INTRODUCTION TO GEOCHEMICAL AND REACTIVE TRANSPORT MODELING

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Principal types of geochemical modeling:

1. Speciation (for exemple, for lead);

2. Inverse geochemical modeling;

3. Direct geochemical modeling;

4. Reactive transport modeling (for example, with oxidation of pyrite, organic matter decay etc.);

A standard program, which includes all types of modeling indicated above, is PHREEQC-2 (Parkhurst and Appelo, 1999; available from U.S. Geological Survey), but includes only transport in 1-D; there are programs like PHT3D and PHAST, which couple PHREEQC-2 and a program of transport in 3-D (generally MT3D);

ad (1) can be performed with only one sample of water, program divides total concentrations between free ions and complexes, for example, lead can present as:

$Pb_{total} = Pb^{2+} + PbSO_4^0 + PbHCO_3^+ + PbCO_3^0$ etc.

and calculates saturation indices SI for different minerals, for example SI_{gypsum} for mineral gypsum

$SI_{gypsum} = [Ca^{2+}]\,[SO_4^{2-}]/K_{sp}$ where K_{sp} is solubility product for specified temperature and [ ] are activities

SI = 0 equilibrium

SI < 0 undersaturation, a mineral can dissolve

SI > 0 supersaturation, a mineral can precipite

problems: kinetic factors are not considered, there can be precipitation of solid solutions instead of pure mineral phases, in most cases data for formation of organic complexes are not available;

Exemple: speciation of arsenic-input

```
DATABASE C:\PROGRAM FILES\USGS\PHREEQC INTERACTIVE 2.8\phreeqc.dat
SOLUTION 1-1
    temp      11.1
    pH        6.87
    pe        1.39
    redox     pe
    units     mg/kgw
    Alkalinity  138.1 as HCO3
    Cl        5.37
    S         169.54 as SO4
    P         0.026 as HPO4
    Na        16.3
    K         5.13
    Mg        24.44
    Ca        50.46
    Fe        9.27
    Mn        0.445
    Al        1.32
    Si        15
    As        0.091
    Zn        0.083
    N(5)      0.9 as NO3
    N(-3)     0.46  as NH4
```

Exemple: continuation

```
SOLUTION_MASTER_SPECIES
As                H3AsO4  -1.0    74.9216         74.9216
    As(+3)        H3AsO3   0.0    74.9216
    As(+5)        H3AsO4  -1.0    74.9216
SOLUTION_SPECIES 1 # Do not change this number it is used by the program!
    H3AsO4 = H3AsO4
        log_k       0
        delta_h     0           kcal
    H3AsO4 + 2e- + 2H+ = H3AsO3 + H2O
        log_k       19.444
        delta_h     -30.015     kcal
    ..
    ..
    ..
    ..
PHASES
    Scorodite
    FeAsO4:2H2O = Fe+3 + AsO4-3 + 2H2O
        log_k       -20.249
    Arsenolite
    As4O6 + 6H2O = 4H3AsO3
        log_k       -2.801
        delta_h 14.330 kcal
    ..
```

Exemple-output:

	Species	Molality	Activity	log Molality	log Activity	log Gamma
Al		4.892e-05				
	Al(OH)4-	3.688e-05	3.352e-05	-4.433	-4.475	-0.042
	Al(OH)2+	8.492e-06	7.717e-06	-5.071	-5.113	-0.042
	Al(OH)3	2.729e-06	2.734e-06	-5.564	-5.563	0.001
As(3)		8.084e-08				
	H3AsO3	8.062e-08	8.078e-08	-7.094	-7.093	0.001
	H2AsO3-	2.268e-10	2.061e-10	-9.644	-9.686	-0.042
	H4AsO3+	5.941e-15	5.399e-15	-14.226	-14.268	-0.042
	HAsO3-2	9.430e-16	6.432e-16	-15.025	-15.192	-0.166
	AsO3-3	2.638e-22	1.116e-22	-21.579	-21.953	-0.374
As(5)		1.134e-06				
	HAsO4-2	7.007e-07	4.780e-07	-6.154	-6.321	-0.166
	H2AsO4-	4.330e-07	3.935e-07	-6.363	-6.405	-0.042
	AsO4-3	1.484e-11	6.273e-12	-10.829	-11.203	-0.374

etc.

