The HPx reactive transport models: A short overview of development and possibilities

D. Jacques\textsuperscript{(1)}, J. Šimůnek\textsuperscript{(2)}, D. Mallants\textsuperscript{(3)}, M.Th. van Genuchten\textsuperscript{(4)}

\textsuperscript{(1)} SCK•CEN, Belgium, \textsuperscript{(2)} UCR, CA, USA, \textsuperscript{(3)} CSIRO, Adelaide, Australia, \textsuperscript{(4)} Federal University of Rio de Janeiro, Brazil
djacques@sckcen.be

4\textsuperscript{th} International HYDRUS Conference
Prague, March 21-22, 2013

Outline

- HPx
  - Flow – Transport
  - Geochemistry

- Recent examples
  - Diffusion in gas phase
  - Two-dimensional flow and transport
  - Inverse optimisation of flow, transport and geochemical parameters
  - Coupling geochemical variables – transport parameters
  - Benchmarking

HPx


Process

- Variable-saturated water flow
  - Richards’ equation with root water uptake

- Convection-dispersion equation for solute transport

- Heat transport

- Thermodynamic equilibrium

- Kinetic Reactions
Water flow and solute transport models
Uniform flow and transport model

- Three phase system
  - Aqueous, solid and gas phase

- Transport
  - Water flow
  - Heat transport
  - Advection-dispersion in aqueous phase
  - Diffusion in gas phase

- Homogeneous sink/source terms $S$
  - Root water uptake $S_{r,w}$
  - Solute root uptake $S_{r,s,i}$
  - Degradation/decay/transformation $S_{d,i}$

- Heterogeneous mass exchange $\Gamma$
  - Aqueous – solid phase $\Gamma_{ws}$
  - Aqueous – air phase $\Gamma_{wa}$

Water flow and solute transport models
Uniform flow and MIM transport model

- Three phase system
  - Aqueous, solid and gas phase

- Two domains
  - Mobile / Immobile

- Transport
  - Water flow
  - Heat transport
  - Advection-dispersion in aqueous phase
  - Diffusion in gas phase
  - Solute exchange $\Gamma_i$

- Homogeneous sink/source terms $S$
  - Root water uptake $S_{r,w}$
  - Solute root uptake $S_{r,s,i}$
  - Degradation/decay/transformation $S_{d,i}$

- Heterogeneous mass exchange $\Gamma$
  - Aqueous – solid phase $\Gamma_{ws,m}$
  - Aqueous – air phase $\Gamma_{wa}$
  - In both mobile and immobile domain

Water flow and solute transport models
Dual-porosity model water flow and solute transport

- Three phase system
  - Aqueous, solid and gas phase

- Two domains
  - Mobile / Immobile

- Transport
  - Water flow
  - Heat transport
  - Advection-dispersion in aqueous phase
  - Diffusion in gas phase
  - Solute exchange $\Gamma_i$

- Homogeneous sink/source terms $S$
  - Root water uptake $S_{r,w}$
  - Solute root uptake $S_{r,s,i}$
  - Degradation/decay/transformation $S_{d,i}$

- Heterogeneous mass exchange $\Gamma$
  - Aqueous – solid phase $\Gamma_{ws,m}$
  - In both mobile and immobile domain
  - Aqueous – air phase $\Gamma_{wa}$

Geochemical processes
Thermodynamic equilibrium

- Aqueous speciation with different activity correction models (Davies, Debye–Hückel, B-Dot, PITZER, SIT)
- Multiple sites
- Linked to equilibrium phases or kinetic reactants
- Surface complexation (no-electrostatic model, diffuse double layer, CD_MUSIC) with different options to calculate composition double layer
- Minerals in equilibrium with the aqueous phase
- Solid solution (multiple ideal solid solution, binary non-ideal solid solution)
- Exchange with gas phase
Geochemical processes
Kinetic processes

- Kinetic dissolution & precipitation of minerals
- Kinetic sorption & desorption processes
- Kinetic degradation (first order (e.g. radionuclides) or Monod, Michaelis-Menten kinetics)

Geochemical processes
Kinetic processes

- Kinetic reaction networks

Geochemical processes
Kinetic processes

- Including ‘bio’processes

Geochemical processes
Kinetic processes

- Including ‘bio’processes and root interaction processes
Conceptual geochemical model
Mercury speciation in soil

Organic matter degradation
Water content and temperature dependency

Porporato et al. 2003

\[ \frac{dC_i}{dt} = k_i + k_2 C_h - k_i C_i \]
\[ \frac{dC_h}{dt} = r_b k_3 C_i C_h - k_i C_i C_h \]
\[ \frac{dC_i}{dt} = (1 - r_r - r_r^2) k_3 C_i C_i + (1 - r_r) k_i C_i C_h - k_i C_h \]
\[ \frac{dC_b}{dt} = r_b k_4 C_i C_i - s_i C_b \]

\[ f(s) = \begin{cases} 0 & s \leq s_B \\ \frac{s - s_B}{s_r - s_B} & s_B < s \leq s_r \\ 1 & s > s_r \end{cases} \]

\[ f(T) = \frac{47.9}{1 + \exp \left( \frac{106}{T + 18.3} \right)} \]
Organic matter degradation

Organic and inorganic C pools

Transport below Mill Tailing pile

High infiltration
Low infiltration

Acid water
Rain water

Constant head (400 cm)
Soil water

Constant head (1200 cm)
Soil water

HP2

Inverse optimisation – Flow, Transport, Exchange

Water absorption and cation exchange in horizontal cores

pH
U
Calcite
Geochemical variables – transport properties

- HP1 allows dynamic updates of porosity, soil hydraulic properties, tortuosity in the aqueous and gaseous phase, dispersivity, heat conductivity and heat dispersivity.

- User has great flexibility in implementing any porosity-parameter relationships via BASIC-functions in input file.

Example – Diffusive leaching of concrete

Portlandite front (Rain W): 
- \( \sim 1.4 \text{ mm/y}^{0.5} \)
  - 100 y -> 1.4 cm.
  - 400 y -> 2.8 cm

Leaching Rain W > Leaching Soil

In case of higher concentration of major anions and cations -> hydrotalcite precipitation

In case of higher \( \text{CO}_2 \) -> calcite precipitation

\( \Rightarrow \) Porosity clogging \( \Rightarrow \) decrease in tortuosity factor
Geochemical variables – transport properties
Example – Diffusive leaching of concrete

Benchmarking
E.g. pyrite oxidation due to Oxygen intrusion

- International Benchmark
- Example: oxygen diffusion, pyrite oxidation with ground water table at 2.5 m.
- Three codes
  - Solid: MIN3P
  - Dotted: HP1
  - Dash-dot: FLOTRAN