Coupling "rich" thermodynamic models (GEM) into reactive transport simulations

Predictive Geosciences Workshop, 25. October 2016, BRGM Orléans
Reactive transport phenomena

- Occur in spatially heterogeneous porous/fractured media where chemical reactions are driven by the advective/diffusive transport of aqueous and/or gaseous fluids
- Reactions such as mineral dissolution and growth influence both aqueous speciation and mass transport via modification of pore geometry and related transport properties
- Such feedbacks require coupling the transport model to (complex) partial equilibrium speciation, resolved simultaneously at every time step in each control volume

Advection/diffusion-driven mineral replacement

Dolomitization of limestones (Canadian Rockies, Sharp ea, 2010)

Hydrothermal alteration of basalt around fractures (Iceland)

Replacement of celestite by barite in a lab sand tank upon advection of BaCl$_2$ solution at room $T$ (Poonoosamy ea, 2016 GCA)
“Rich” chemistry: CO₂ binding in basalt

- Complex systems at given T, P and complete mass balance for all phases
- Heterogeneous, many minerals possible, some (glass) under kinetic controls
- Solid solutions – aqueous solution – non-ideal gaseous fluid

Progress of reaction of basaltic glass with CO₂-saturated water

Computed with GEM-Selektor

From (A. Gysi, Pure Applied Chemistry, 2016, submitted), http://tdb.mines.edu
“Rich” plausible chemistry: Cement hydration

Thermodynamic modelling

• Hydration of cement clinker
• Blended / alternative cements
• Degradation / durability
• Cemdata’07 and ‘14 TDBs

Provided by Barbara Lothenbach, Empa (www.empa.ch/cemdata)

Lothenbach ea (2008), CCR 38, 1162-1186

Portland cement (OPC)

Deschner ea (2012), CCR 42
Another example of “rich” geochemistry

High-enthalpy geothermal systems

Two-phase non-isothermal fluid (water, steam) with enthalpy constraints, at $P < 200$ bar, $T < 360$ °C

Equilibrium partitioning of gases ($H_2, H_2S, CO_2, HCl, CH_4$), $Si(OH)_4, B(OH)_3$ between water and steam.
Account for redox & formation of secondary minerals governed by kinetics of basalt (glass) dissolution

COTHERM project (Switzerland-Iceland)

Efficiently modeled by HKF+PRSV EoS TDB
Why Gibbs Energy Minimization (GEM)?

**Problem:**

Find \( n \) (equilibrium amounts of chemical species in phases)
at \( T, P, b \) (bulk elemental composition)
s.t. mass balance \( A^T n = b, \ n \geq 0 \),
such that \( G(n) \to \text{min} \)

\[
G(n) = \sum_j \mu_j n_j
\]

Chemical potential is linear for pure substances only:

\[
\mu_j = \mu_j^0 = \frac{g_{j,T,P}^0}{RT}
\]

General case:

\[
\mu_j = \mu_j^0 + \ln C_j + \ln \gamma_j
\]

\[
C_j = f(n)
\]

\[
\gamma_j = f(n, T, P)
\]

Caveat: Precision of summation in elemental mass balance

**Purpose:**

Calculation of chemical equilibria in complex systems with:

- aqueous electrolyte;
- non-ideal gaseous fluids;
- non-ideal solid solutions;
- non-ideal (ionic) melts;
- adsorption, ion exchange;
- Many pure phases (s, l);
- metastable species / phases, kinetics

**Features:**

- Non-linear \( G(n) \) function
- Multi-component phases
- Non-ideal solutions
- Multi-phase systems

Page 6
TSolMod library for activity models


- Provides activity coefficients etc.
- Easy to add new activity models
- Flexible parameter exchange
- Transfer via I/O files to GEMS3K solver in coupled codes
- Multi-site (sublattice) solid solutions and melts
- Models of real gaseous fluid

Miscibility gap in a non-ideal ternary feldspar – aqueous system as $f(T)$

Under construction:
- Integral phase properties
- Derivatives of activities on x, T, P
- Calphad-style mixing models
- Adsorption, ion exchange, Donnan
Examples of using GEM in RT simulations

