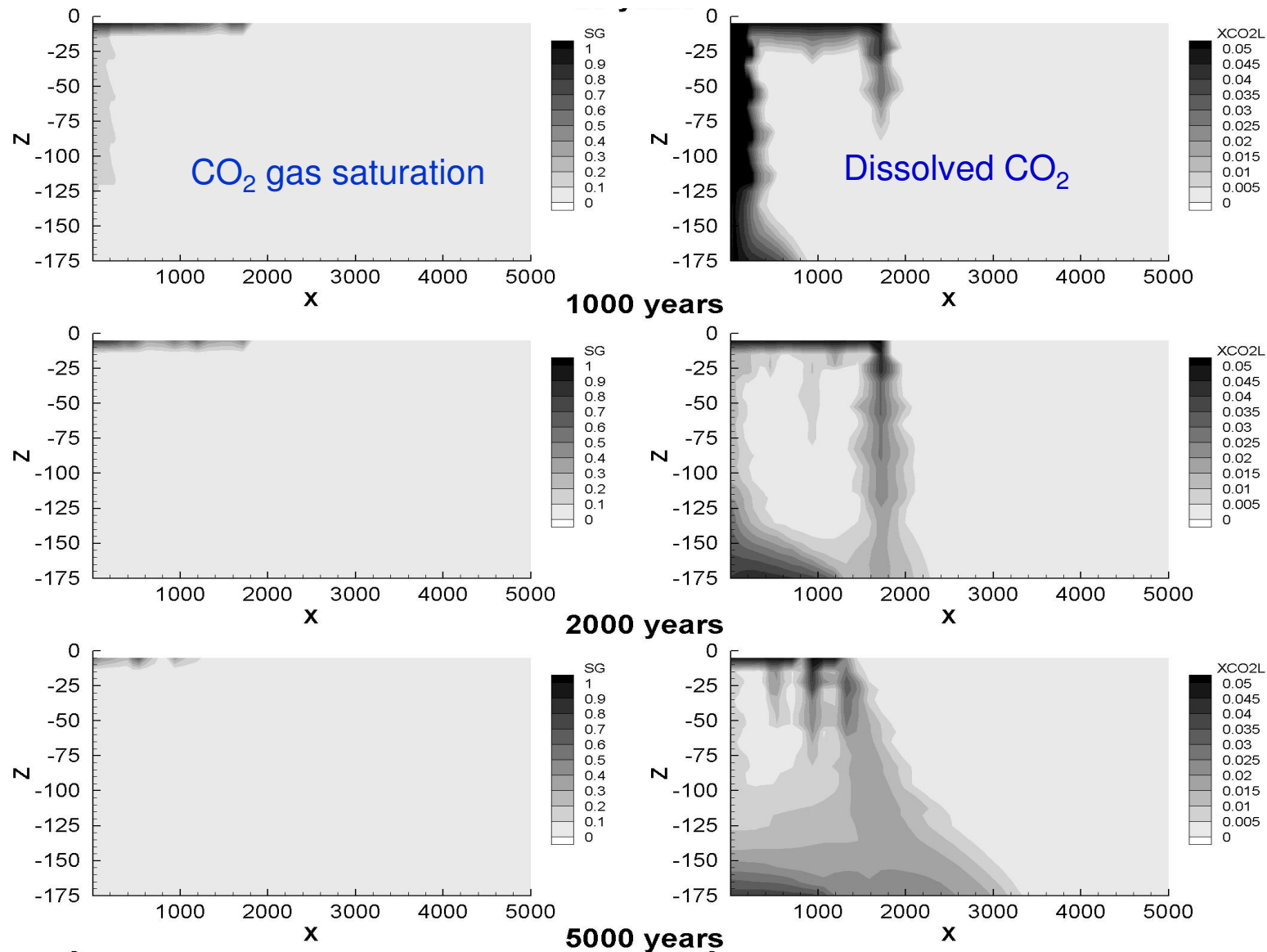# Modelling of CO_2 injection in a saline aquifer at the Sleipner

Sleipner A

Sleipner T

Gas from Sleipner West

1 M tons/yr

CO_2-injection well

Nordland Shale Caprock

700-1000 m

Utsira Formation

CO_2

Sleipner East Production and injection Wells

Sleipner East Field
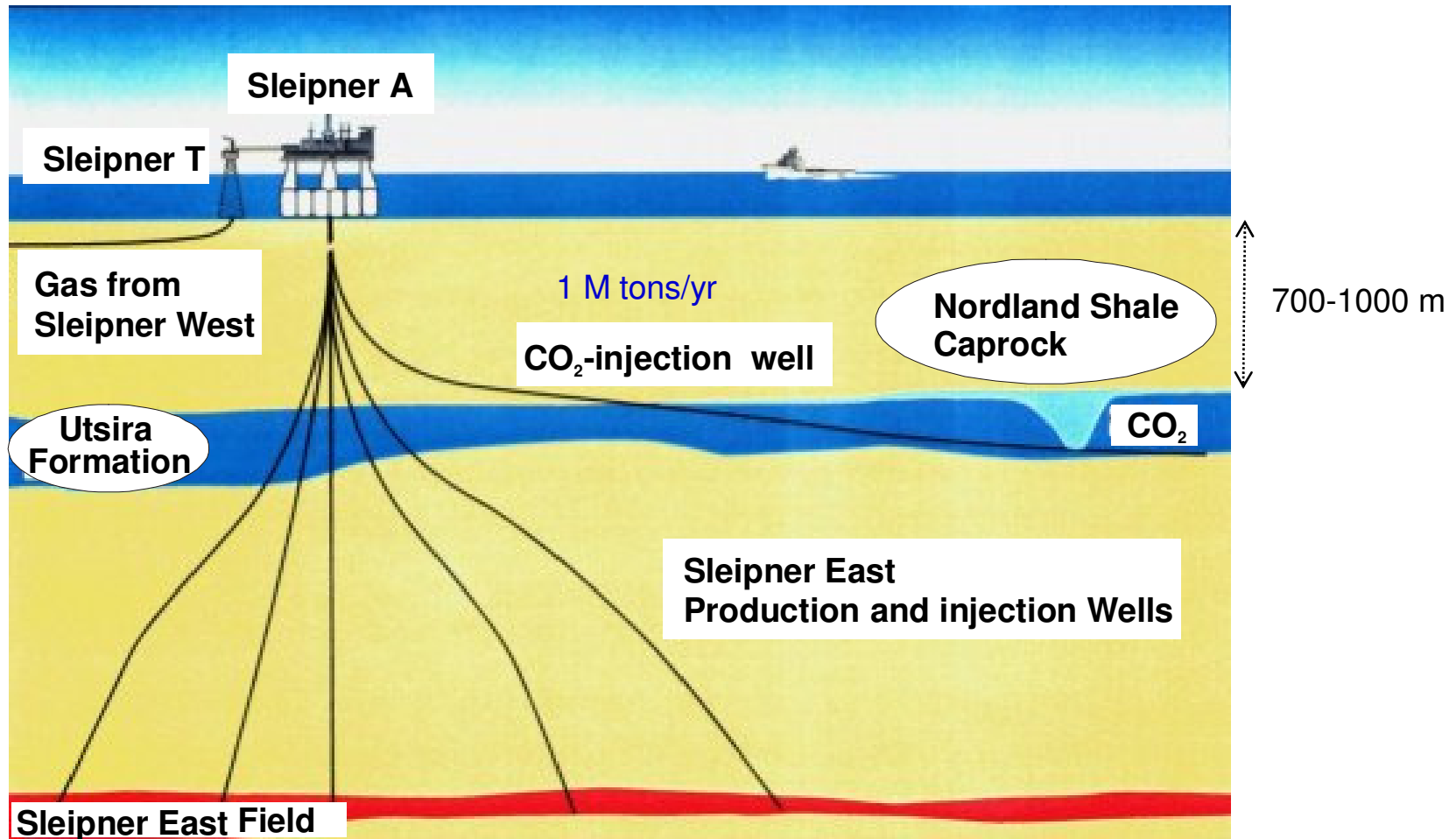
Audigane et al., 2007; AJS

