STANFORD UNIVERSITY
ENERGY RESOURCES ENGINEERING
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Chemical Reaction Modeling in CO_2 Storage Simulation

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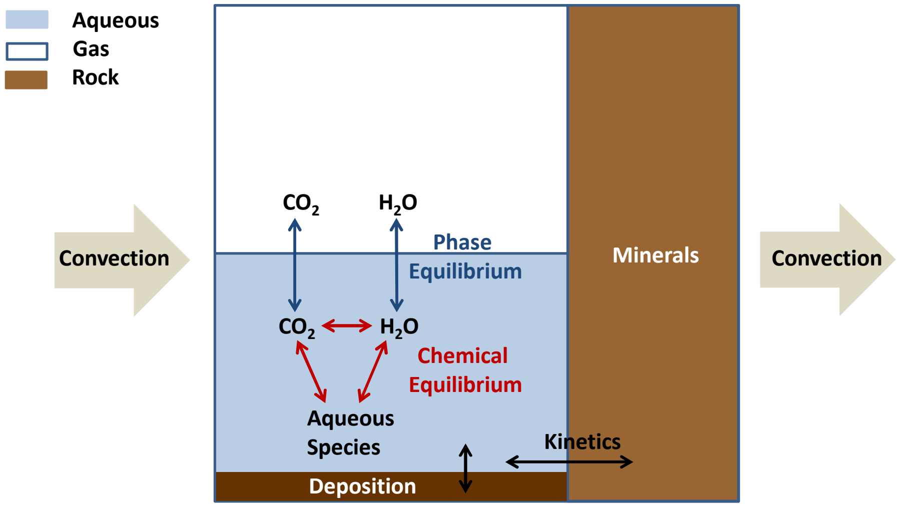
Outline

- Reactive transport modeling
- Overall-composition variable formulation
- Problem of water disappearance
- Porosity change modeling
- Simulation case results
- Future work

Reactive Transport Modeling in GPRS

- ❑ GPRS implementation (Fan, 2010): Applied to in-situ oil-shale upgrading and CO_2 sequestration in saline aquifers
- ❑ AD-GPRS developments:
  - Natural variable formulation
  - Deposition modeling
  - Overall-composition variable formulation
  - Modeling porosity change

Model Description



🟦 **Aqueous**
☐ **Gas**
🟫 **Rock**

Convection

CO_2 **H_2O**

Phase Equilibrium

CO_2 ⟷ **H_2O**

Chemical Equilibrium

Aqueous Species

Kinetics

Deposition

Minerals

Convection

Chemical Reaction in AD-GPRS

Fluid Species $\frac{\partial M_i}{\partial t} + \nabla . \sum_{j=1}^{n_p} \rho_j X_{ij} u_j + q_{i,well} = \sum_{l=1}^{n_R} v_{i,l} r_l$

Minerals $\frac{\partial M_j}{\partial t} = \sum_{l=1}^{n_R} v_{j,l} r_l$

$$\Downarrow$$

$$\frac{\partial \boldsymbol{M}}{\partial \boldsymbol{t}} + \boldsymbol{\nabla . F} + \boldsymbol{q_{well}} = \boldsymbol{Vr}$$

Phase equilibrium and phase constraints remain unchanged

Chemical Reaction Treatment

$\boldsymbol{E}$: Equilibrium Rate Annihilation Matrix (ERA matrix)

$$\boldsymbol{E} = \underset{\xrightarrow{\quad\text{Species}\quad}}{\begin{pmatrix} a_{1,1} & \cdots & a_{1,n_s} \\ \vdots & \ddots & \vdots \\ a_{n_e,1} & \cdots & a_{n_e,n_s} \end{pmatrix}} \Big\downarrow \text{Elements}$$

$$\boldsymbol{E} = \begin{array}{c|ccc|c} & \mathbf{CO_2} & \mathbf{CH_4} & \cdots & \\ \hline & 1 & 1 & \cdots & \mathbf{C} \\ & 0 & 4 & \cdots & \mathbf{H} \\ & 2 & 0 & \cdots & \mathbf{O} \end{array}$$

$$V = \underset{\xrightarrow{\quad\text{Reactions}\quad}}{\begin{pmatrix} v_{1,1} & \cdots & v_{1,n_r} \\ \vdots & \ddots & \vdots \\ v_{n_s,1} & \cdots & v_{n_s,n_r} \end{pmatrix}} \Big\downarrow \text{Species}$$

