Chemical and Thermal Non-Equilibrium: Kinetic Mass & Energy Transfer

International Research Training Group nupus

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Motivation

Modeling Non-Equilibrium

- Limits of *thermodynamic equilibrium assumption*
  → confidence in existing models
- Being able to model situation of clear non-equilibrium
  → extending range of applicability

Current Work

Chemical Non-Equilibrium

- Comparing implemented model with [1]:

$$\frac{\partial\left(\phi S_w \varrho_w x_w^w\right)}{\partial t} + \nabla\cdot\left(\varrho_w x_w^w \mathbf{v}_w + \mathbf{j}_w^w\right) = \varrho_w^{w,\mathrm{pure}} q_w^w - D_w^w \varrho_n a_{wn} \frac{x_{n,\mathrm{sat}}^w - x_n^w}{d}$$

$$\frac{\partial\left(\phi S_w \varrho_w x_w^a\right)}{\partial t} + \nabla\cdot\left(\varrho_w x_w^a \mathbf{v}_w + \mathbf{j}_w^a\right) = \varrho_w^{a,\mathrm{pure}} q_w^a + D_w^a \varrho_w a_{wn} \frac{x_{w,\mathrm{sat}}^a - x_w^a}{d}$$

$$\frac{\partial\left(\phi S_n \varrho_n x_n^w\right)}{\partial t} + \nabla\cdot\left(\varrho_n x_n^w \mathbf{v}_n + \mathbf{j}_n^w\right) = \varrho_n^{w,\mathrm{pure}} q_n^w + D_n^w \varrho_n a_{wn} \frac{x_{n,\mathrm{sat}}^w - x_n^w}{d}$$

$$\frac{\partial\left(\phi S_n \varrho_n x_n^a\right)}{\partial t} + \nabla\cdot\left(\varrho_n x_n^a \mathbf{v}_n + \mathbf{j}_n^a\right) = \varrho_n^{a,\mathrm{pure}} q_n^a - D_n^a \varrho_w a_{wn} \frac{x_{w,\mathrm{sat}}^a - x_w^a}{d}$$

$$\text{with: } p_c = p_c\left(S_w\right),$$

$$a_{wn} = a_{wn}\left(S_w, p_c\right),$$

$$x_{w,\mathrm{sat}}^a = p_n^a H_{w-n}^a \quad \textsc{Henr}$$

$$x_{n,\mathrm{sat}}^w = \frac{p_{v,\mathrm{sat}}^w}{p_n} \quad \textsc{Raoult}$$

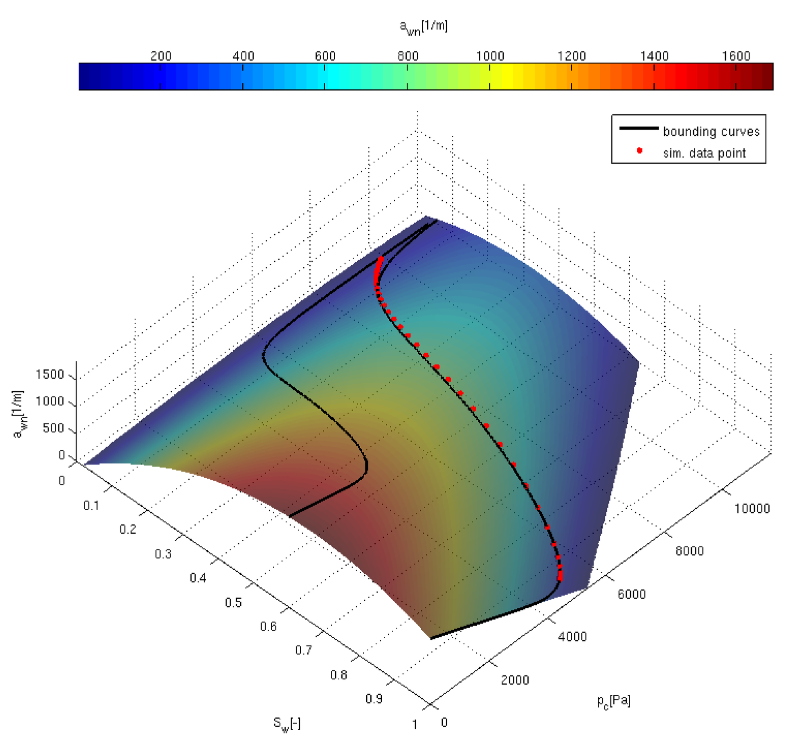


Figure 1: Constitutive relation for volume specific interfacial area.