CO$_2$ injection at the Sleipner (2)

a) Mesh

b)

Seismic images (1999, 3 years of injection)

North view

Top view

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).
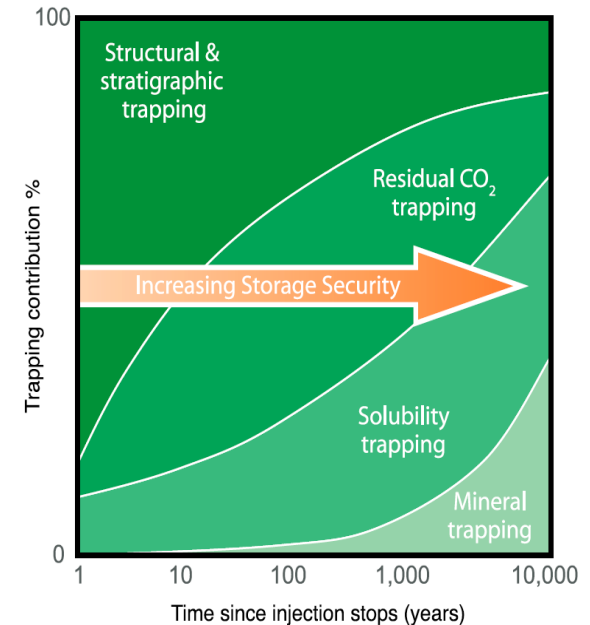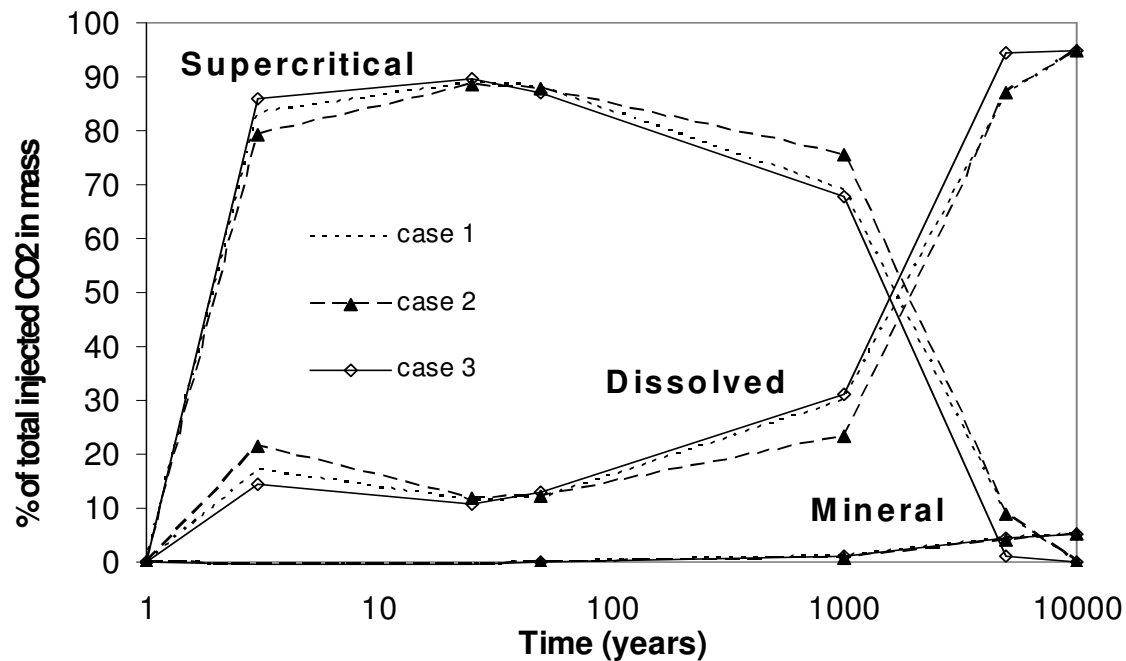
CO$_2$ injection at the Sleipner (3)

CO$_2$ gas saturation

Dissolved CO$_2$

1000 years

2000 years

5000 years

CO$_2$ injection at the Sleipner (4)

