Geochemical Modeling and Its Applications to Groundwater Resources and Quality

A NGWA Webinar
January 18, 2017

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Bloomington, Indiana, USA
Introduce myself: Chen Zhu, Professor at Indiana University

- Ph.D., Johns Hopkins, Geochemistry & hydrogeology
- M.Sc., University of Toronto, geochemistry
- B. Eng, Chengdu College of Geology, China
- Post-doctoral fellowship, Woods Hole Oceanographic Institution

- Five years as Senior Geochemist, GeoTrans, Inc. (part of now Tetra Tech)
Book by Cambridge University Press
May, 2002

sold over 200 copies
Adopted as textbook in USA, Canada, Poland, South Africa etc
Chemical processes in the hydrologic cycle

- upper atmosphere
- cosmogenic induced $^3\text{H}$ and $^{14}\text{C}$
- atmospheric $\text{O}_2$, $\text{N}_2$, $\text{He}$, $\text{Ne}$, $\text{Ar}$, $\text{Kr}$, $\text{Xe}$
- sea spray
- industrial waste, sewage, pesticides, fertilizers
- bomb $^3\text{H}$ and $^{14}\text{C}$
- pollution $^1\text{H}$, $^{16}\text{O}$
- well $^{18}\text{O}$
- spring
- water table
- ocean
- freshwater
- salt water
- interface
- soil $\text{CO}_2$
- dissolved ions
- interaction with rocks
- temperature increase
- decay of $^3\text{H}$ and $^{14}\text{C}$ (aging)
- accumulation of radiogenic $^4\text{He}$ and $^{40}\text{Ar}$ (aging)

After Mazor (1991)
Why to use geochemical models?

❖ Predicting the future
❖ Complicated processes, coupling of processes, feedback of different processes

Water Quantity: To use chemical and isotope tracers to quantify fluxes across reservoirs in the hydrologic cycle;
Water Quality: To determine the concentrations and speciation of chemicals in water. Sources and fate of contaminants;
Figure 6.2. Plan view of the mine site and tailings impoundment.
Figure 6.3. Cross-section A—A’ from Figure 6.2. Water level was recorded on January 5, 1995.
The role of geochemical modeling

Overall

⇒ Prediction of chemical concentrations and speciation in space and time
⇒ Time coordinate
⇒ Spatial coordinate
Types of geochemical models

- Speciation-solubility models
- Surface adsorption models
- Reaction-path models
- Inverse mass balance models
- Coupled reactive transport models
Figure 2.3. Different levels of complexity of geochemical models. After Raffensperger (1996).
Types of Geochemical Models

1. Speciation-solubility model
   - What are the concentrations and activities of ionic and molecular species in an aqueous solution?
   - What are the saturation states with respect to various minerals in the system, and hence the directions of reactions that might occur toward achieving equilibrium?
   - What is the stable species distribution on surfaces or ion-exchangers that is at equilibrium with the aqueous solution?

Closed, static, batch, or beaker type system or a snap shot in a dynamic system

Read Anderson & Crerar (1993) and Bethke (1996) for equilibrium constants and free energy minimization approaches.
Figure 3.1. Molalities of $\text{H}_2\text{CO}_3$, bicarbonate, and carbonate ions as a function of pH, for a total concentration of $10^{-5}$ m.
Types of Geochemical Models (continued)

2. Reaction Path Models
   - A sequence of equilibrium states involving incremental or step-wise mass transfer between phases
   - Incremental addition or subtraction of a reactant
   - Increase or decrease of $T$, $P$.

Simulate processes versus speciation-solubility only calculations that simulate equilibrium states

Chemical equilibrium and kinetics + mass balance principles

Read Helgeson (1968), Helgeson et al. (1969)
Types of Geochemical Models (continued)

❖ Reaction Path Models

◆ Titration model

• after each aliquot of the reactant, the aqueous solution is re-equilibrated by precipitating or dissolving a solid or gas phase or phases.

• The reactant can be a mineral, a chemical reagent, a glass, a gas, another aqueous solution, a `rock", or anything for which the chemical stoichiometry can be defined.

• Evaporation is considered as a negative titration of water.
Figure 2.4. Schematic representation of a mixing or titration model.
Types of Geochemical Models (continued)

❖ 3. Inverse Mass Balance Models

❖ Initial water + reactants → final water + products

❖ Based on principles of mass balance only;
❖ Thermodynamics and equilibrium not considered
Figure 2.6. Schematic representation of the inverse mass balance model.