$$\sum_\alpha \frac{\partial\left(\phi S_\alpha \varrho_\alpha x_{\alpha,\mathrm{sat}}^w\right)}{\partial t} + \sum_\alpha \nabla\cdot\left(\varrho_\alpha x_{\alpha,\mathrm{sat}}^w \mathbf{v}_\alpha + \mathbf{j}_\alpha^w\right) = \sum_\alpha x_{\alpha,\mathrm{sat}}^w \varrho_\alpha q_\alpha$$

$$\sum_\alpha \frac{\partial\left(\phi S_\alpha \varrho_\alpha x_{\alpha,\mathrm{sat}}^a\right)}{\partial t} + \sum_\alpha \nabla\cdot\left(\varrho_\alpha x_{\alpha,\mathrm{sat}}^a \mathbf{v}_\alpha + \mathbf{j}_\alpha^a\right) = \sum_\alpha x_{\alpha,\mathrm{sat}}^a \varrho_\alpha q_\alpha$$

- "Baseline" example
  → Injecting pure gas
  → Injection at high rate
  → Initially fully water saturated domain
  → Comparison to standard model shows differences

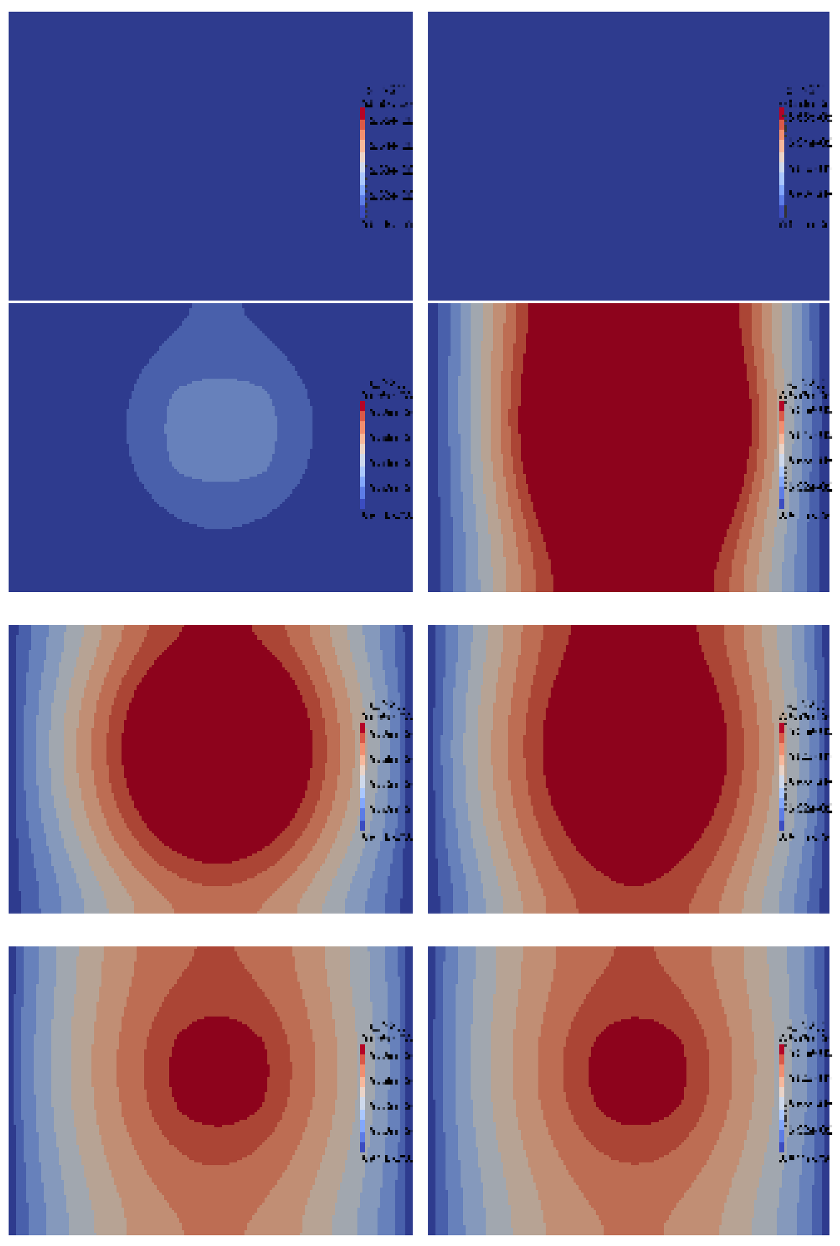


*Figure 2: Comparing the kinetic mass transfer (**left**) model to the standard (**right**) model.*

Future Work

Thermal Non-Equilibrium

- Comparing implemented model with [2]:

$$\frac{\partial\left(\phi \varrho_w S_w u_w\right)}{\partial t} + \nabla\cdot\left(\varrho_w \mathbf{v}_w h_w + \sum_\kappa \mathbf{j}_w^\kappa h_w^\kappa\right) - \nabla\cdot\left(\phi S_w \lambda_w \nabla T_w\right) =$$

$$\varrho_w^{w,\mathrm{pure}} h_w^w q_w^w + \varrho_w^{a,\mathrm{pure}} h_w^a q_w^a + a_{wn}\lambda_{wn}\frac{\left(T_n - T_w\right)}{d_{wn}^{\mathrm{therm}}} + a_{ws}\lambda_{ws}\frac{\left(T_s - T_w\right)}{d_{ws}^{\mathrm{therm}}}$$