Calcite — 5000 years

Dawsonite — 5000 years

Mineral trapping — 10 000 years

Porosity Change
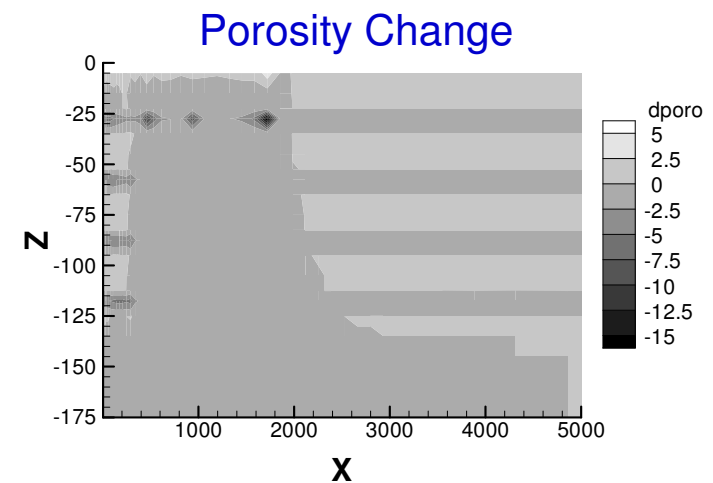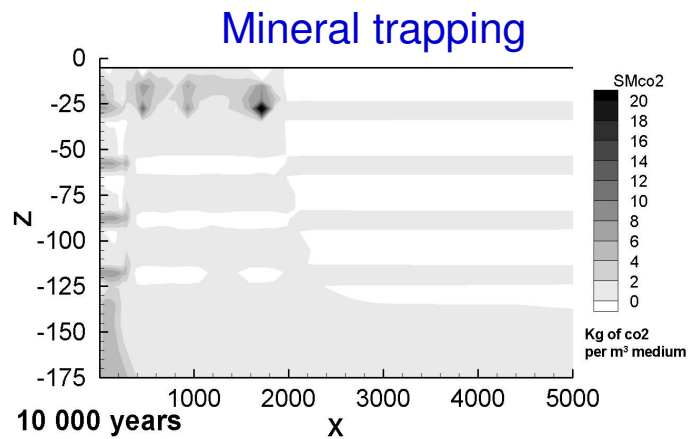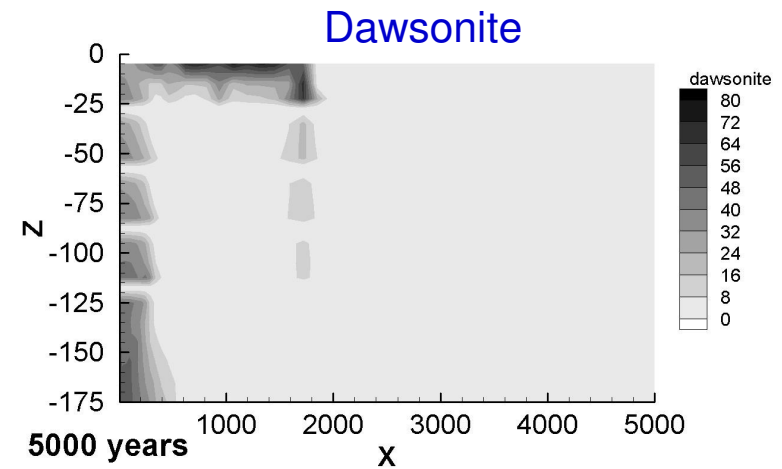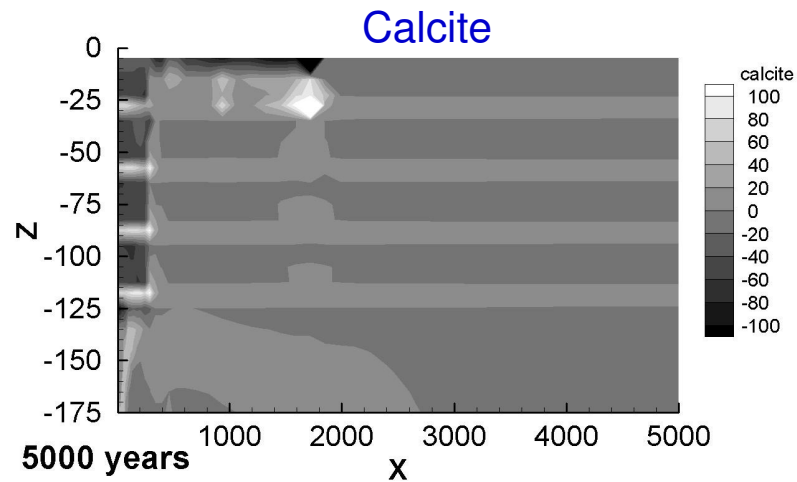
CO$_2$ injection at the Sleipner (5)

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.
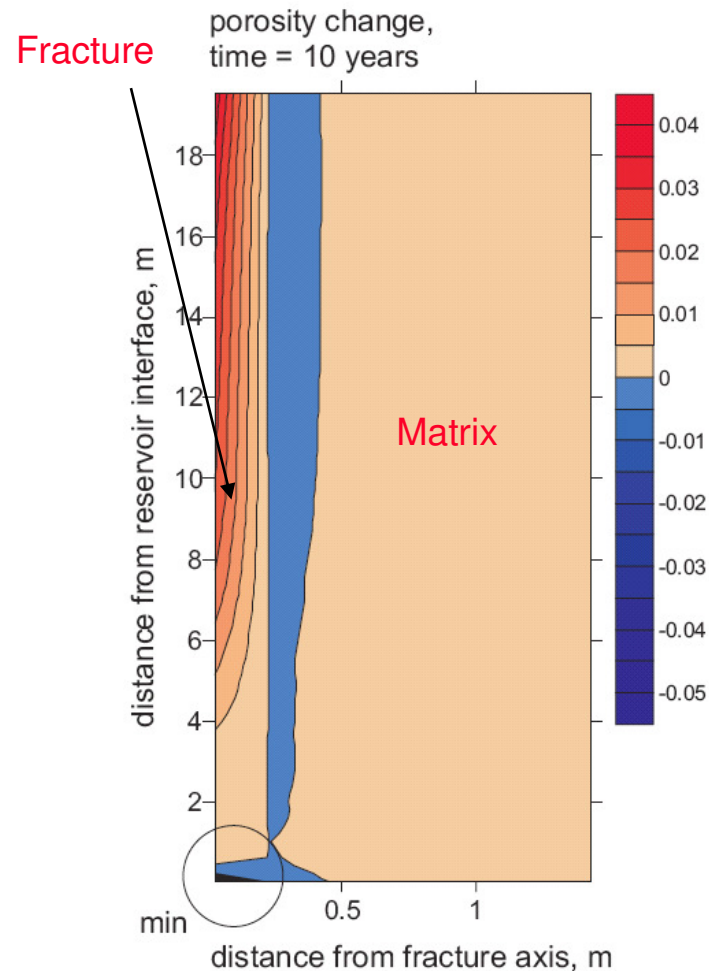
Cap Rock Alteration due to CO₂ Storage