Exemple-output (continuation):

Phase	SI	log IAP	log KT	
Al(OH)3(a)	1.09	12.84	11.75	Al(OH)3
Albite	0.46	-18.47	-18.93	NaAlSi3O8
Alunite	7.63	8.03	0.40	KAl3(SO4)2(OH)6
Anhydrite	-1.77	-6.10	-4.33	CaSO4
Anorthite	0.86	-19.27	-20.13	CaAl2Si2O8
Aragonite	-1.19	-9.45	-8.26	CaCO3
Arsenolite	-25.06	-28.37	-3.31	As4O6
As2S3(am)	-108.19	-155.18	-46.99	As2S3
Calcite	-1.04	-9.45	-8.41	CaCO3

etc.

ad (2) inverse geochemical modeling is used for interpretation of processes, which have already happened, we enter chemistry of water at 2 hydraulically connected points and composition of solid phase between these points; program produces reactions, which may explain changes of water chemistry:

Water 1 + reactants = Water 2 + products

Problems: stoichiometry of minerals in solid phase is not often well known, solution may be non-unique and program produces several possible models;

Exemple: data from PRB, Milovice, Czech Republic

```
DATABASE C:\PROGRAM FILES\USGS\PHREEQC INTERACTIVE 2.8\phreeqc.dat
TITLE PRB-inverse modeling 0-21 cm
SOLUTION 1 Entry
units mg/kgw
temp  13.2
pH 7.33
pe 5.427
Alkalinity  402.6 as HCO3
Ca  169
Na  18.4
Cl 55
Fe   1.2
N(5)  12
density 1
SOLUTION 2 Outflow
units mg/kgw
temp  12.4
pH 7.56
pe -2.797
Alkalinity 317.2 as HCO3
Ca  131
Na  18.2
Cl  53
Fe   42
N(5)  0.1
density 1
```

Exemple (continuation):

```
INVERSE_MODELING
-solutions 1 2
-uncertainty 0.149
-range
-balances
  pH   0.1
  Na
  Cl
-phases
calcite precip
siderite precip
Fe dissolv
N2(g)    precip
  H2(g)    precip
Fe6(OH)12CO3  precip
PHASES
Fe
Fe + 2.0H2O = 1.0Fe++ + 2.0OH- + H2
-log_k 0
Fe6(OH)12CO3
Fe6(OH)12CO3 + 12.0H+ = 4.0Fe++ + 2.0Fe+++ + 1.0CO3-2 + 12.0H2O
log_k -376
END
```

Exemple-output (transfer coeffcients in mmol/L):

Phase	mole transfers:	Minimum	Maximum
Calcite	-1.829e-03	-2.009e-03	-1.449e-03
Fe	1.916e-03	1.640e-03	2.205e-03
N2(g)	-4.248e-04	-4.892e-04	-3.604e-04
Fe6(OH)12CO3	-2.163e-04	-2.629e-04	-1.572e-04

Redox mole transfers:

Fe(3)	-4.150e-04
H(0)	3.833e-03
N(0)	-8.496e-04

ad (3) this type of modeling is used for prediction of water chemistry, we enter initial water composition and reactive phases (minerals, gases etc.), then program calculates predicted water chemistry:

Water 1 + reactants = Predicted water 2 + products

Problems: as in case (1), kinetic data are often missing and also adsorption data are frequently limited;

this modeling can be performed in batch mode or in column mode, but modeling in column mode already belongs to group (4), e.g., to the modeling of reactive transport;

Exemple-neutralization of AMD by calcite: input

```
SOLUTION 1-1
        temp      11.1
        pH        2.4
        pe        10.2
        redox     pe
        units     mmol/kgw
        S(6)      14.95
        Na        0.2
        Mg        1.1
        Fe        6.3
        Al        1.32
EQUILIBRIUM_PHASES
Calcite  0   10
Gypsum  0   0
Fe(OH)3(a) 0   0
Siderite 0    0
END
```

Output:

Phase	SI	log	Moles in assemblage Initial	Final	Delta
Calcite	0.00		1.000e+01	9.986e+00	-1.443e-02
Fe(OH)3(a)	0.00		0.000e+00	9.554e-05	9.554e-05
Gypsum	-0.02		0.000e+00	0.000e+00	
Siderite	0.00		0.000e+00	6.139e-03	6.139e-03

pH = 6.709
pe = 2.828

Elements	Molality
Al	1.320e-03
C	8.293e-03
Ca	1.443e-02
Fe	6.517e-05
Mg	1.100e-03
Na	2.000e-04
S	1.495e-02

ad (4) in this case geochemical module is connected to transport module; so called split operator approach is used: advection-dispersion equation (ADE) is solved first and then geochemical step calculation is performed,

there are special reactive transport programs (TOUGH AMD, SULFIDOX etc.) which may include, for example, oxidation of pyrite or decay of organic matter;

A necessary condition: flow parameters (flow direction, velocity) has to be determined before reactive transport modeling!