Coupled RMT codes using GEMS3K kernel from GEMS

- **OpenGeoSys-GEM**: clay-cement interfaces in geological waste repositories; transport-induced dissolution-precipitation phenomena in experiments

- **CSMP++GEM**: element partitioning upon two-phase transport in high-enthalpy geothermal systems; non-isothermal dolomitisation of limestones

- **COMSOL-GEMS**: Engesgard-Kipp benchmark (1-D calcite-dolomite column); cement-clay interface (Marty et al., 2015) benchmark

* Developed without any participation of GEMS Development Team (Azad et al., Computers & Geosciences 92 (2016), 79-89)

GEMS3K code with TNode API and TNodeArray API is open-source (LGPL v3): http://gems.web.psi.ch/GEMS3K; https://bitbucket.org/gems4/gems3k
OpenGeoSys-GEM

- Fully and partially saturated liquid flow (H) in fractured and porous media
- Multi-species solute transport (T)
- Heat transport (T)
- Chemistry (C) with GEMS3K

-> coupled T-H-C (feedback between processes)

OpenGeoSys parallelization:

- PETSc (overlapping domain decomposition approach)
- In addition, boost-threads (spawns multiple GEMS worker threads for solving chemistry in each domain)

Modeling long term evolution of material interfaces: Engineered gas transport system (EGTS)

2D model with variable fluid saturation & geochemical reactions

Figure 10: Conceptional two-dimensional model considering spatially varying fluid saturation
Long term evolution after 100,000 years: advective transport in fluid-saturated bottom drives cement leaching.

Modeling long-term evolution of material interfaces: Engineered gas transport system (EGTS).

- Calcite precipitation
- C-S-H dissolution
- Fluid flow
- Gypsum precipitation

Long term evolution
RT modelling: prediction vs experiment

Barite precipitation; 2 celestite phases with different reactive surface area

Experimental sand tank 1x10x10 cm

OpenGeosys-GEM coupled code (OGS-GEM)

10 Hours 100H 200H
Barite profiles with a barium enrichment zone at the interface

Fault-controlled hydrothermal dolomitisation

Helicopter photograph of an outcrop (approx. 200m high) from the Canadian Rocky Mountains (Sharp et al., 2010)

Alternating mudstone-wackestone and packstone-grainstone layers displaced by a normal fault. Top boundary open for the outflow. Simulation results after 2.5kyr at 100°C, uniform RSA 10 000cm²/g. Initial “Christmas-tree” pattern gets smeared off later. Note overdolomitisation at the bottom of the fault.

**Permeability update is important!**

The self-accelerating nature of the dolomitisation process results in a strong deviation of the front geometry from the straight vertical line. The increase in porosity and therefore permeability provides a positive feedback on the fluid flow, increasing the difference between dolomitisation rates in the upper and the lower parts of the 2D domain.

Dolomite (min. vol%) after 25 kyr (0.9 relative time) at 100°C, RSA 10000 cm²/g
(a) with k update – 87 vol% dolomite (b) without k-update – 63 vol% dolomite

Hydrothermal dolomite is, in fact, a **solid solution** with CaMg, CaFe, CaMn end members.
Geothermal reactive transport with boiling

Heat-transport + Hydrology

RT simulator of
two-phase non-isothermal flow (water, steam) with enthalpy constraints,
at P < 200 bar, T < 360 °C

New version of coupled code

Equilibrium partitioning of gases (H₂, H₂S, CO₂, HCl, CH₄), Si(OH)₄, B(OH)₃ between water and steam; account for redox, formation of secondary minerals governed by kinetics of basalt (glass) dissolution

Alina Yapparova, Sinergia COTHERM-2 SP2 project
Two-phase reactive transport simulations

**CSMP++GEM**

1D simulation:
Hot 300°C vapor is injected from the left into the 200°C warm liquid, a boiling zone develops in the middle part of the model, volatiles partition between the liquid and vapor phases.