Self sealing
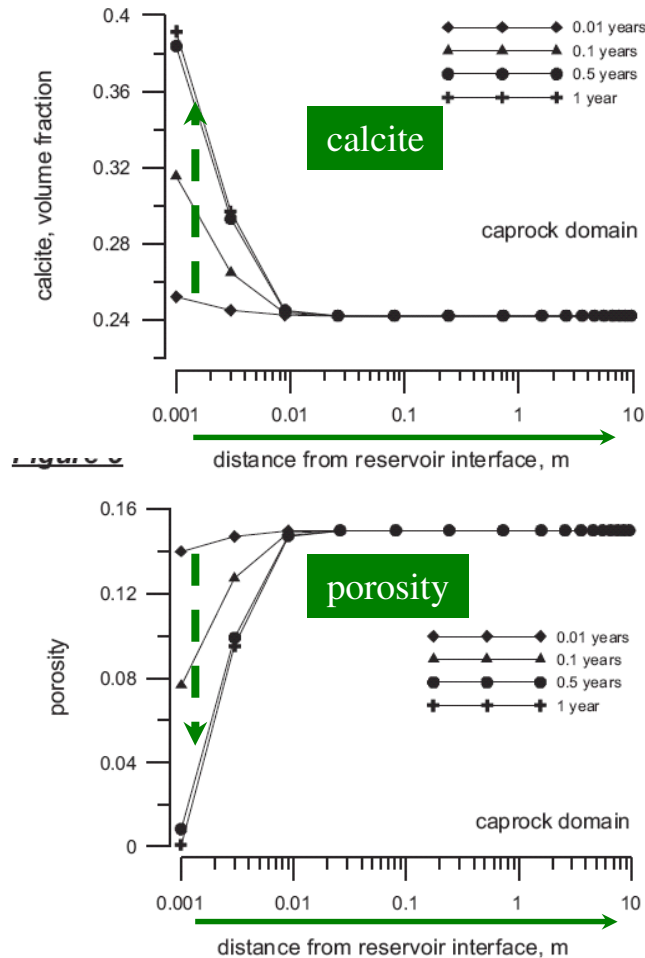
Fracture enhanced dissolution

(F. Gherardi, T. Xu and K. Pruess, 2007; *Chem. Geol.*)

Acid (H$_2$S) Gas Injection

(Google images)

• (Reuters - 2002) 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.

• (Reuters – 4/5/07) 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.

• (Reuters – 4/15/07) 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.
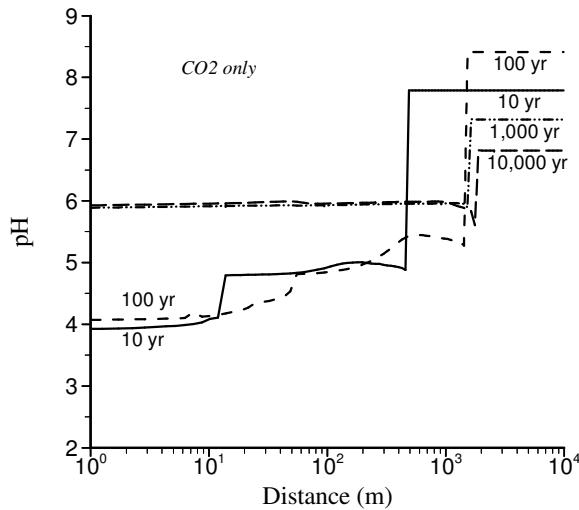
Acid Gas Injection and Mineral Trapping

➢ Sequestering less-pure flue gas (CO_2) containing H_2S and/or SO_2 requires less energy to separate.

➢ pH conditions are important for well corrosion.

➢ Here we present simulation results on sequestration of CO_2, H_2S and SO_2 in a Gulf Coast Frio formation.

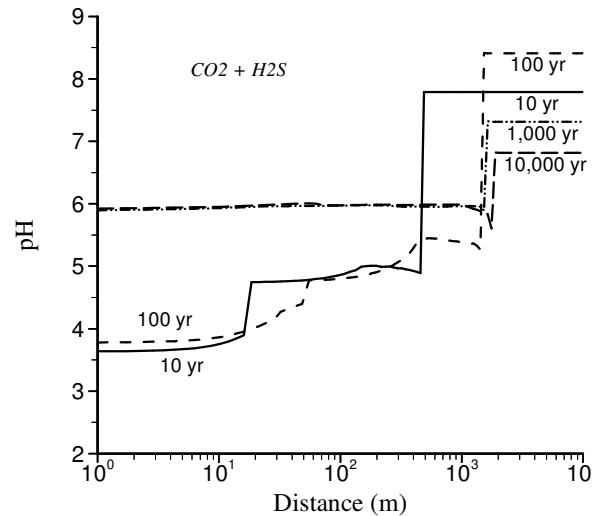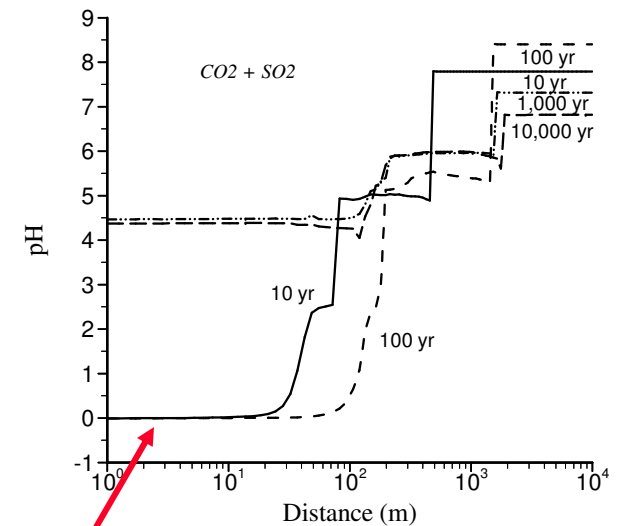➢ Use conditions and parameters encountered in brine aquifers at a depth of order 2 km.

Injection well

10 m	$\phi = 0.1$ $k = 10^{-18}$ m^2	Shale
10 m	$\phi = 0.3$ $k = 10^{-13}$ m^2	Sandstone

z

x
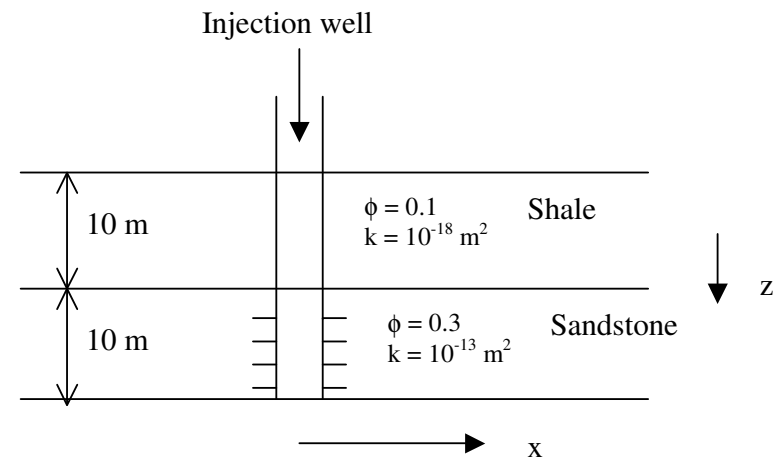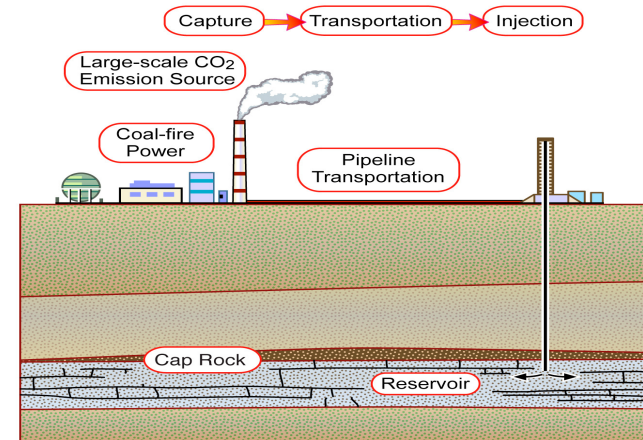
Xu et al., 2007; Chem Geol.