Mass Transfer Reactions

2K-feldspar + CO₂ + 2H₂O + H⁺ →

kaolinite + 2K⁺ + 4SiO₂ + HCO₃⁻
4. Coupled Mass Transport Models

- Partial differential equations describing physical transport processes
- Algebraic equations describing chemical equilibrium and kinetics
- Heat conduction
- Fluid flow
Figure 2.7. Schematic diagram of a one-dimensional reactive transport model.
State of geochemical modeling

- Geochemical modeling useful
- Grossly under used
- Limitations mostly from kinetics and surface adsorption
- Model is useful in integrating data, quantifying processes
The “rule of three” for geochemical modeling

- A computer code
- A thermodynamic, kinetic, and surface property database
- Chemical and physical measurements of the system of concern
PHREEQC

- U.S. Geological Survey, public domain
- C Language
- Three versions
  - phreeqc-interactive, will be used in class
  - Batch win32
    - Windows by Vincent Post
- Manual in PDF format
- Databases
- Example input files (18)
MINTEQA2
http://www2.lwr.kth.se/English/OurSoftware/vminteq/

❖ U.S. Environmental Protection Agency (EPA), public domain
❖ Fortran Language
❖ Three versions
  ◆ MS-DOS version by EPA, free
  ◆ Visual MINTEQ by the Swedish, free, will be used in class
  ◆ MINTEQA2 for Windows by Allison, at cost
❖ Manual in PDF format
❖ Visual MINTEQ has guides in html format
Part 2: database

- LLNL.dat: Jim Johnson, EQ3/6
- Minteq.dat: Minteq
- MINteqv.4.dat: ver. 4.02 of MINTEQA2
- Waterq4f.dat: From Ball and Nordstrom (1990)
- Pitzer.dat: with Pitzer equation
Internal consistency of thermodynamic data
(Nordstrom and Munoz, 1986)

- Data are consistent with thermodynamic relationship (the basic laws and their consequences)
- Common scales are used for T, energy, atomic mass, and fundamental physical constants
- Conflicts among measurements have been resolved
- The mathematical model is used to fit different data sets
- The same chemical model is used to fit different data sets
- Appropriate consideration has been given to starting point in applying item 1
- Appropriate choice of standard states has been made, and the same standard states have been used for all similar substance
5.9.3 Who Produced the Model?

The common perception among environmental practitioners, that a modeling program produces a model, is not correct. *It is always the modeler, not the computer code, that produces a model.* In environmental practice, this misconception, and sometimes misrepresentation, borders on deception of the public, regulators, or clients because most popular modeling codes are distributed by regulatory or federal agencies and therefore carry an air of authority.
in fact we make a distinction between computer programs and models. A model is produced by a human being aided by computer programs. He or she must choose what data to use, what computer program options are appropriate, and must select the results which seem reasonable, and reject those which do not.
Code ≠ Model
database (maybe) = model(s)

- Code = appliance (David Sherman)
  - Oven: bake fish, beef, or sweet potato
- Input file is your model design
- “Databases” imply models
  - Activity coefficient models (ion association vs ion interactions, Davis vs. B-dot)
  - Aqueous speciation (Tagoriv and Schott (2001) for Al or Shock et al. (1989) or Pokrovskii and Helgeson (1995)
1. Speciation – solubility modeling

- Solving a set of mass balance and mass action equations
- Need an activity coefficient model
- A number of computer codes available: Eq3/6, PHREEQC, MINTEQ family, Geochemist’s Workbench©, etc

- Snap shot of the state of the chemical system at a point in time
- Building blocks for more advanced process modeling
Speciation and Solubility Modeling

Water chemical analysis

Saturation Indices

Speciation calculation

Species distribution

Thermodynamic database
Speciation-solubility model

- What are the concentrations and activities of ionic and molecular species in an aqueous solution?
- What are the saturation states with respect to various minerals in the system, and hence the directions of reactions that might occur toward achieving equilibrium?
- Closed, static, batch, or beaker type system
What is a speciation calculation?

