Simulation of Radionuclide Transport in Fractured Porous Media

Seminar presentation

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Outline





Cladding tube Spent nuclear fuel Bentonite clay Surface facility Surface facilit

Introduction

(SKB, 2006)

- High-level radioactive waste (HLW) contains highly radioactive materials with long half-lives and high toxicity, necessitating special disposal methods to ensure safety for current and future generations.
- Deep geological disposal with engineering barrier is generally adopted worldwide for final disposal of HLW management.
- In order to estimate the safety of the disposal system, we need to simulate the radionuclide transport in fractured porous media (host rock).
 - Advection, Dispersion, matrix diffusion
 - Chemical reaction (decay, sorption, ...)



Introduction

- Radioactive decay is when unstable atoms lose energy by emitting radiation until they become stable.
- Sorption is the process of adsorption or absorption of species onto the surface of solids or liquids, which can be quantified by a sorption distribution coefficient (Kd) for linear sorption.
- Also, chemical reactions will affect the concentration and distribution of substances.
- To understand these processes, laboratory experiments have been applied to determine relevant parameters. Then, we can use some chemical reaction software to help us to simulate chemical reaction, e.g. PHREEQC.

$$\frac{\partial(\theta C)}{\partial t} = -\lambda\theta C$$

$$\frac{\partial(\theta C)}{\partial t} = -\rho_b \mathbf{K}_d \frac{\partial C}{\partial t}$$

$$\frac{\partial(\theta C)}{\partial t} = \mathbf{R}_i$$

Chemical reaction

- Chemical reaction simulations are based on the conservation of mass, energy, and charge, and the laws of thermodynamics.
- Thermodynamic reactions

$$a\mathrm{A} + b\mathrm{B} \leftrightarrow c\mathrm{C} + d\mathrm{D}$$
 $K_\mathrm{c} = rac{[C]^c [D]^d}{[A]^a [B]^b}$ Equilibrium constant

Kinetic reactions

A+B
$$\rightarrow$$
C $\frac{d[C]}{dt} = k(T)[A]^m [B]^n$ Reaction rate constant

 A thermodynamic database is a collection of data providing information on the thermodynamic properties of chemical species and reactions (eg. ΔG, K), used to model and predict the behavior of substances under various conditions.



A partial screenshot of the "Pitzer.dat" thermodynamic data

```
1 # Pitzer.DAT for calculating pressure dependence of reactions
2 # and temperature dependence to 200 °C. With
3 # molal volumina of aqueous species and of minerals, and
   # critical temperatures and pressures of gases used in Peng-Robinson's EOS.
4
    # Details are given at the end of this file.
 6
   SOLUTION MASTER SPECIES
   Alkalinity CO3-2
                     1 Ca0.5(CO3)0.5 50.05
 7
8
    В
           B(OH)3 0 B
                             10.81
9
    Ba
           Ba+2
                   0 Ba
                             137.33
10
    Br
           Br- 0 Br
                          79.904
11
                   2 HCO3
                                 12.0111
   С
           CO3-2
12 C(4)
               CO3-2
                       2 HCO3
                                     12.0111
13
           Ca+2
                   0 Ca
                             40.08
   Ca
14 Cl
           Cl- 0 Cl
                          35.453
15
   Е
           e- 0 0.0
                          0.0
16 Fe
           Fe+2
                   0 Fe
                             55.847
17 H
           H+ -1 H
                          1.008
               H+ -1 0.0
18 H(1)
19 K
           K+ 0 K
                          39.0983
20
   Li
           Li+ 0 Li
                          6.941
21 Mg
           Mg+2
                   0 Mg
                             24.305
22 Mn
                   0 Mn
                             54.938
           Mn+2
23 Na
           Na+ 0 Na
                          22.9898
24
   0
           H2O 0 O
                          16.00
25
   0(-2)
               H2O 0 0.0
26 S
           SO4-2 0 SO4
                             32.064
27
   S(6)
               SO4-2
                       0 SO4
28
   Si
           H4SiO4 0 SiO2
                                 28.0843
29
   Sr
           Sr+2
                   0 Sr
                             87.62
   # redox-uncoupled gases
31 Hdg
                          2.016 # H2 gas
           Hdg 0 Hdg
32
                          32 # Oxygen gas
    Oxg
           Oxg 0 Oxg
                             16.032 # CH4 gas
33 Mtg
           Mtg 0.0 Mtg
                                                                                 Manual addition is OK.
           H2Sg
34
   Sg
                 1.0
                        H2Sg
                                     34.08 # H2S gas
35 Ntg
           Ntg 0 Ntg
                          28.0134 # N2 gas
36
37 SOLUTION SPECIES
38 H+ = H+
39
       -dw 9.31e-9 1000 0.46 1e-10 # The dw parameters are defined in ref. 4.
40 # Dw(TK) = 9.31e-9 * exp(1000 / TK - 1000 / 298.15) * TK * 0.89 / (298.15 * viscos)
41 # Dw(I) = Dw(TK) * exp(-0.46 * DH A * |z H+| * I^0.5 / (1 + DH B * I^0.5 * 1e-10 / (1 + I^0.75)))
42 e- = e-
43 H2O = H2O
44 Li+ = Li+
       -dw 1.03e-9 80
45
46
      -Vm -0.419 -0.069 13.16 -2.78 0.416 0 0.296 -12.4 -2.74e-3 1.26 # ref. 2 and Ellis, 1968, J. Chem. Soc. A, 1138
```

