Instructions on ETLM INTERFACE for Visual MINTEQ

(ETL(MIN)$_2$) version 1.0.1

Shigeyori Kosugi and Keisuke Fukushi*

Corresponding Author: * fukushi@staff.kanazawa-u.ac.jp

April 27th, 2021

Contents

Acknowledgement

Financial support was provided to KF by a Grant-in-Aid for Scientific Research (KAKENHI) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) (no. JP17H06458 and JP21H04515) and the Japan Society for the Promotion of Science (JSPS) (no. JP15K21019). This development of ETL(MIN)$_2$ was performed under the cooperative research program of the Institute of Nature and Environmental Technology, Kanazawa University (no. 18042).

1. What is ETL(MIN)$_2$?

ETL(MIN)$_2$ (**ETLM IN**TERFACE for Visual **MIN**TEQ) is a program to support the Extended Triple Layer Model (ETLM) within the free software Visual MINTEQ 3.1 (Gustafsson, 2019). ETLM is a sub-model of the surface complexation models and was developed by D.A. Sverjensky (The Johns Hopkins University) and co-workers. ETL(MIN)$_2$ is a user-friendly program to perform ETLM for quantitative descriptions and predictions of adsorption of dissolved major and trace elements on mineral surfaces.

The Visual MINTEQ program requires the equilibrium constants of surface complexation and aqueous reactions, as well as the solution condition input file to conduct ETLM. ETL(MIN)$_2$ enables the generation of these dataset files and input files via simple operations in EXCEL spreadsheets. In addition, ETL(MIN)$_2$ contains databases required for specific ETLM calculations for numerous adsorbates over a wide range of oxides from previous studies. The current version is 1.0.1 (distributed in 2021/4/27).

2. Feature of ETL(MIN)$_2$

ETL(MIN)$_2$ enables the following via the inherent functions of Visual MINTEQ:

- Serial calculations as functions of various parameters (pH, ionic strength, solid concentration and component concentrations) using the Multi Problem function.
- Calculations in an open system under variable CO_2 partial pressures, which was not possible in the previous ETLM calculation code GEOSURF.
- Spreadsheet output of the modeling results such as dissolved component concentrations, extent of adsorption, and surface potentials of minerals as function of arbitrary parameters.
- Optimization of equilibrium constants via the PEST function in Visual MINTEQ.

ETL(MIN)$_2$ disables the following because of Visual MINTEQ functional limitations:

- Calculations of closed systems of liquid and/or gas phases at arbitrary volumes and pressures.
- Kinetics and transport modeling.

The current version of ETL(MIN)$_2$ (ver. 1.0.1) disables the following, although these functions are available in the Visual MINTEQ program:

- Redox reactions
- Advanced configurations of mineral formation (infinite/finite/possible solids)
- Inclusion of gases other than CO_2
- Adsorption models other than the Triple Layer Model
- pH calculations based on mass and/or charge balance equations
- Addition of dissolved organic soil matter
- Calculations in binary sorbent systems

ETL(MIN)$_2$ requires the installation of Visual MINTEQ. The operation is confirmed with Visual MINTEQ 3.1 (modified on 23 February 2019 and 17 May 2018) under Windows 10 and is not supported with other versions of Visual MINTEQ and Windows.

3. Constitution of ETL(MIN)$_2$ worksheets

ETL(MIN)$_2$ consists of several spreadsheets:

- Default Databases sheets: **"thermo" and "comp_2008"**

  The contents in the sheets are copied from the standard (default) database thermo.vdb and comp_2008.vdb in Visual MINTEQ 3.1 (modified on 23 February 2019). ETL(MIN)$_2$ generates databases for specific problems from the default datasets (see Ch. 4.5). Content revision should be done for the generated database in the directory of the Vminteq31 database, instead of the datasets in the default database sheets.

- INTERFACE sheet: **"INTERFACE for ETLM"**

  This is the main sheet for ETL(MIN)$_2$ that has configurations of the required ETLM parameters, surface complexation reactions, and output parameters. The on/off switch of the Control Center is also placed on the sheet. See details in Ch. 4.3.

- DATASET sheet: "**Multi Problem DATASET"**

  This sheet contains solution condition configurations for the calculations. The calculated results are also shown in the sheet. See details in Ch. 4.4.