(a) CO_2 Only

(b) CO_2 + H_2S

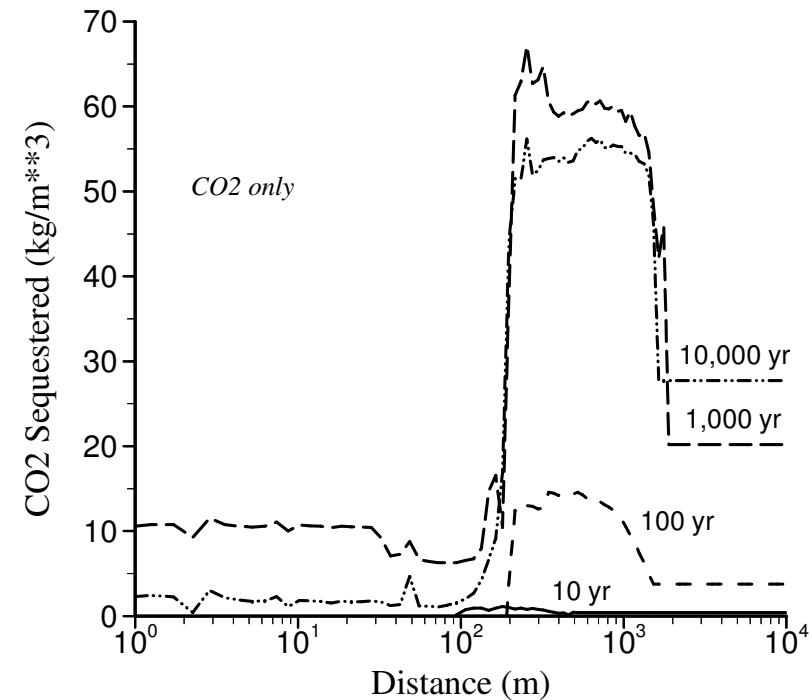(c) CO_2 + SO_2

pH = 0

- Co-injection of $SO_2 \rightarrow$ stronger acidic zone close to the well. Corrosion and well abandonment are issues.
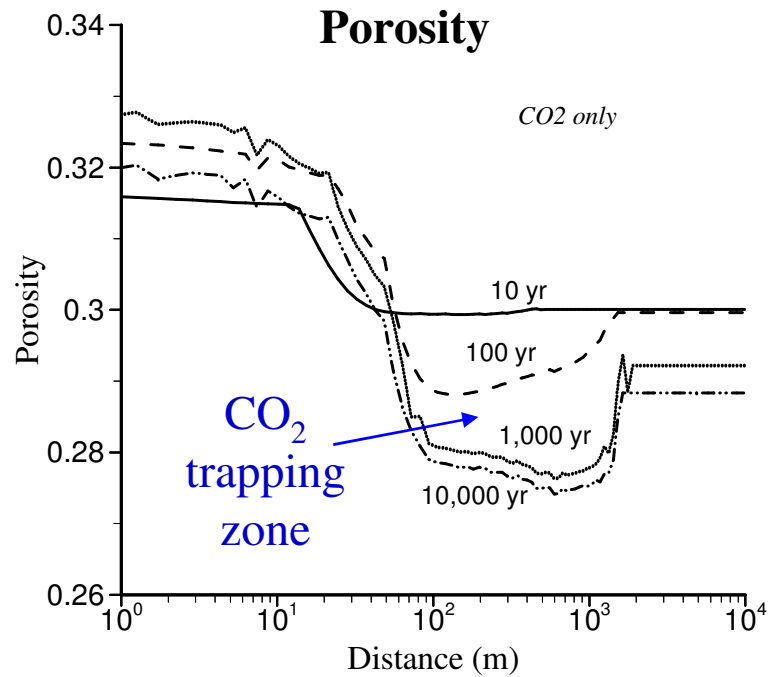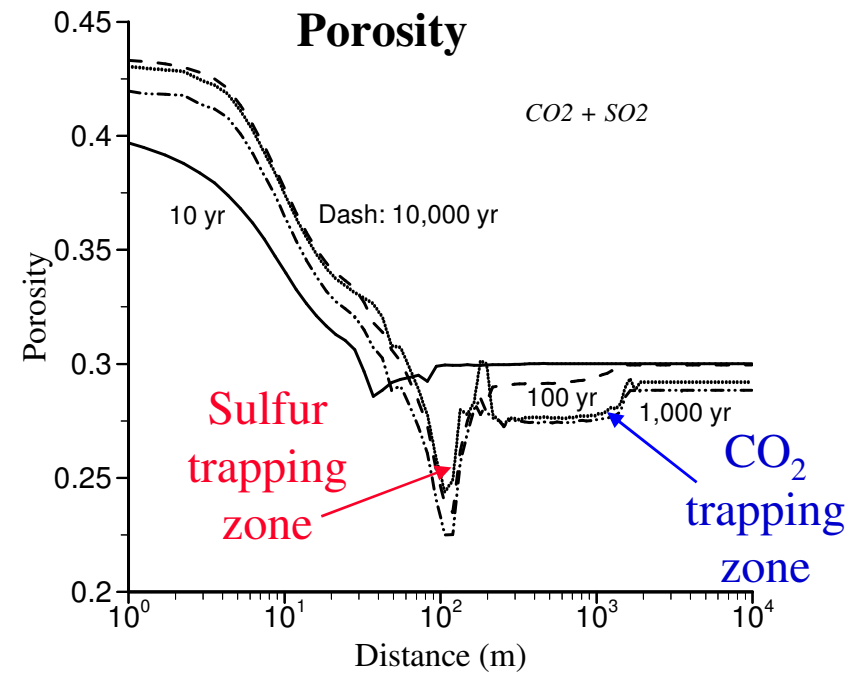
Acid Gas: Results (2)
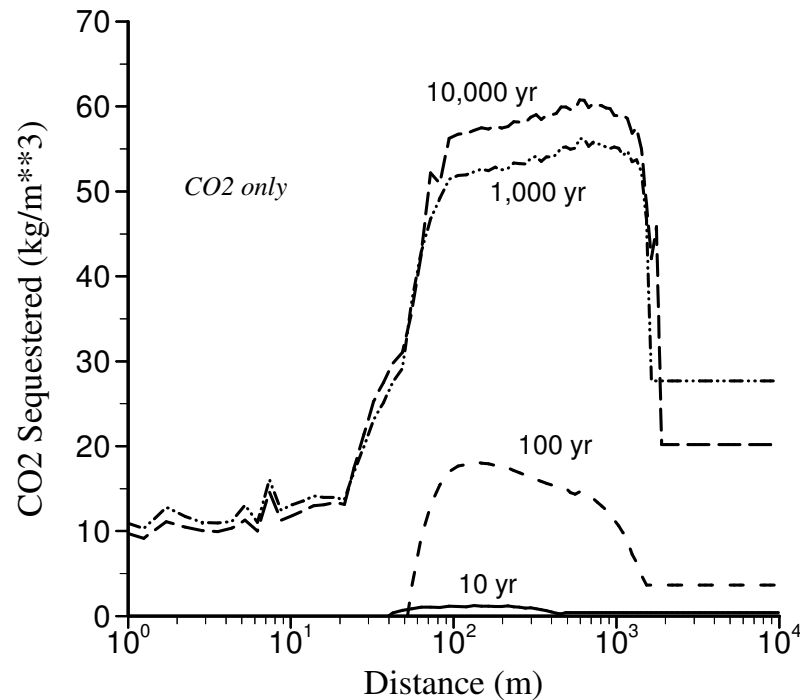
(a) CO$_2$