❖ **Input:**
  - pH
  - pe
  - Elemental Concentrations

❖ **Equations:**
  - Mass-balance—total calcium= sum of the calcium species
  - Mass-action—activities of products divided by reactants = equilibrium constant
  - Newton-Raphson Iteration
  - Activity coefficients—function of ionic strength and ion properties

❖ **Output**
  - Molalities, activities of all aqueous species
  - Saturation indices
Figure 6.2. Plan view of the mine site and tailings impoundment.
Figure 6.3. Cross-section A—A’ from Figure 6.2. Water level was recorded on January 5, 1995.
Figure 6.4. Changes of species distribution in groundwater samples from Cross-section A—A’ of Figure 6.3.
Figure 6.5. Saturation Indices for carbonate minerals from MINTEQA2.
Figure 6.6. Saturation Indices for sulfate minerals from MINTEQA2.
Modeling Surface Adsorption

- Adsorption onto mineral surfaces generally is the process controlling the concentration of most metal contaminants
  - Concentrations of contaminants (e.g., Pb, As) are at the ppm to ppb level (not controlled by solubility)
  - The subsurface has large surface areas
- Fe and Mn oxyhydroxides commonly play a major role even when constituting a minor fraction of the bulk rocks, soils, or sediments
- Tied to the redox cycle

Zhu and Anderson, 2002
Significance of surface adsorption in environmental studies

- Low concentrations of pollutants
- Large surface areas in porous media
- Trace elements or contaminants not controlled by mineral solubility, but by surface adsorption
- Dissolution and precipitation reactions are thought to be controlled by surface reactions
Surface complexation models

- Adsorption onto hydrous ferric oxides (HFO)

\[ \equiv Fe^{w}OH^{o} + Pb^{2+} = \equiv Fe^{w}OPb^{+} + H^{+} \]

\[
K = \frac{[\equiv FeOPb^{+}]a_{H^{+}}}{[\equiv FeOH^{o}]a_{pb^{2+}}} e^{(\Delta ZF\Psi/RT)}
\]

- Law of mass action, $\Delta_r G$ activity, log $K$
- Analogous to aqueous complex formation
- Electrostatic correction term later
Equilibrium phase modeling

GAS_PHASES
EQUILIBRIUM_PHASES
Ion EXCHANGE
SURFACE
SOLID_SOLUTIONS

Aqueous Solution
Types of Geochemical Models (continued)

- **Reaction Path Models**
  - A sequence of states involving incremental or step-wise mass transfer between phases
  - Incremental addition or subtraction of a reactant
  - Increase or decrease of T, P.

- **Simulate processes versus speciation-solubility calculations that simulate equilibrium states**

- **Chemical equilibrium and kinetics + mass balance principles**

- **Read Helgeson (1968), Helgeson et al. (1969)**
Fig. 2.4. Schematic representation of a mixing or titration model.
• Simulate limestone treatment of AMD
• Simulate reactions, albeit without flow, when AMD encounter calcite in soils and aquifers
Figure 8.4. Results of titration of calcite into TS-3 water.
Titration of calcite to pore water + Fe(OH)3 with adsorbed acidity

Zhu et al., 2002, *Ground Water*
Chap. 11 Kinetics Modeling – put reaction on a time scale
Experiment of feldspar hydrolysis
Dual furnace rocker autoclave for gas/water/rock interaction experiments

In situ sampling solution

Fu et al., Chem. Geology (accepted)
Time-series solution chemistry for major and trace elements (200 °C, 300 bars)
Modeling kinetics with PHREEQC

❖ PHREEQC Keywords

❖ Kinetics
  • Keyword call for kinetic calculation
  • Pass parameters to RATES

❖ Rates
  • The Basic function
  • Completely programmable
CO$_2$-alkali feldspar-brine experiments at 200 °C 300 bars, 50 mM CO$_2$, 0.2M KCl

$k*_{\text{clay}}/k*_{\text{feldspar}} \ll 1$
General Rate Law (Lasaga, 1981)

\[ R_j = k_j S_j a_{H^+}^{nH^+} g(I) \prod_a a_i^{n_i} f(\Delta G_r) \]

- \( R_j \) is the rate of dissolution of the \( j \)th mineral (mol m\(^{-2} \) s\(^{-1} \))
- \( k_j \) the respective rate constant
- \( S_j \) the reactive surface area
- \( a_{H^+} \) -- activity of hydrogen in the aqueous solution
- \( g(I) \) accounts for possible ionic strength dependence of the rates
- catalytic and inhibitory effects of all aqueous species e.g., Al
- \( \Delta G_r \) stands for the Gibbs free energy of the reaction
- \( f(\Delta G_r) \) accounts for the variation of the rate with the deviation from equilibrium
$f(\Delta G_r)$ - the thermodynamic drive

Far from eqbm

Albite dissolution at 300 °C, pH 9

Congruent stage

$r_i = k_1S_1(1 - e^{\Delta G_r/RT})$

➢ Transition State Theory
➢ Linear
➢ Simple

$\Delta G = -RT \ln \left( \frac{N_2}{N_1} \right)$

$r = k' \left( 1 - e^{-\frac{\Delta G_1}{RT}} \right)^{n+1} + k'' \left( 1 - e^{-\frac{\Delta G_2}{RT}} \right)^{m+1}$