- Information sheets for minerals and solutions: "**Ext-DH", "Solids INFO" and "Capacitance"**

  The "Ext-DH" sheet has configurations of the Extended Debye-Hückel equation. The contents are used to generate the Component and the Thermodynamic databases.

  The "Solids INFO" sheet has intrinsic parameters for specific minerals including zero point of charge (pH_{ZPC}), differences between $\log K_2^{\theta}$ and $\log K_1^{\theta}$ (ΔpK_n^{θ}), site densities of surface hydroxyls (N_S), and bulk dielectric constants of minerals (ε_S). The contents are linked to the "Surface phase" in "INTERFACE for ETLM".

  The "Capacitance" sheet has mineral capacitances.

  Each sheet has space for new minerals and electrolytes.

- Reaction database sheets

  Serial sheets with mineral names such as "HFO" and "FeOOH(goethite)" are databases for surface complexation reactions and equilibrium constants compiled from previous studies. The reactions with equilibrium constants can be copied and pasted into the "INTERFACE for ETLM" sheet to fill out the surface complexation reactions. The literature sources for the surface complexation reactions and corresponding constants are cited in the end of the manual (Ch. 0).

4. Performing ETLM calculations

4.1. Install Visual MINTEQ 3.1 (modified on 23 February 2019)

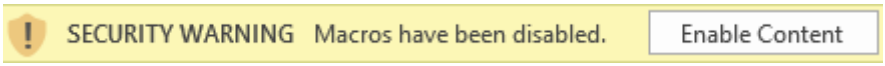
Install Visual MINTEQ 3.1 (modified on 23 February 2019) in your PC.

Visual MINTEQ Home Page (KTH: Royal Institute of Technology, Sweden): https://vminteq.lwr.kth.se/

4.2. Download and open ETL(MIN)$_2$ file

Download and open ETL(MIN)$_2$ file.

The "SECURITY WARNING" appears at the top of the sheet.

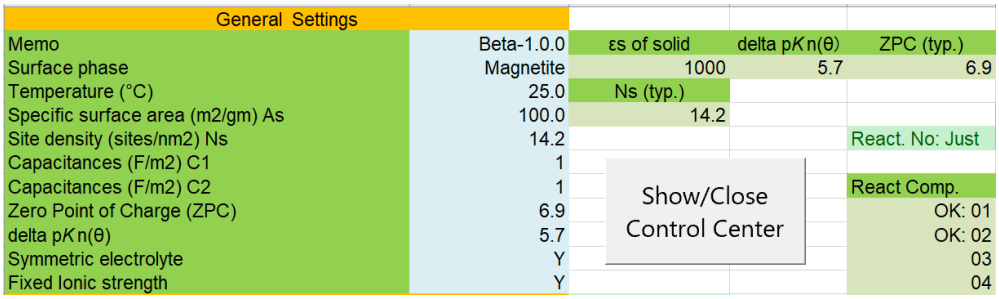


The Control Center of ETL(MIN)$_2$ automatically opens by clicking "Enable Content".

The Control Center can be opened or closed with "Show/Close Control Center" in the "INTERFACE for ETLM" sheet.

4.3. Fill out the INTERFACE sheet—"INTERFACE for ETLM"

4.3.1. General Settings



Memo: Free comments

Surface phase: Select minerals from the drop-down list

The mineral-specific parameters in the "Solid INFO" sheet are copied in the green area at right ["εs of solid", "delta p*K*n(θ)", "ZPC (typ.)" and "Ns (typ.)"]. Contents in the "Solids INFO" sheet can be revised. In addition, new minerals can be added in the free Space of "Solids INFO".

Temperature: Choose in the range 0-40 °C, although all the surface complexation constants reactions included in ELT(MIN)2 are obtained at 25°C.

Specific surface area: Enter specific surface area of the sorbent

Site density: Enter site density of the sorbent. You can refer to typical values in the green area at right that come from "Solid INFO".

Capacitances: Enter inner and outer capacitances (C_1 and C_2).

One can refer to the wide variety of oxide C_1 values for various electrolyte solutions (theoretical or experimental values: Sverjensky, 2001; Sverjensky, 2005) summarized in the "Capacitance" sheet.

It is recommended to use the same C_2 value as C_1 (Kitadai *et al*., 2018). The data cell of the C_2 value directly refers to that of the C_1 value.