(b) CO$_2$+ SO$_2$

- The CO$_2$ mineral trapping capability can reach 60 kg/m^3 medium.
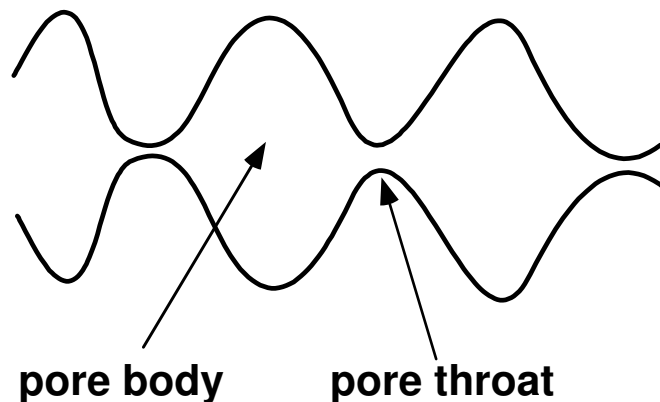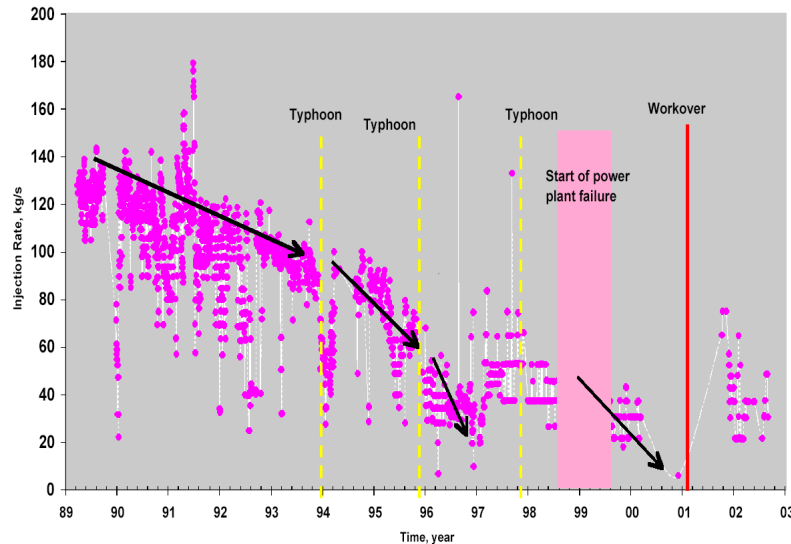
Acid Gas: Results (4)

(a) CO_2

(b) $CO_2+ SO_2$

- Increase in porosity close to the well.
- Decrease at distances.

Geothermal Injectivity at Tiwi Field (1)

Injection Rate, kg/s vs Time, year

Typhoon   Typhoon   Typhoon   Workover

Start of power plant failure
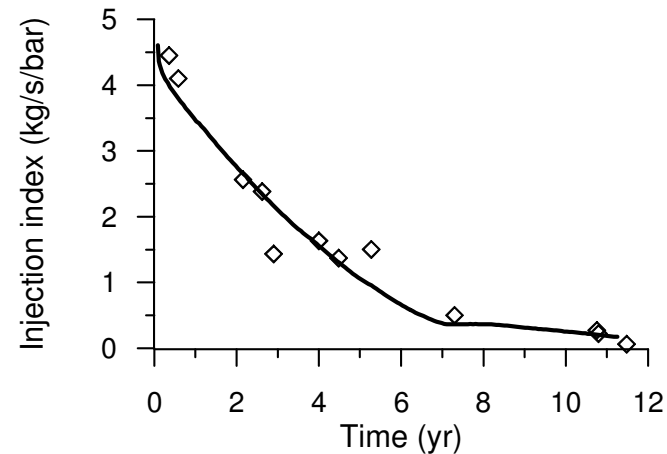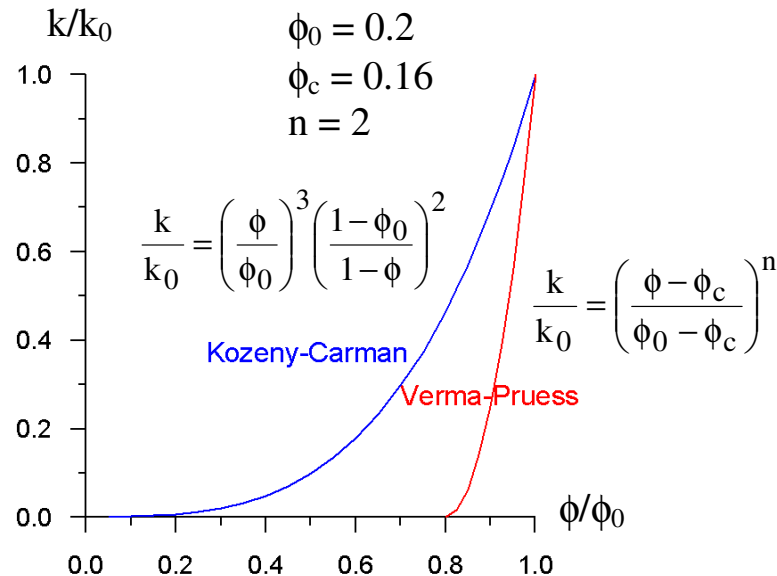

pore body   **pore throat**

- 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)