Aquifer fluid composition was calculated from the liquid and steam sample analysis of the K-14 well from the Krafla geothermal field (Iceland).

Effects of condensation on gases partitioning are visible after the temperature front.

Alina Yapparova et al., Sinergia COTHERM-2 SP2 project
GEMS vs LMA speciation codes

- Chemical species taken as master (primary) and product (secondary)
- A **product species** is defined by LMA (Law-of-Mass-Action) of its formation reaction from **master species** with equilibrium constant \( \log K(T) \) as thermodynamic data (TD)
- TD for master species (aqueous ions or minerals) are ignored, hence additional inputs to set the system state are necessary

<table>
<thead>
<tr>
<th>++ LMA codes pros</th>
<th>-- LMA codes cons</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fast and simple</strong> (minimizes mass balance residuals by keeping LMA)</td>
<td>Limited to aquatic systems with low S/L, mostly low-P, low-T</td>
</tr>
<tr>
<td>Widely used in aquatic chemistry and in hydrogeochemical reactive transport simulations (HYTEC, TOUGHREACT, OGS-PHREEQC)</td>
<td>Limited to ideal gaseous, liquid or solid solutions; only binary non-ideal solutions (PHREEQC); no solid solutions at all (GWB)</td>
</tr>
<tr>
<td>Can easily compute metastable aqueous or surface speciation</td>
<td>pH and Eh can be set at input to any values; no intrinsic redox</td>
</tr>
<tr>
<td>Public domain, very popular (PHREEQC)</td>
<td>Need many trial runs to find all stable minerals</td>
</tr>
</tbody>
</table>
Conventional Law of Mass-Action (LMA) Methods

Product species \[ \text{CaCO}_3 + \text{H}^+ = \text{Ca}^{2+} + \text{HCO}_3^- \]

Master species

\[ K_{\text{CaCO}_3} = \frac{a_{\text{Ca}^{2+}} \cdot a_{\text{HCO}_3^-}}{a_{\text{H}^+} \cdot a_{\text{CaCO}_3}} \]

\[ K_{\text{CaCO}_3} \neq \frac{a_{\text{Ca}^{2+}} \cdot a_{\text{HCO}_3^-}}{a_{\text{H}^+} \cdot a_{\text{CaCO}_3}} \]

Calcite (end-member) stable

\[ 0 < a \leq 1 \]

Calcite is unstable

\[ \text{Is this 0?} \]

- Speciation algorithms based on conventional LMA equations require tentative addition and removal of phases so that the LMA expressions are always valid.

- Efficient, if presumed aspects of the chemical system are known (e.g., aqueous phase is always present; minerals are added/removed according to their saturation indices).

- Common practice for >30 years in geochemical modeling literature (Morel & Morgan, 1972; Reed, 1982; Bethke 2007); codes MINEQL, PHREEQC, GWB, MINTEQ, etc.
xLMA equations were derived from the general GEM problem:

\[ \mu(n) - A^T y - z = 0 \]
\[ An = b \]
\[ n_i z_i = 0 \quad (i = 1, \ldots, N) \]
\[ n_i \geq 0, z_i \geq 0 \]

Stability-related factor: renders xLMA the power of GEM!

Conventional LMA equations:

\[ K_m = \prod_{i=1}^{N} a_i^{\nu_{im}} \quad 0 \Leftrightarrow \sum \nu_{mi} \alpha_i \]

Extended xLMA equations:

\[ K_m = \prod_{i=1}^{N} (a_i \omega_i)^{\nu_{mi}} \]

"extended activity"

Missing in all old LMA codes
Reaktoro algorithms and NextGEMS

Allan M.M. Leal
(PSI; ETHZ IG GEG since 09.2015)

**Chemical Equilibrium Problem**

Fundamental Gibbs energy minimization problem

\[
\text{min } G(n) \quad \text{subject to} \quad \begin{cases} 
An = b \\
n \geq 0
\end{cases}
\]

**GEM**

Direct Gibbs energy minimization approach using chemical potentials

\[
\mu(n) - ATy - z = 0
\]

\[
An = b
\]

\[
n_i z_i = 0
\]

\[
n_i, z_i \geq 0
\]

**rLMA**

Revised law of mass action approach using equilibrium constants

\[
\ln K = \nu \ln a(n) + \nu z
\]

\[
An = b
\]

\[
n_i z_i = 0
\]

\[
n_i, z_i \geq 0
\]

These equations assume general multiphase systems.