Zero Point of Charge: Enter pH_{ZPC}. One can refer to the typical value in the green area at right.

delta p*K*n(θ): difference between $\log K_2^{\theta}$ and $\log K_1^{\theta}$ (ΔpK_n^{θ}).

pH_{ZPC} and ΔpK_n^{θ} of some minerals are obtained from potentiometric titration curves or are predicted from Born solvation theory (Sverjensky, 2005).

After the input of these parameters, $\log K_1^{\theta}$, $\log K_2^{\theta}$ and $\log K_1^{VM}$, and $\log K_2^{VM}$ are automatically calculated (see Ch. 6.1.3).

logK1(θ)	4.05	V_MIN logK1	2.9
logK2(θ)	9.75	V_MIN logK2	-10.9

Select Y/N from the drop-down list for the following two items.

Symmetric electrolyte (1:1)

Settings for Gouy-Chapman (G-C) equation

Y: Assumes 1:1 electrolyte solution that simplifies the G-C equation.

N: Use general G-C equation.

Fixed Ionic strength

Settings for ionic strength calculations

Y: Fixed ionic strength

N: Calculate from total concentrations of each species

4.3.2. Aqueous Components

Aqueous Components		Comp. No: Just	
Components to use (from 1 to ~)	2	V_MIN ID	React
Compnent name 1 (electrolyte anion)	NO3-1	492	Y
Compnent name 2 (electrolyte cation)	Na+1	500	Y
Compnent name 3			
Compnent name 4			
Compnent name 5			
Compnent name 6			
Compnent name 7			
Compnent name 8			
Compnent name 9			
Compnent name 10			
Fixed CO2 gas	N	log10(press.)	
Fixed CO2 gas pressure (atm)	3.8.E-04	-3.420216403	

AJ	AK	AL	AM	AN	AO
V_MIN ID	Compone	Valence	Ion Size	b	Mole Wt.
20	Ag+1	1	0	0	107.868
30	Al+3	3	9	0	26.9815
45	Am+3	3	0	0	243
61	AsO4-3	-3	0	0	138.92
80	Au+3	3	0	0	196.967
100	Ba+2	2	5	0	137.34
110	Be+2	2	0	0	9.0122

Component name:

Select a maximum of ten components from the drop-down list. The first (name 1) and second (name 2)

components should be major anions and cations, respectively, in the electrolyte. An error message appears if duplicate components are selected.

The available components ("basis" of Visual MINTEQ) with ID numbers are listed as AJ to JO in the INTERFACE for ETLM sheet, which come from the inorganic and organic dissolved species listed in the "comp_2008.vbd" database in Visual MINITEQ.

V_MIN ID and React

These properties automatically appear in the cells after component selections. Y in React suggests that components considered in the surface complexation reactions are in the lists of Aqueous Components.

Components to use

Enter the number of aqueous components. If it exceeds the number of selected components, an error message will appear.

Fixed CO_2 gas

Select presence or absence of CO_2 from drop-down list (Y or N). If Y is selected, the partial pressure must be specified in the cell below. In addition, the component "CO3-2" must be included in the aqueous components.

4.3.3. Directories & Databases

Directories & Databases	
Directory of Vminteq31 Databases	C:\Users\username\Documents\Vminteq31
Directory of Vminteq31 Program	C:\Program Files (x86)\Vminteq31
ETLM Database Name	ETLM
V_MIN Component Database Name	comp_2008_Na+1NO3-1H3AsO3
V_MIN Main Thermodynamic Database Name	thermo_Na+1NO3-1H3AsO3
V_MIN Solids Database Name	type6
V_MIN Gaussian DOM Database Name	gaussian
V_MIN Executable File	Mintrun17.exe

Directory of Databases

Specify the directory for the databases generated and/or used by ETL(MIN)$_2$. The name of the directory folder must be "Vminteq31," and is created in the "My Documents" folder during Visual MINTEQ 3.1 installation.

Directory of Vminteq31 Program

Input the directory name of the Visual MINTEQ 3.1 program. The name of folder must be "Vminteq31".

ETLM Database Name

Input the name of the surface complexation reactions database. The default is "ETLM".

V-MIN Component Database Name and V_MIN Main Thermodynamic Database Names

Input the names of the Component and Thermodynamic databases generated by ETL(MIN)$_2$ for the specific problems. These databases depend on the components considered in the calculations. Therefore, the file names are automatically selected from components inputted above cells. The names can be changed.