Equilibrium
Albite dissolution – sanidine precipitation, 300 °C, pH 9, Alekseyev et al. (1997)

\[ NaAlSi_3O_8 (\text{albite}) \rightarrow Al^{3+} + H^+ + k \]

\[ \rightarrow Al^{3+} + Na^+ + 3SiO_2 + 2H_2O \]

\[ \rightarrow KAlSi_3O_8 (\text{sanidine}) + 4H^+ \]

◆ a quasi-steady state is reached
◆ \( k^*_\text{Ab}/k^*_\text{San} \approx 10 \)

\( k^* = k \times S_A \)
Albite dissolution and sanidined precipitation (Alek97
Far from eqbm

Zhu et al., GCA, 2010
Albite dissolution – sanidine precipitation, 300 °C, Alekseyev et al. (1997)
Reactive Transport Computational Approach

FLOW
(TOUGH2)

TRANSPORT

Sequential Iterative (SIA)

Sequential Non-Iterative (SNIA)

CHEMISTRY
Multicomponent Chemical System

- Multicomponent Reactions (water must be present)
  - Aqueous Species
  - Minerals
  - Gases
  - Exchange Species
  - Surface Complexes (v2.0 beta)

- Aqueous Speciation: equilibrium (v2.0 beta with kinetics)

- Surface Complexation/Exchange: equilibrium

- Mass Transfer:
  - Minerals: equilibrium or kinetic constraints
  - Gases: equilibrium

- External Thermodynamic Database: reaction stoichiometries, equilibrium constants, activity coefficient data, etc.
Figure 2.1. Schematic representation of different processes.
Tailings Fluids

- pH 1.5 ~ 3.5
- Contaminants: As, Be, Cd, Cr, Pb, Mo, Ni, Se, $^{226}$Ra, $^{228}$Ra, $^{230}$Th, U
- Fe 2,000 mg/L, Al ~1,000 mg/L, $\text{SO}_4^{2-}$ ~20,000 mg/L
Model to Evaluate Remediation Alternatives

❖ “Cover and attenuate” reclamation plan
❖ Approval from NRC
❖ Will it work?

❖ Concentration distribution in time and space
❖ 1D coupled reactive transport model, with PHREEQC
Discretization of the simulated domain
Flow and transport model parameters

- Uniform Darcy velocity 15 m/yr
- Porosity 30%
- Dispersivity 10 m
- Cauchy flux boundary
  - first 5 years infiltration of tailings fluid
  - another 200 years flushing by uncontaminated upgradient water
Reaction Model

- **11 Components:** H, Ca, Mg, Cl, C, Al, S, Fe, Na, K, and Si
- **6 Minerals:** Al(OH)$_3$(a), Fe(OH)$_3$(a), calcite, gypsum, SiO$_2$(a), and illite
- **Surface adsorption:** Dzombak and Morel’s double diffuse layer model
- **Successive pH buffer reactions with calcite, Al(OH)$_3$(a), and Fe(OH)$_3$(a)**
Initial and Boundary Conditions

- 1994 pore fluid measurements
- Bulk mineral analysis and postulations
- Third-type or Cauchy boundary condition at both ends
- Five years infiltration and 200 years flushing by clean groundwater
The graphs depict the change in $K_d$ (ml/g) and pH with distance (m) over different time periods:

- **Top Graph**: $K_d$ values for a 100-year period, showing a steep increase followed by a decrease.
- **Middle Graph**: pH values for 100 and 200 years, indicating a gradual decrease followed by stabilization.
- **Bottom Graph**: pH values at 0 year, illustrating a sharp increase and subsequent stabilization.

These graphs suggest that both $K_d$ and pH are significantly influenced by distance and time, with distinct trends for each period.
Summary and Conclusions

- Simulated reactive mass transport of the natural attenuation of an acid groundwater plume at a uranium mill tailings site under a reclamation scenario.
- In different time-space domains, the transport of reactive constituents is dominated alternatively by chemical reactions or physical processes.
- Geochemical evolution of the contaminated aquifer produces multiple concentration waves.
Geochemical Modeling and Its Applications to Groundwater Resources and Quality

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Geochemical modeling was transformed from expert only exercise to nearly everyone’s tool
Example calculations

❖ Carbon sequestration

❖ Acid mine drainage

❖ Naturally occurring radioactive materials (NORM)