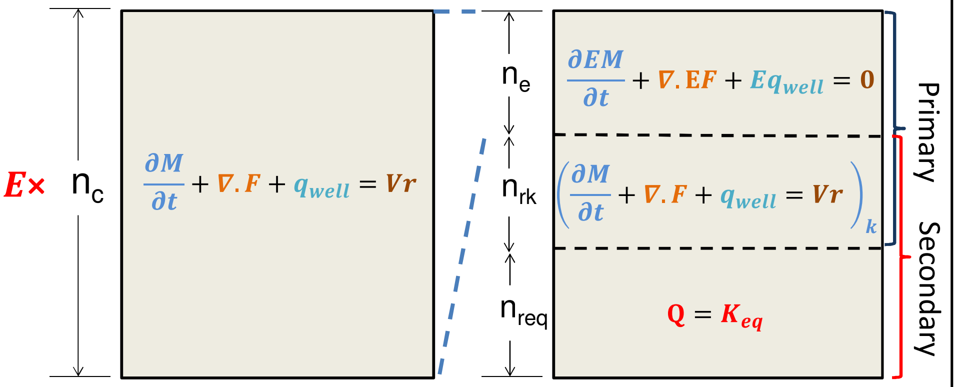
$$\boldsymbol{EV} = \boldsymbol{0}$$

$$\boxed{\frac{\partial \boldsymbol{EM}}{\partial \boldsymbol{t}} + \boldsymbol{\nabla . EF} + \boldsymbol{Eq_{well}} = \boldsymbol{EVr} = \boldsymbol{0} \quad \text{Element Balance}}$$

Fan et al., Advances in Water Resources, 2012

Species to Element Balance

$$n_c = n_e + n_{rk} + n_{req}$$



$E\times$ n_c

$$\frac{\partial M}{\partial t} + \nabla . F + q_{well} = Vr$$

n_e

$$\frac{\partial EM}{\partial t} + \nabla . \mathbf{EF} + Eq_{well} = 0$$

n_{rk}

$$\left(\frac{\partial M}{\partial t} + \nabla . F + q_{well} = Vr\right)_k$$

n_{req}

$$\mathbf{Q} = K_{eq}$$

Overall-Composition Variable Formulation

$$v_p = \frac{S_p \rho_p}{\sum_j S_j \rho_j}$$

$$\rho_T = \sum_{j=1}^{n_p} S_j \rho_j = \left(\sum_{j=1}^{n_p} \frac{v_j}{\rho_j}\right)^{-1}$$

$$z_c = \frac{\sum_j S_j \rho_j x_{cj}}{\sum_j S_j \rho_j} = \sum_{j=1}^{n_p} v_j x_{cj}$$

$$\longleftarrow \quad M_c = \phi \sum_{p}^{n_p} S_p \rho_p x_{cp}$$

$$\longrightarrow \quad M_c = \phi \rho_T z_c$$

$$S_p = v_p \rho_T / \rho_p$$

Overall-Composition Variable Formulation, FIM

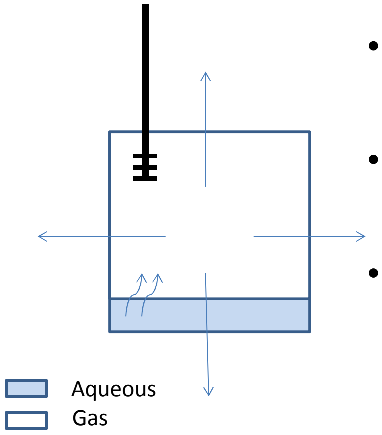
In Each Newton iteration

1 Globally solve for primary variables $x_p = \{P, T, z_c\}$
- Mass conservation equations

2 Solve local constraints for each individual block to update secondary unknowns $x_s = \{x_{cp}, \nu_p\}$
- Phase equilibrium
- Phase constraints