ETL(MIN)$_2$ is designed to solve problems by using the minimum number of components considered. See Ch. 4.5 for the generation of the databases.

V_MIN Solids Database Name and V_MIN Gaussian DOM Database Name

Input the names of the Solids and Dissolved Organic Matters databases. The current version of ETL(MIN)$_2$

does not consider these functions.

V_MIN Executable File

The name of the executable (exe) file of Visual MINTEQ 3.1 (modified on 23 February 2019).

* The file name of Visual MINTEQ updated before 23 February 2019 is different from "Mintrun17.exe." Although it may be possible to execute the program by changing the name to a previous version of Visual MINTEQ, this not recommended.

4.3.4. V-MINTEQ Settings

V-MINTEQ Settings	
Terminate if imbalance exceeds 30 %?	N
the number of iterations	2000
Activity correction method	Debye-Huckel
Davis b parameter	0.2
Over saturated solids precipitation	0
Min. concentration for aqueous species (mol/L)	1.00E-300
Min. value of saturation index for solids	-500
Max. value of saturation index for solids	500
Spreadsheet program	Excel

Generally, these parameters should not be changed.

Activity Correction Method

Select the activity model for aqueous species. The use of "Debye-Hückel" is recommended for ETLM. The "Davies" equation with a 0.2 Davis b parameter should be used when the Debye-Hückel parameters (see next section) are unavailable.

Precipitation of over-saturated solids

Select the manner of mineral precipitation in supersaturation conditions. The default is 0.

0: do not allow precipitation

1: precipitate after final calculations

2: calculate dissolution/precipitation at each step

4.3.5. Extended Debye-Hückel Parameters for New Databases

The activity model adopted in ETLM is the Extended Debye-Hückel equation developed by Helgeson *et al.* (1981) (Criscenti and Sverjensky, 1999) for z:z-type electrolytes.

Extended Debye-Hückel equation from Helgeson *et al.* (1981):

$$\log\gamma_i = \frac{-A_\gamma (z_i)^2 \sqrt{I}}{1 + aB_\gamma \sqrt{I}} + bI + \Gamma_\gamma \qquad (1)$$

where I is ionic strength (m) and z_i is valence of the ith ions. A_γ and B_γ are temperature-dependent parameters incorporated into Visual MINTEQ. a and b are parameters that depend on the type of electrolyte, and Γ_γ is a term for very high ionic strength solutions, as given by:

$$\Gamma_\gamma = -\log\left(1 + 0.0180153\sum_i m_i\right) \quad (2)$$

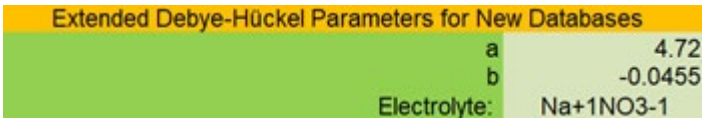
where m_i is the molarity (m) of the ith ions.

Visual MINTEQ 3.1 cannot consider the Γ_γ term. Alternatively, the following Extended Debye-Hückel equation is available:

Extended Debye-Hückel equation (used in Visual MINTEQ 3.1):

$$\log\gamma_i = \frac{-A(z_i)^2\sqrt{I}}{1 + B_{DH}a\sqrt{I}} + bI \quad (3)$$

Eqs. (1) and (3) provide equivalent activity coefficients at low ionic strengths (up to 0.5 m for 1:1 electrolytes).



ETL(MIN)$_2$ automatically refers to the a and b parameters based on the types of electrolytes from the aqueous components. Displays of "0" in the a and b parameter cells indicate no available parameters from the "Ext-DH" sheet. In this case, the Davies equation should be used (see Ch. 4.3.4).

The parameters for the activity models are automatically considered in the Component and Thermodynamic databases (see Ch. 4.5).