Species activity.

Mass balance constraints for elements or primary species.

Complementary conditions for each chemical species.

**solver for chemical kinetics with adaptive time steps**

GPL-3 license, http://www.reaktoro.org

**Missing in old LMA codes!**


Psi LES and ETHZ IG GEG cooperate on mutual development of Reaktoro & GEMS.
Conclusions

- Chemistry is more than just a few reactions if non-ideal aqueous, gaseous, melt, solid solutions; (ad)sorption, ion exchange are involved in a “rich” heterogeneous system

- Using “rich” chemically plausible systems with “rich” TDBs cannot be avoided in realistic RT simulations

- GEM can solve for “rich” partial-equilibrium chemical speciation especially if using thermochemical input database

- RT-GEM coupled codes are already in use (OGS-GEM, OGS-ChemApp, CSMP++GEM, COMSOL-GEMS)

- Conventional LMA methods are simple, fast, but may be too limited for “rich” multiphase chemical systems

- New xLMA method in Reaktoro and next GEMS4R kernel has the power of GEM and can re-use the existing (e.g. PHREEQC) LMA (logK) thermodynamic data and problems
We thank all past and present contributors in the GEMS Development Team

- Berner, Urs
- Chudnenko, Kostya
- Damiani, Leonardo
- Dmytrieva, Sveta
- Gruen, Gillian
- Gysi, Alex
- Hingerl, Ferdinand
- Leal, Allan
- Miron, Dan
- Nichenko, Sergii
- Rysin, Andy
- Thoenen, Tres
- Wagner, Thomas
- Yapparova, Alina
Simulating kinetics as series of partial equilibria

- Time step duration $\Delta t$, time $t$, net kinetic rate $R_{n,k,t}$
- Surface area $A_{k,t}$ of $k$-th solid (solution) phase

$$\bar{n}_{k,t+\Delta t} = n_{k,t} + A_{k,t} R_{n,k,t} \Delta t \quad \text{if} \quad \log_{10} \Omega_k > \varepsilon$$

$$n_{k,t+\Delta t} = n_{k,t} - A_{k,t} R_{n,k,t} \Delta t \quad \text{if} \quad \log_{10} \Omega_k < -\varepsilon$$

- $A_{S,k}$: specific surface area; $M_{M,k}$: molar mass; $n_{k,t}$: amount (mol) of $k$-th phase

- $A_{k,t} = A_{S,k} M_{M,k} n_{k,t}$
- Reactive surface area

- $\Omega_k = \sum_j \hat{\chi}_j = \sum_j \exp \left( \hat{\eta}_j - \frac{g_j^o}{RT} - \ln \lambda_j - \Xi_k \right)$
- Stability index of $k$-th phase

- $R_{n,k,t} = f(\text{stability index, activities})$

- Dual chemical potential $\hat{\eta}_j = \sum_i a_{ij} \hat{\phi}_i^{(b)}$
- $\hat{\phi}_i^{(b)}$ conversion term

- TKinMet library of rate models
- GEMS SELECTOR
- AMR
- GEM
- $T_{\text{KinMet}}$ library of rate models
No single algorithm is best for all chemical systems.

Linear or quadratic convergence rates are critical for RT modeling.

Better mass-balance precision is essential.

Robustness, stability and speed are critical for RT modeling.

Feasible warm-start initial guess (fast, but may fail).

Cold-start initial guess (slow, but always works).

If a chosen GEM algorithm fails, equilibrium can still be solved by switching to xLMA or another GEM method.

Using the same activity models and TD data by all algorithms is essential!