3 Update $$\frac{\partial x_s}{\partial x_p} = -\left(\frac{\partial R_s}{\partial x_s}\right)^{-1} \frac{\partial R_s}{\partial x_p}$$

Water Disappearance



- Some species exist only in the aqueous phase
- Such species must be tracked upon full disappearance of water
- Natural variable formulation suffers from near-singular/ singular Jacobian at very low to zero water saturations

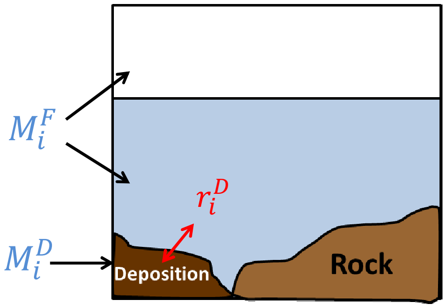
- Special treatment developed for natural variables, not needed for overall-composition variables

Deposition Term for Aqueous Species

$$\frac{\partial M_i^F}{\partial t} + \nabla.(\rho_w X_{iw} u_w) + q_{i,well} = \sum_{l=1}^{n_R} \upsilon_{i,l} r_l - r_i^D$$

$$\frac{\partial M_i^D}{\partial t} = r_i^D$$

$$r_i^D = c_i k_D \phi S_w \left(1 - \frac{I}{I_{max}}\right)$$



I : Ionic Strength

c_i : molar fraction in deposited phase

F : Fluid

D : Deposited

Generalized Treatment of Solid Species

$$\frac{\partial \boldsymbol{M}}{\partial \boldsymbol{t}} + \boldsymbol{\nabla}.\boldsymbol{F} + \boldsymbol{q_{well}} = \boldsymbol{Vr} \qquad \boldsymbol{M_c} = \sum_{p}^{n_p} \boldsymbol{V_p \rho_p x_{cp}}$$

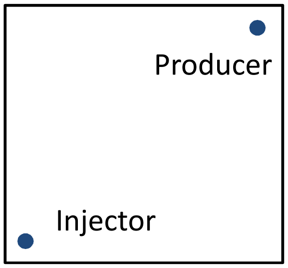
$$\boldsymbol{V_p} = \begin{cases} \boldsymbol{\phi_f S_p} & \boldsymbol{1 \le p \le n_{p,fluid}} \\ \boldsymbol{\phi_{rs} S_p} & \boldsymbol{n_{p,fluid} < p \le n_{p,fluid} + n_{p,solid}} \end{cases}$$

$$\boldsymbol{\phi_f + \phi_{rs} \le 1}$$

- Fluid and reactive solid phase saturations defined wrt the corresponding porosity
- Time dependent porosity values
- Enhanced convergence

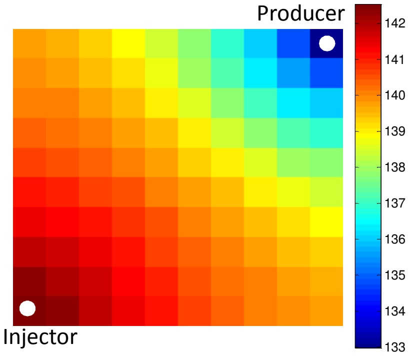
Case 1

- 12 species: 9 aqueous species and 3 minerals
- 6 elements
- 6 reactions
  - 3 equilibrium reactions (homogeneous, aqueous)
  - 3 kinetic reactions (heterogeneous, mineral dissolution and precipitation)
- 2D, 100 grid blocks, injection and production wells at two corners, injecting pure CO_2 for 1 year