4.3.6. Surface Reactions

The general expression of the surface complexation reaction, the corresponding equilibrium constant, and the PSI factor are given by:

Surface complexation reaction:

$$a(\mathrm{SOH_2^+ or SOH or SO^-}) + b(\mathrm{SOH}) + c\mathrm{H^+} + d\mathrm{H_2O} + \sum_i e_i\,[\mathrm{Comp.}]_i = [\mathrm{PRODUCTS}] \quad (4)$$

Equilibrium constant:

$$K^\theta_{[\mathrm{PRODUCTS}]} = \frac{a_{[\mathrm{PRODUCTS}]}}{\left(a_{(\mathrm{SOH_2^+})\mathrm{or}(\mathrm{SOH})\mathrm{or}(\mathrm{SO^-})}\right)^a (a_{\mathrm{SOH}})^b (a_{\mathrm{H^+}})^c \left(a_{\mathrm{H_2O}}\right)^d \prod_i \left(a_{[\mathrm{Comp.}]_i}\right)^{e_i}} 10^{\frac{F(\Delta\psi_r)}{2.303RT}} \quad (5)$$

$${}^*K^\theta_{[\mathrm{PRODUCTS}]} = \frac{a_{[\mathrm{PRODUCTS}]}}{(a_{\mathrm{SOH}})^{a+b}(a_{\mathrm{H^+}})^{(c+a)\mathrm{or}(c)\mathrm{or}(c-a)}\left(a_{\mathrm{H_2O}}\right)^d \prod_i \left(a_{[\mathrm{Comp.}]_i}\right)^{e_i}} 10^{\frac{F(\Delta\psi_r)}{2.303RT}} \quad (6)$$

PSI factor for electric term:

$$\Delta\psi_r = l\psi_0 + m\psi_\beta + n\psi_d \quad (7)$$

where K^θ and ${}^*K^\theta$ are the equilibrium constants based on site-occupancy standard states (Sverjensky, 2003). The superscript (*) represents the reaction relative to neutral surface hydroxyls (>SOH) (see Ch.6.1).

The maximum number of the surface complexation reactions is eighteen.

React Comp.		PRODUCTS	log Kθ		a Surf. 1	b (Surf. 2)	c (H+)	d (H2O)	l (PSI-0)	m (PSI-B)	n (PSI-d)
OK:	01	SOH2+_NO3-1		2.8	1 SOH2+				1	-1	
OK:	02	SO-_Na+1		2.5	1 SO-				-1	1	
	03										
	04										

Aqueous Components : NO3-1,Na+1,,,,,,,,
Only reactions whose all components included in Aqueous Components will be calculated.

e	Prim. Comp.	e	Comp.	e	Comp.	e	Comp.	e	Comp.	e	Comp.
1	NO3-1										
1	Na+1										

PRODUCTS: Name of surface complex formed by the reaction. Names are not necessary to express the exact chemical formula of the complexes.

log Kθ: Equilibrium constant based on site-occupancy standard states (see Ch.6.1)

Enter the values of constants corresponding to Eq. (5).

Surf. 1 and Surf. 2: Cells for surface hydroxyls

Input the coefficients *a* and *b* in the sheet.

Surf. 1: Select one from "SO-, SOH, SOH2+" in the drop-down list.

Surf. 2: Only for "SOH". This cell is for reactions with mixtures of charged and un-charged surface hydroxyls (e.g., Sverjensky 2006 and Fukushi et al. 2013).

H+, H2O, PSI-0, PSI-B, PSI-d

Input the coefficients *c, d, l*, *m* and *n* in the sheet.

Note: The coefficients of PSI factors corresponding to Eq. (6) must be values obtained **relative to >SOH** (see Ch. 6.2).

Reaction components

Enter components (basis) and reaction coefficients (e_i)

The "Reaction Components" must be identical to those in "Aqueous Components". When these are not included in "Aqueous Components", the "React.Comp." cells display "?".

Each reaction needs "PRODUCTS", "logKθ", "Surf.1" and "Prim. Comp.". An error message appears when the input is insufficient.

Reactions #01 and #02 are surface complexation (outer-sphere) reactions with major anions and cations.

	Considering H2O in reactions	N
React. No: Just	Reactions to use (from 1 to ~)	2

Considering H2O in reaction

Select whether the H_2O component is included in the equilibrium calculation (default setting is N).

Except for extremely high ionic strength solutions, the H_2O activity is almost unity. (Therefore, it is not necessary to consider it in mass action expressions.)

Reactions to use

Enter the number of surface complexation reactions included in the ETLM database. An error message appears if the number increases the number of the reactions.

Cs for log *K0 (gm/L)
1.6
log *K0 for GEOSURF
5.70
-8.40

log *K0 for GEOSURF

Display the equilibrium constants log $*K^0$ based on hypothetical 1.0-M standard states (Sverjensky, 2003) used in classic geochemical codes such as GEOSURF (see Ch. 6.1).