$$\frac{\partial\left(\phi \varrho_n S_n u_n\right)}{\partial t} + \nabla\cdot\left(\varrho_n \mathbf{v}_n h_n + \sum_\kappa \mathbf{j}_n^\kappa h_n^\kappa\right) - \nabla\cdot\left(\phi S_n \lambda_n \nabla T_n\right) =$$

$$\varrho_n^{w,\mathrm{pure}} h_n^w q_w^w + \varrho_n^{a,\mathrm{pure}} h_n^a q_n^a - a_{wn}\lambda_{wn}\frac{\left(T_n - T_w\right)}{d_{wn}^{\mathrm{therm}}} + a_{ns}\lambda_{ns}\frac{\left(T_s - T_n\right)}{d_{ns}^{\mathrm{therm}}}$$

$$\frac{\partial\left(\left(1-\phi\right)\varrho_s c T_s\right)}{\partial t} - \nabla\cdot\left(\left(1-\phi\right)\left(\left(1-\left(S_n + S_w\right)\lambda_s \nabla T_s\right)\right) =$$

$$- a_{ws}\lambda_{ws}\frac{\left(T_s - T_w\right)}{d_{ws}^{\mathrm{therm}}} - a_{ns}\lambda_{ns}\frac{\left(T_s - T_n\right)}{d_{ns}^{\mathrm{therm}}}$$

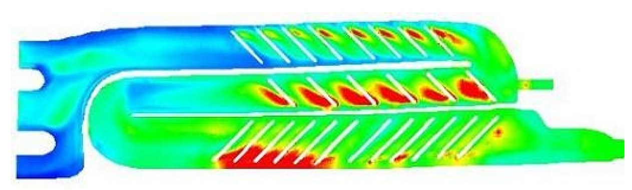
- Standard compositional energy equation (one Temperature per REV):

$$\frac{\partial\left(\left(1-\phi\right)\varrho_s c T\right)}{\partial t} + \sum_\alpha \frac{\partial\left(\phi \varrho_\alpha S_\alpha u_\alpha\right)}{\partial t} - \nabla\cdot\left(\bar{\lambda}_{\mathrm{pm}} \nabla T\right)$$

$$+ \sum_\alpha \nabla\cdot\left(\varrho_n \mathbf{v}_n h_n + \sum_\kappa \mathbf{j}_n^\kappa h_n^\kappa\right) = \sum_\kappa \sum_\alpha x_{\alpha,\mathrm{sat}}^\kappa q_\alpha \varrho_\alpha h_\alpha$$

Example Applications

- Industrial Cooling Devices
- Thermally enhanced remediation



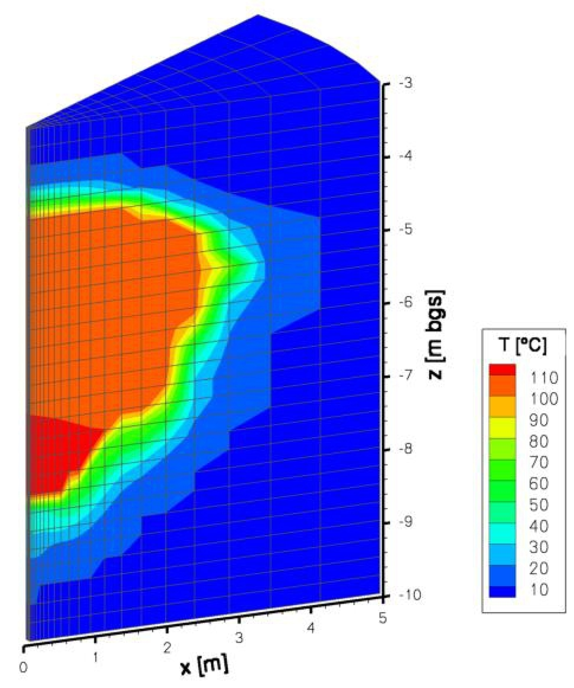


*Figure 3: Cooling Device (**left**), steam injection into an aquifer (**right**)*

Outlook

Identify Need for Complex Model

- Under which circumstances is thermodynmic equilibrium a good assumption?
- Mass transfer is actually driven by difference in chemical potential
  → influence of thermal non-equilibrium on kinetic mass transfer
- Adaptivity of numerical model

Literature

[1] *Niessner, J.; Hassanizadeh, S.M.:* Modeling kinetic interphase mass transfer for two-phase flow in porous media including fluid-fluid interfacial area. *Transport in Porous Media 80 (2009)*

[2] *Niessner, J.; Hassanizadeh, S.M.: Non-equilibrium heat and mass transfer during two-phase flow in porous media–Theoretical conciderations and modeling*. Advances in Water Resources 32 (2009), p. 1756-1766

[3] Ochs, S.O. et al.: Methods for predicting the spreading of steam below the water table during subsurface remediation. Water Resources Research 46, (2010)

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