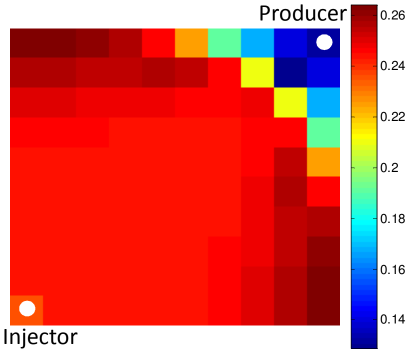


Pressure Profile, 200 days

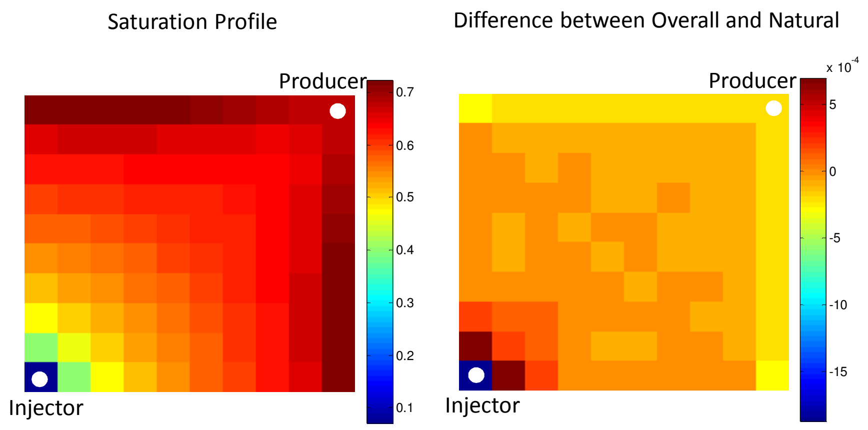
Pressure Profile



Difference between Overall and Natural

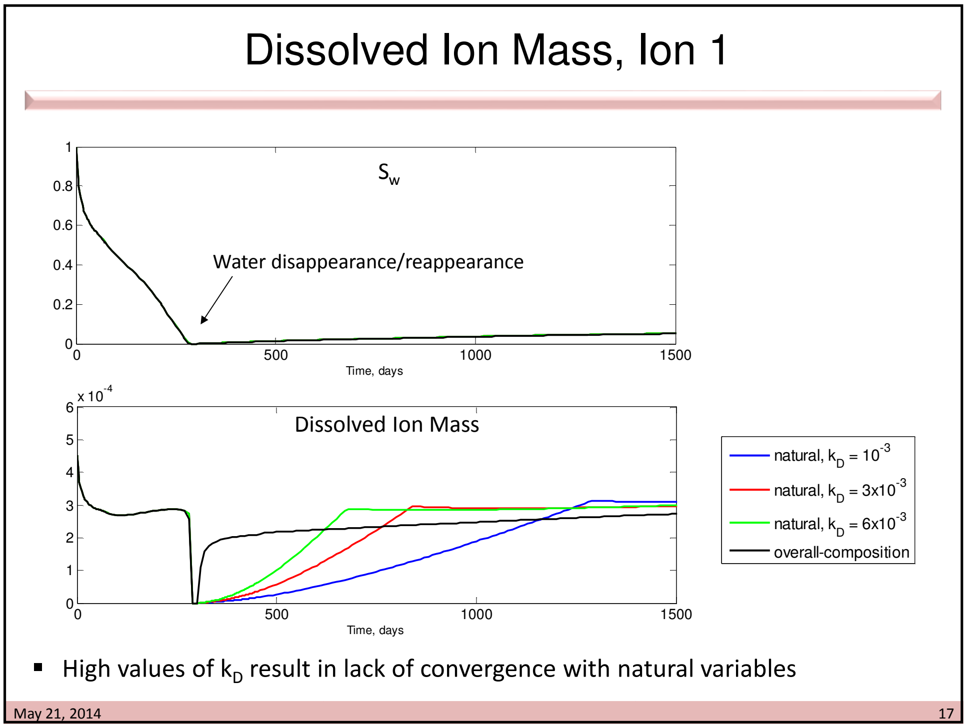


Water Saturation Profile, 365 days



Case 2

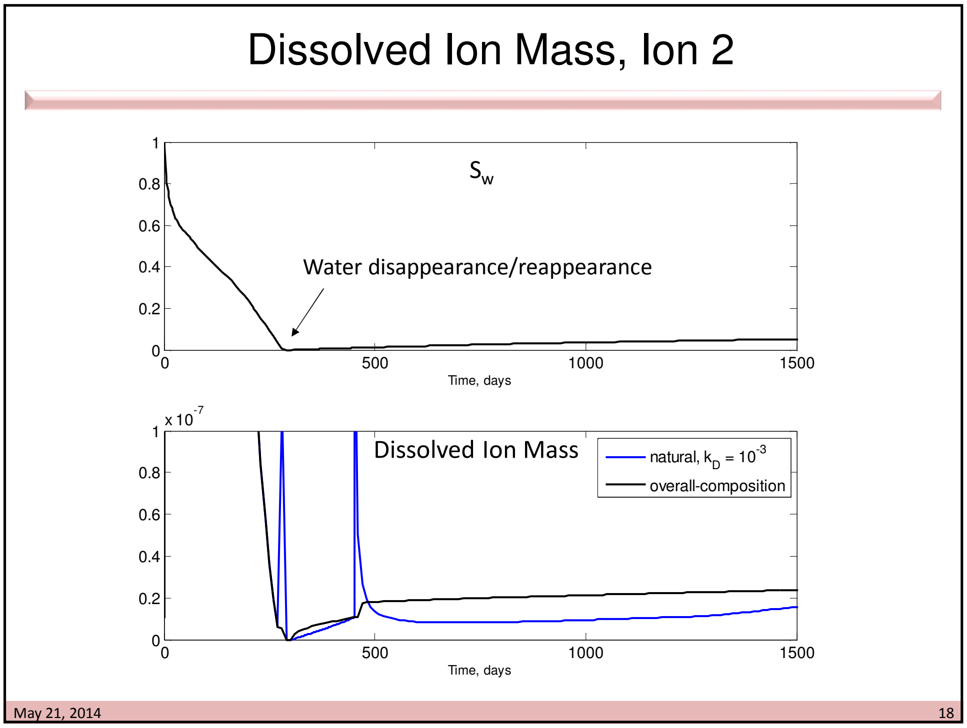
- 12 species: 9 aqueous species and 3 minerals
- 6 elements
- 6 reactions
  - 3 equilibrium reactions (homogeneous, aqueous)
  - 3 kinetic reactions (heterogeneous, mineral dissolution and precipitation)
- 1D, 10 grid blocks, injection and production wells at the two ends, Injecting pure CO_2 for 290 days