The influence of the different thermodynamic database

- PHREEQC (Parkhurst et al., 2013)
 - PHREEQC is a widely-used computer program for simulating chemical reactions in aqueous systems.
- Here are the results of ion strength for groundwater and seawater, using different databases.







A partial screenshot of the "Pitzer.dat" thermodynamic data

	1	<pre># Pitzer.DAT for calculating pressure dependence of reactions</pre>									
	2	# and temperature dependence to 200 °C. With									
	3	# molal volumina of aqueous species and of minerals, and									
	4	# critical temperatures and pressures of gases used in Peng-Robinson's EOS.									
	5	# Details are given at the end of this file.									
	6	SOLUTION MASTER SPECIES									
	7	Alkalinity CO3-2 1 Ca0.5(CO3)0.5 50.05									
	8	B B(OH) 3 0 B 10.81									
	9	Ba Ba+2 0 Ba 137.33	Λ11 +1								
	10	Br Br- 0 Br 79.904									
	11	C CO3-2 2 HCO3 12.0111									
	12	C(4) CO3-2 2 HCO3 12.0111	prop								
	13	Ca Ca+2 0 Ca 40.08									
	14	Cl Cl- 0 Cl 35.453	can o								
-											

(Lu et al., 2022)

Table 1 Comparison of thermodynamic data files discussed in this study

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Database	T-P range	Pressure correction	Corrected P range	Aqueous activity coefficient model	Fugacity coefficients	Number of species	Sources	Especially radio
phreeqc.dat	${<}200\ensuremath{^\circ\text{C}}\xspace,{<}1\ensuremath{\text{kb}}\xspace$	Appelo et al. (2014)	up to $\sim 1 \mathrm{kb}$	mixed WATEQ ¹ and Davies equation	Peng- Robinson	$\sim 310^{2}$	Appelo et al. (2014)	
amm.dat	${<}200\ ^{\circ}\text{C}\text{, }{<}1\ \text{kb}$	Appelo et al. (2014)	up to ${\sim}1kb$	mixed WATEQ and Davies equation	Peng- Robinson	$\sim 310^{2}$	Appelo et al. (2014)	
iso.dat	0.01–100 $^{\circ}\mathrm{C}$ at 1 bar	N.A.	N.A.	mixed WATEQ and Davies equation	Ideal gas law	~330	Thorstenson and Parkhurst (2002, 2004)	
wateq4f.dat	0.01–100 $^\circ\text{C}$ at 1 bar	N.A.	N.A.	mixed WATEQ and Davies equation	Ideal gas law	~770	Ball and Nordstrom (1991)	
llnl.dat	0.01–100 °C at 1 bar, 100–300 °C along P _{SAT}	SUPCRT92	N.A.	B-dot	Ideal gas law	~2590	Greg M. Anderson; EQ3/6 ³	
core10.dat	0.01–100 °C at 1 bar, 100–300 °C along P _{SAT}	Appelo et al. (2014) & P _{sat} log K in Supert92	up to $\sim 1 \text{kb}$	B-dot	Peng- Robinson	~630	Neveu et al. (2017)	
carbfix.dat	0.01–100 °C at 1 bar, 100–300 °C along P _{SAT}	Appelo et al. (2014) & P _{sat} log K in Supert92	up to $\sim 1 \text{ kb}$	B-dot	Peng- Robinson	~660	Voigt et al. (2018)	
sit.dat	15–80 °C at 1 bar	N.A.	N.A.	SIT	Ideal gas law	~2300	Amphos 21, BRGM and HydrAsa for ANDRA	
minteq.dat	0.01–100 °C at 1 bar	N.A.	N.A.	mixed WATEQ and Davies equation	Ideal gas law	~1610	Allison et al. (1991)	
minteq.v4. dat	0.01-100 °C at 1 bar	N.A.	N.A.	Mostly Davies equation	Ideal gas law	~1990	Allison et al. (1991)	
pitzer.dat	${<}200\ensuremath{^\circ C},{<}1\ensuremath{\mathrm{kb}}$	Appelo et al. (2014)	up to $\sim 1 \text{kb}$	Pitzer equation	Peng- Robinson	~120	Plummer et al. (1988)	
frezchem. dat	–73–25 °C at 1 bar	Appelo et al. (2014)	up to ~1 kb	Pitzer equation	Peng- Robinson	~70	Spencer et al. (1990), Marion and Farren (1999), and Marion (2001)	
ColdChem. dat	–73–25 °C at 1 bar	N.A.	N.A.	Pitzer equation	N.A.	~40	Toner and Catling (2017)	ed in ref. 4.
geothermal. dat	0.01–100 °C at 1 bar, 100–300 °C along P _{SAT}	SUPCRTBL	N.A.	B-dot	Ideal gas law	~ 1050	SUPPHREEQC (Zhang et al., 2020)	(298.15 * viscos) 1^0.5 * 1e-10 / (1 + 1^0.75)))
diagenesis. dat	0.01–100 °C at 1 bar, 100–200 °C along P _{SAT}	Appelo et al. (2014) & $P_{\text{sat}} \log K$ in SUPCRTBL	up to ~1 kb	WATEQ equation	Peng- Robinson	~1050	SUPPHREEQC (Zhang et al., 2020)	
bL.dat	Up to 1000 °C and 5 kb (variable <i>T</i> isobaric)	SUPCRTBL	up to 5 kb	B-dot	Ideal gas law	~1050	SUPPHREEQC (Zhang et al., 2020)	