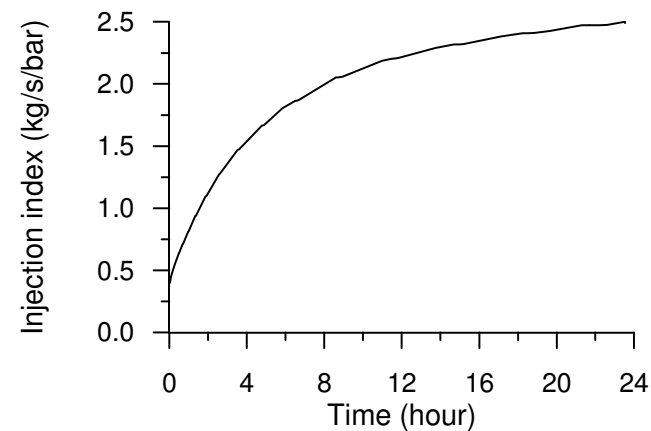$$\frac{k}{k_0} = \left(\frac{\phi - \phi_c}{\phi_0 - \phi_c} \right)^n$$

Geothermal Injectivity at Tiwi Field (2)

$\phi_0 = 0.2$
$\phi_c = 0.16$
$n = 2$

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

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

Kozeny-Carman

Verma-Pruess

k/k$_0$ vs ϕ/ϕ_0

➤ Injectivity loss

➤ Injectivity recovery due to acid

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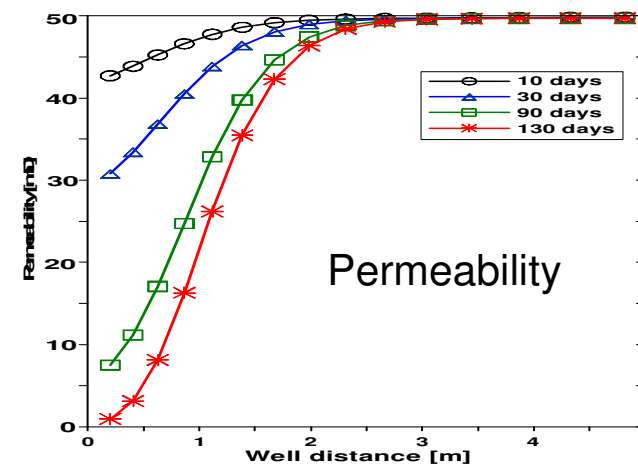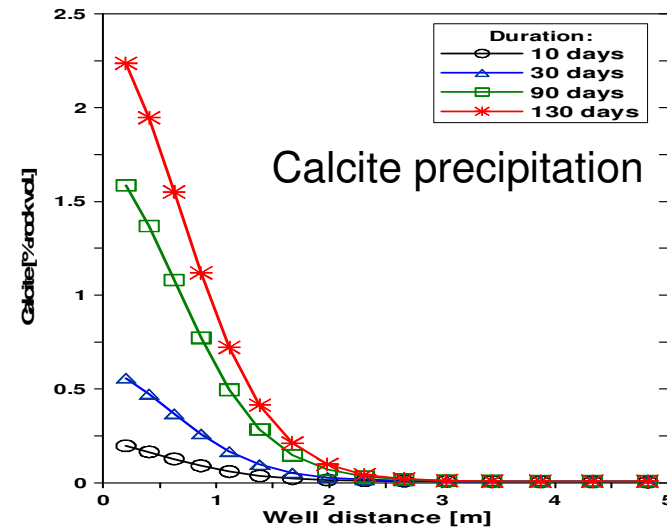
Formation Damage from Waterflooding

- ➤ 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
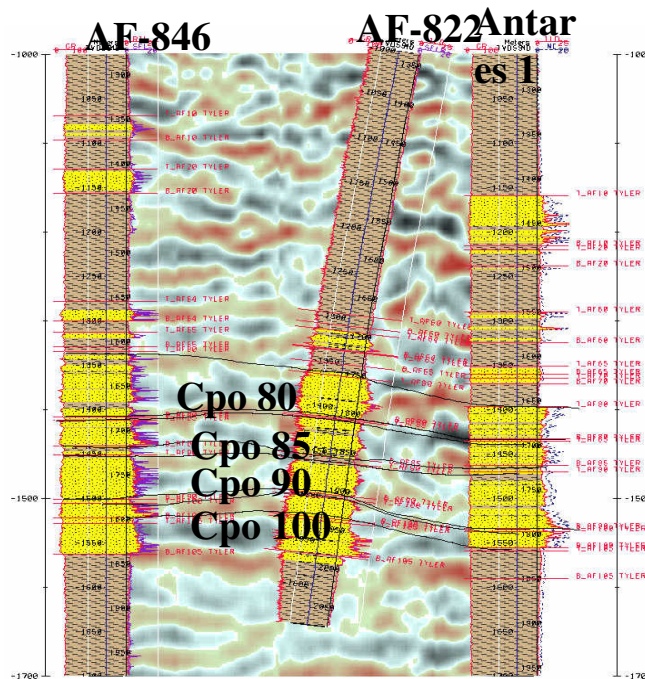
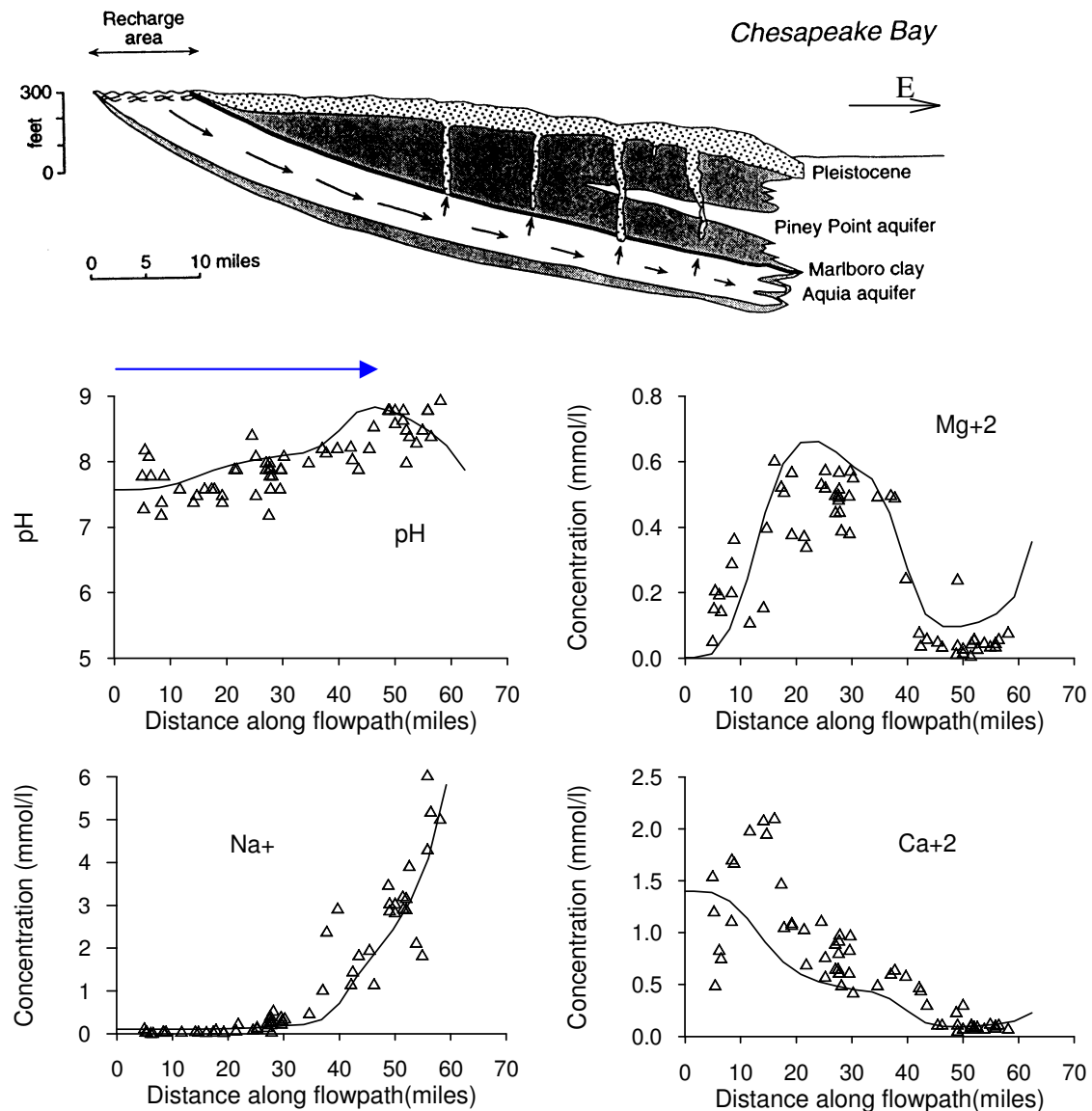Birkle (IE, Mexico), …,, Xu , 2006; SPE paper