Dissolved Ion Mass, Ion 1

- High values of k_D result in lack of convergence with natural variables

May 21, 2014 17



Dissolved Ion Mass, Ion 2

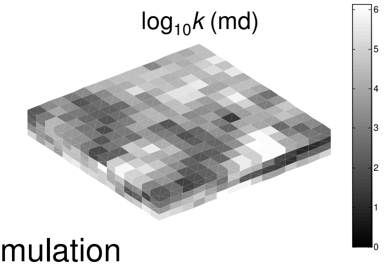
May 21, 2014 18

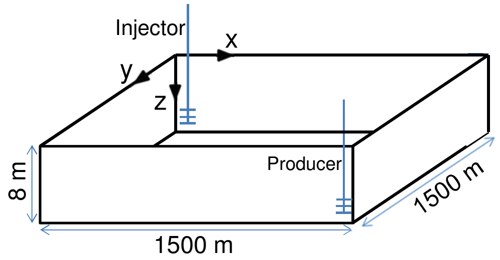
Numerical Results

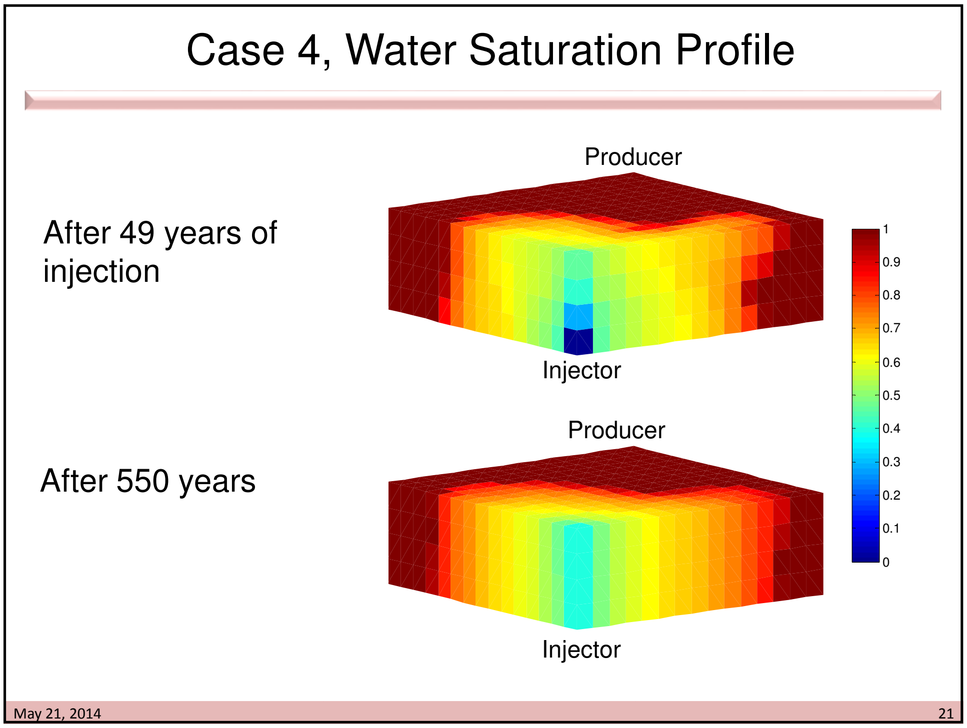
Formulation	Time Steps	Newton Iterations	Linear Solves	EoS
Natural ($k_D=10^{-4}$)	523	835	835	1182
Natural ($k_D=6x10^{-3}$)	1226	3744	3744	1194
Overall-composition	553	1906	1906	50399

Case 4

- Same reaction system as before
- 1.5 km x 1.5 km x 8 m
- 15×15×4 (900) grid blocks
- Heterogeneous permeability field
- Injecting pure CO_2 for 49 years
- Employing overall-composition formulation