he information on the thermodynamic erties of chemical species and reactions only be obtained from experiments.

radionuclides

-Vm -0.419 -0.069 13.16 -2.78 0.416 0 0.296 -12.4 -2.74e-3 1.26 # ref. 2 and Ellis, 1968, J. Chem. Soc. A, 1138

Sorption of U and Tc in bentonite

- Experimental data and modeling was developed to confirm the multi-site surface complexation/ion exchange of MX 80 bentonite. (Grambow et al, 2006)
- We use PHREEQC with the NEA-TDB (OECD Nuclear Energy Agency Thermochemical Database) and thermodynamic data in this paper to replicate the research findings.



Surface species		$\log K$	log K B&B Na	log K B&B Ca			
$S-OH+H^+ = S-OH^{2+}$		4.5	4.5		Table 3. Site dense	ities and quantity of dissolving n	unerals in bentonite
S-OH	$= S - O^{-} + H^{+}$	-7.9	-7.9		MX-80.	. , .	
$W1 - OH + H^+ = W1 - OH_2^+$		4.5	4.5				
W1-OH	$= W1 - O^{-} + H^{+}$	-7.9	-7.9		Site densities in m	nol/g dry bentonite	
$W2-OH+H^+$	= W2 $-$ OH ₂ ⁺	6	6			,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	
W2-OH	$= W2 - O^{-} + H^{+}$	-10.5	-10.5		10.3		2.510-6
$S1-OH+H^+$	= S1 $-$ OH ₂ ⁺	4.5			S-OH		2.3×10^{-5}
S1-OH	$=$ S1 $-$ O $^{-}$ $+$ H $^{+}$	-7.9			W2_OH		3.2×10^{-5}
$S1-OH+Cs^+$	$=$ S1 $-$ OCs $+$ H $^+$	-0.1			S1-OH		7.5×10^{-8}
S-OH+Ni ²⁺	$=$ S $-$ ONi $^+$ $+$ H $^+$	-1.2	-0.6	-0.9	X		6.96 × 10 ⁻⁴
$S-OH+Ni^{2+}+H_2O$	= Si-ONiOH + 2H ⁺	-10.2	-10	-10	Y		2.5×10^{-3}
$W1 - OH + Pb^{2+}$	$=$ W1 $-$ OPb $^+$ $+$ H $^+$	-1	-1.3				
$W1 - OH + Pb^{2+} + H_2O$	= W1-OPbO ⁻ + 3H ⁺	-18			Minerals which di	issolve/precipitate until equilibri	um
S-OH+Eu ³⁺	$=$ S $-OEu^{2+}+H^{+}$	0.4	1.6	0.8		// 1 1	
$S-OH+Eu^{3+}+H_2O$	= S-OEuOH ⁺ + 2H ⁺	-6.5	-6.4	-6.4	Calcite	Quantity max in mol/g	9×10^{-5}
$S - OH + Eu^{3+} + 3H_2O$	$=$ S $-OEu(OH)_3^- + 4H^+$	-24.5					
$W1 - OH + Eu^{3+} + 3H_2O$	$= W1 - OEu^{2+} + H^+$	-1.6	-0.5	-1.4	Phases which diss	which dissolve entirely in mol/g dry bentonite	
S-OH+Am ³⁺	$= S - OAm^{2+} + H^{+}$	1.5	1.6				
$S-OH+Am^{3+}+H_2O$	= S-OAmOH ⁺ + 2H ⁺	-7	-6.8		Pyrite		1 × 10 ⁻⁵
$S - OH + Am^{3+} + 2H_2O$	= S-OAm(OH) ₂ + 3H ⁺	-15.4	-15		Siderite		2 × 10 ⁻⁵