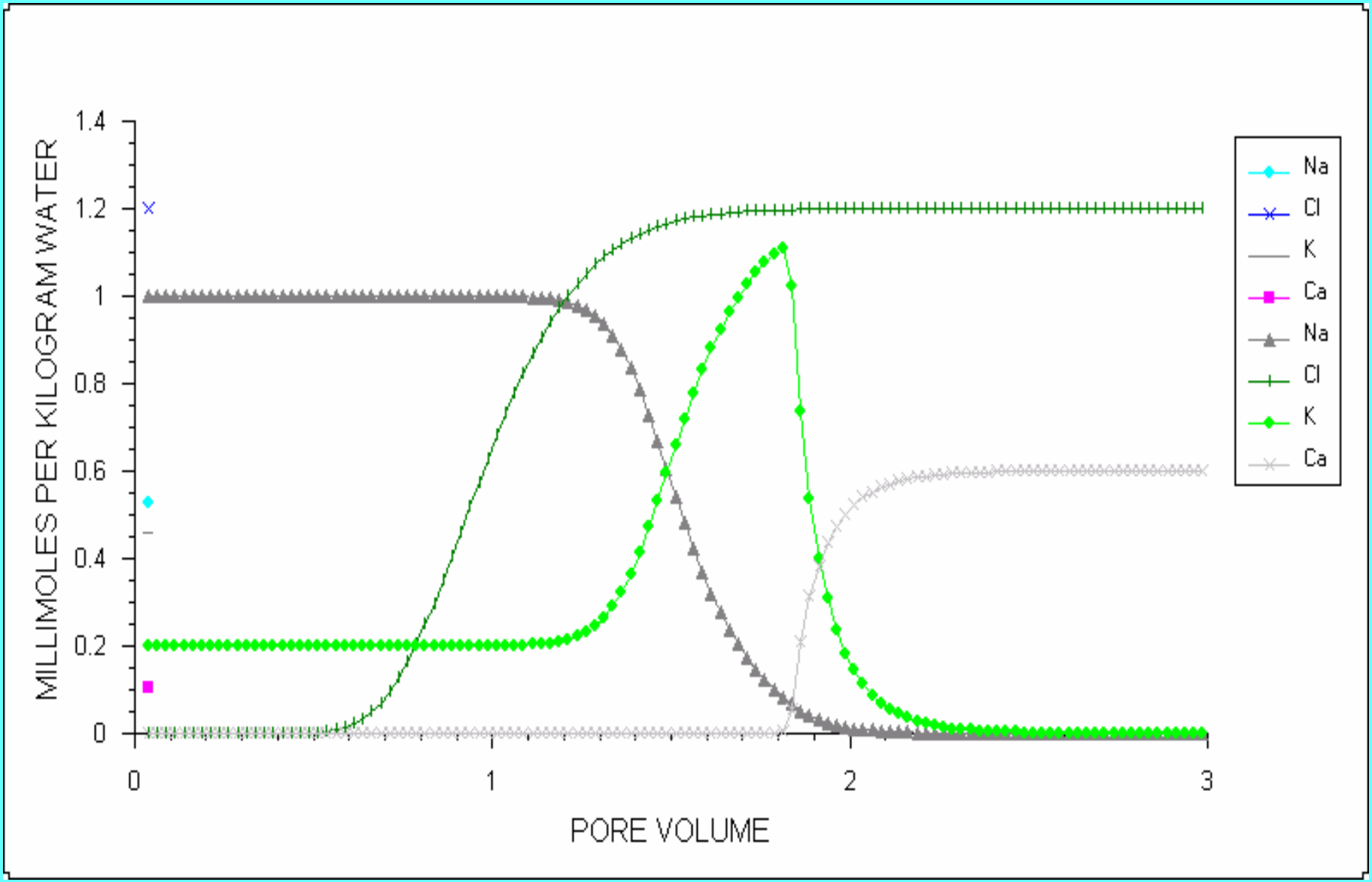
Exemple-cation exchange in a column, input:

```
TITLE Transport and ion exchange.
SOLUTION 0  CaCl2
        units           mmol/kgw
        temp            25.0
        pH              7.0     charge
        pe              12.5    O2(g)   -0.68
        Ca              0.6
        Cl              1.2
SOLUTION 1-40  Initial solution for column
        units           mmol/kgw
        temp            25.0
        pH              7.0     charge
        pe              12.5    O2(g)   -0.68
        Na              1.0
        K               0.2
        N(5)            1.2
EXCHANGE 1-40
        equilibrate 1
        X               0.0011
PRINT
        -reset          false
SELECTED_OUTPUT
        -file           ex11adv.sel
        -totals         Na Cl K Ca
```

Exemple-input (continuation):

```
TRANSPORT
        -cells          40
        -length          0.002
        -shifts         120
        -time_step       720.0
        -flow_direction  forward
        -boundary_cond   flux    flux
        -diffc          0.0e-9
        -dispersivity    0.002
        -correct_disp    true
        -punch           40
        -punch_frequency 1
        -print          40
        -print_frequency 20
END
```

Exemple-output for the end of column (1 pore volume, PV)



CONCLUSIONS

- Speciation modeling is used for calculation of free ions, complexes, and saturation indices values, it requires good thermodynamic database;

- inverse geochemical modeling is used for interpretation of water chemistry changes between hydraulically connected points, data on solid phase composition are necessary;

- direct geochemical modeling is used for prediction of water chemistry after pre-determined reactions, can be performed in batch or in column (this is already reactive transport modeling);