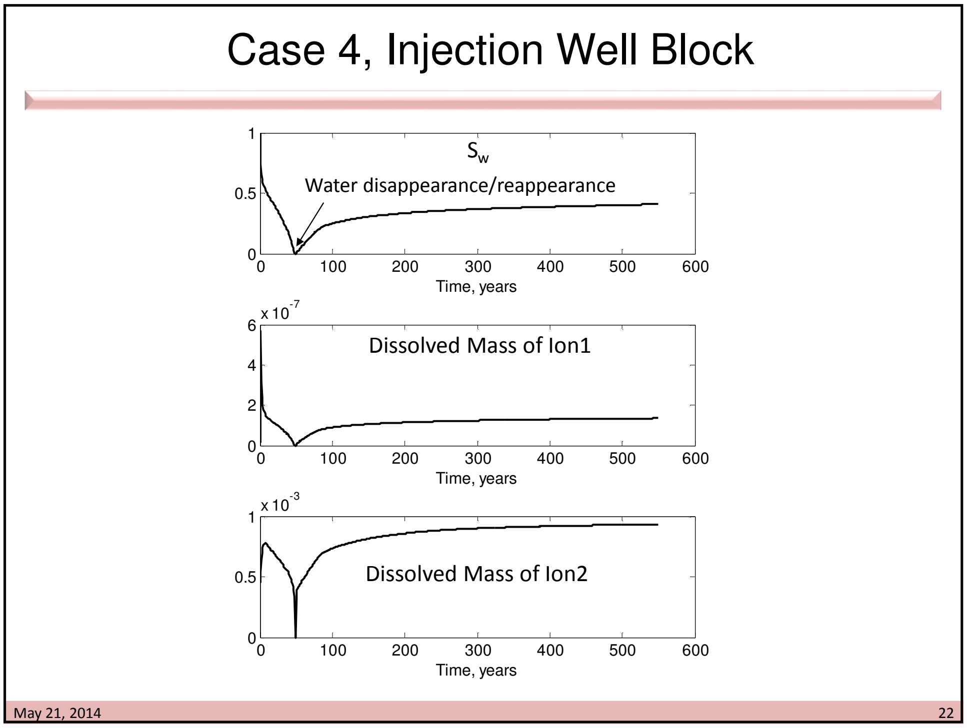




Case 4, Water Saturation Profile

After 49 years of injection

After 550 years



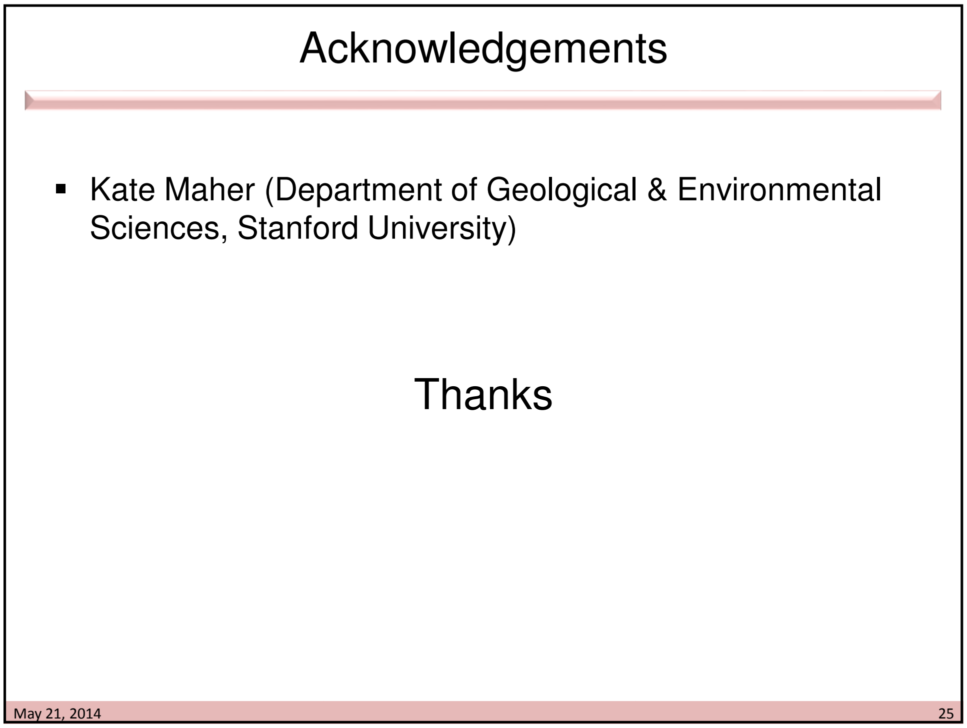
Case 4, Injection Well Block

Conclusions

- Implemented both natural and new overall-composition formulations in AD-GPRS
- Verified consistent solutions in cases with no aqueous-phase disappearance
- Illustrated behavior of overall-composition formulation for cases with aqueous phase disappearance
- Applied to 3D heterogeneous example

Future Work

- Investigate robustness, nonlinear behavior, and time stepping behavior of the overall-composition formulation; address the EOS cost
- Model realistic heterogeneous geological formations with more comprehensive reaction systems
- Apply sequential iteration for reaction modeling
- Model effects of geochemistry on formation properties



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