$S - OH + Am^{3+} + 3H_2O$	= S-OAm(OH) ₃ ⁻ + 4H ⁺	-25.5	-25.6		Magnesite		3.1×10^{-3}
S-OH+Cm ³	$= S - OCm^{2+} + H^{+}$	1.2			MgSO ₄		2.5×10^{-3}
$S-OH+Cm^3+H_2O$	$=$ S $-$ OCmOH $^{+}$ $+$ 2H $^{+}$	-7.2			CaSO ₄		2.4×10^{-3}
$S-OH+Cm^3+2H_2O$	= S $-$ OCm(OH) ₂ $+$ 3H ⁺	-15.4		Exchange species			
$S-OH+Cm^3+3H_2O$	$= S - OCm(OH)_{3}^{-} + 4H^{+}$	-25.5		Exchange species			
S-OH+Ac ³	$= S - OAc^{2+} + H^{+}$	0		$X^- + Na^+$	= NaX	0 0	
$S-OH+Ac^3+H_2O$	= S-OAcOH ⁺ + 2H ⁺	-7.2		$X^{-} + H^{+}$	= HX	0 0	
$S-OH+Ac^3+2H_2O$	$=$ S $-OAc(OH)_2 + 2U^+$	15 /		$\mathbf{X} + \mathbf{K}$	= KX	0.4 0.5 0.6	
$S-OH+Ac^3+3H_2O$	$=$ S $-OAc(OH)_3^-$ - 1	We don't n	eed to rea	to all experim	ente unlege	0.3	
$S-OH+Th^4$ = $S-OTh^{3+}+H^+$ 1. We don't meed to redo an experiments unless 0.7							
$s - OH + Th^4 + H_2O = s - OThOH^{2+} + 1$ considering specific conditions (e.g. Taiwan's 0.7)							
$S-OH+Th^4+2H_2O$ = $S-OTh(OH)_2^+$ -							
$s-OH+Th^4+3H_2O = s-OTh(OH)_3+$ groundwater and / or bedrock).							
$S-OH+Th^4+4H_2O$	= S $-$ OTh(OH) ₄ $-$ -		· · · ·	, · · · ·	11	0.3 0.6	
$S-OH+U^{4+}+3H_2O = S-OU(OH)_3+4$ 2. PH		PHREEQC	can conc	luct simulatio	ons well.	18	
$S-OH+Zr^4+3H_2O$	$=$ S $-OZr(OH)_3 + 4$	- 2.2	V./	24 1 1 11	- 111113	1.6 1.7-2.5	
$S-OH+TcO^{2+}+H_2O$	= S-OTcO(OH) + 2H ⁺	2.38					
$2S-OH+TcO^2++H_2O$	$=(S-O)_2TcO(OH)^-+3H$	H ⁺ -4.27					

(Grambow et al, 2006)



Transport in column experiment



Pore Volumes

Pore Volumes

Pore Volumes

(Shih et al., 2024)

Conclusion

- In the issue of radionuclide transport in solid host rock, we need to consider solute transport and chemical reactions in fractured porous media.
- Thermodynamic data can influence the results of chemical reaction simulations. We can obtain relevant parameters from literature or experiments, but pay attention when using such data (including thermodynamic databases).
- PHREEQC is a valuable and practical geochemical simulation program that can effectively replicate experimental results under known conditions.

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Thank you for your attention!

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