Water Quality in the Aquia Aquifer (Maryland)

- ➢ Validation
- ➢ NaHCO$_3$ 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.

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
  ▪ CO_2 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

LAWRENCE BERKELEY NATIONAL LABORATORY

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
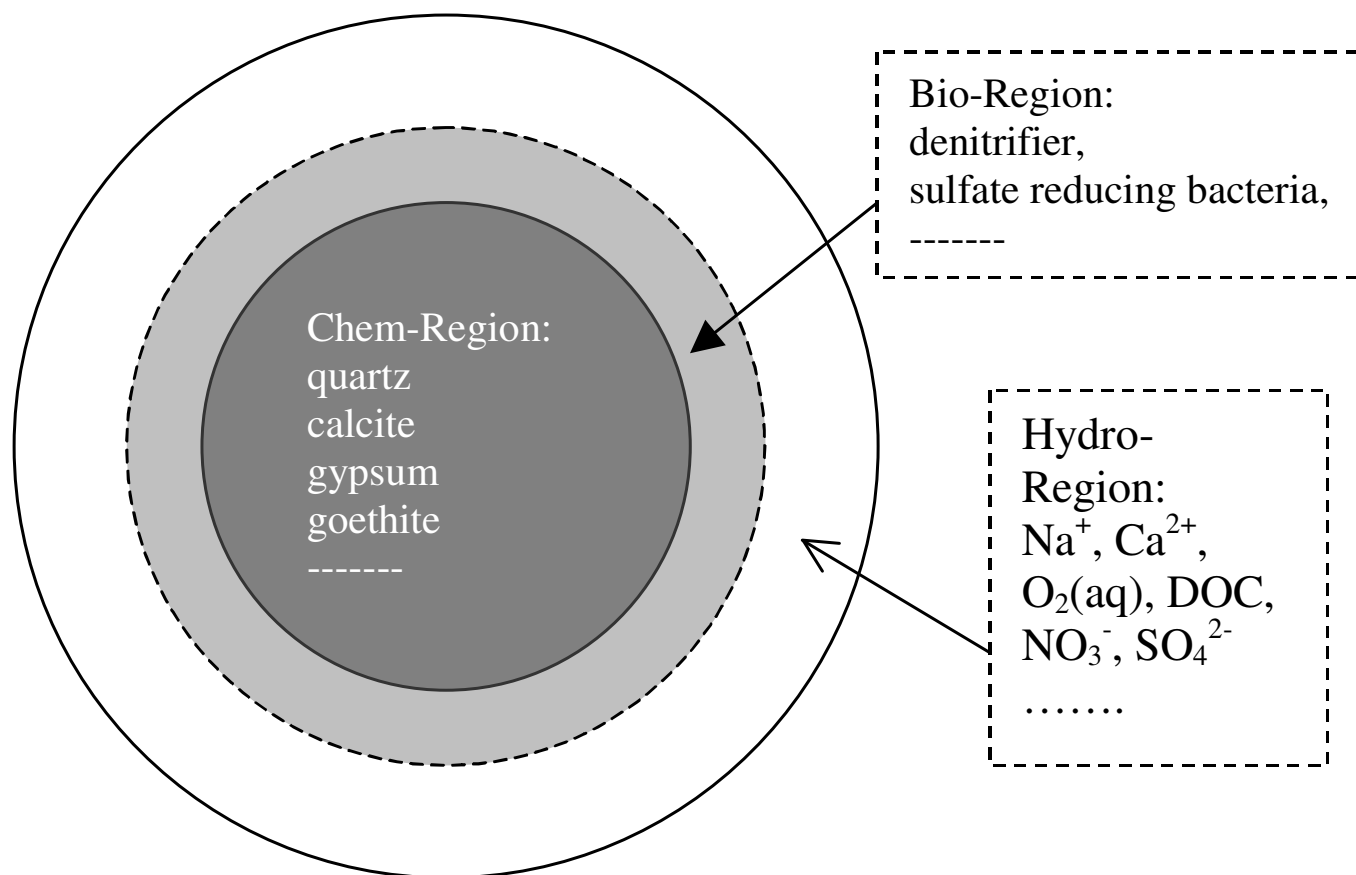- Fortran 90 code upgrading

➢ 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

Bio-Region:
denitrifier,
sulfate reducing bacteria,

Hydro-
Region:
Na^+, Ca^{2+},
$O_2(aq)$, DOC,
NO_3^-, SO_4^{2-}
....

Chem-Region:
quartz
calcite
gypsum
goethite

Xu, Vadose Zone Journal 2008

Biogeochemistry: Denitrification and Sulfate Reduction

➢ ## Rate law

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

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

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

$$r_b = r_b^{O_2} + r_b^{NO_3} + r_b^{SO_4} - bX_b$$

Xu, Vadose Zone Journal 2008