The log $*K^0$ calculation needs the solid concentration in the cell for "Cs for log *K0." The log $*K^0$ values depend on the solid concentration for multidentate reactions.

The input reactions convert to the Visual MINTEQ format and the information is displayed as:

Sp. Num.	PRODUCTS	V_MIN logK	>SOH	H2O	H+
5	SOH2+_NO3-1	5.70	1 =SOH(1)		1 H+
5	SO-_Na+1	-8.40	1 =SOH(1)		-1 H+
0					
0					

EXPSI0	EXPSIB	EXPSID	Prim. Comp.
1 PSIo(1)	-1 PSIb(1)		1 NO3-1
-1 PSIo(1)	1 PSIb(1)		1 Na+1

4.3.7. Sweep Components

	Sweep Components (max13)	
0	pH	Type (Unit)
1	Ionic strength	M
2	NO3-1	Total sorbed
3	NO3-1	Concentration
4	Sigma-o(1)	C/m2
5	Psi-d(1)	mV
6		
7		
8		
9		
10		
11		
12		
13		

Input the output components and units in "Sweep Components" and "Type (Unit)," respectively. The unit can be selected from the drop-down list. The maximum number of output components for each run is fourteen, including pH.

Selectable Components					Example		
Basic Species	Sigma	Psi	I	Surface	Dissolved Spe.	Gas	Mineral
H+1	Sigma-o(1)	Psi-o(1)	Ionic streng	=SOH(1)	OH-	CO2 (g)	Halite
NO3-1	Sigma-b(1)	Psi-b(1)		=SOH2+(1)			Calsite
Na+1	Sigma-d(1)	Psi-d(1)		=SO-(1)	H2CO3* (aq)		
	Sigma-ddl(1)			SOH2+_NO3-1(1)	HCO3-		
				SO-_Na+1(1)	NaCO3-		
				(1)	NaHCO3 (aq)		
				(1)	CO3-2		
				(1)			
				(1)	H3PO4		
				(1)	H2PO4-		
				(1)	HPO4-2		
				(1)	NaHPO4-		
				(1)	Na2HPO4 (aq)		
				(1)	Na2PO4-		
				(1)	NaH2PO4 (aq)		
				(1)	NaPO4-2		
				(1)			
				(1)	NaCl (aq)		
				(1)			
				(1)			
				(1)			
Selectable Types (Unit)							
Concentration	C/m2	mV	M	Concentration	Concentration	Partial pre	Saturation index
Log Concentration				Log Concentration	Log Concentration		logIAP
Activity				Activity	Activity		
Log Activity				Log Activity	Log Activity		
Total dissolved							
Log Total Dissolved							
Total sorbed							
Bound to Oxide							

Selectable components and the corresponding units are given in the table above.

4.4. Fill out “Multi Problem DATASET” sheet

Multi Problem List													PEST
Solid Conc. gm/L	pH	Fixed Ion.Str. M	NO3-1 Molar	Na+1 Molar	Comp.3 Molar	Comp.4 Molar	Comp.5 Molar	Comp.6 Molar	Comp.7 Molar	Comp.8 Molar	Comp.9 Molar	Comp.10 Molar	Memo %
1.00E+00	2.0	1.00.E-01	1.00.E-01	1.00.E-01									
1.00E+00	3.0	1.00.E-01	1.00.E-01	1.00.E-01									
1.00E+00	4.0	1.00.E-01	1.00.E-01	1.00.E-01									
1.00E+00	5.0	1.00.E-01	1.00.E-01	1.00.E-01									
1.00E+00	6.0	1.00.E-01	1.00.E-01	1.00.E-01									
1.00E+00	7.0	1.00.E-01	1.00.E-01	1.00.E-01									
1.00E+00	8.0	1.00.E-01	1.00.E-01	1.00.E-01									
1.00E+00	9.0	1.00.E-01	1.00.E-01	1.00.E-01									
1.00E+00	10.0	1.00.E-01	1.00.E-01	1.00.E-01									
1.00E+00	11.0	1.00.E-01	1.00.E-01	1.00.E-01									
1.00E+00	12.0	1.00.E-01	1.00.E-01	1.00.E-01									

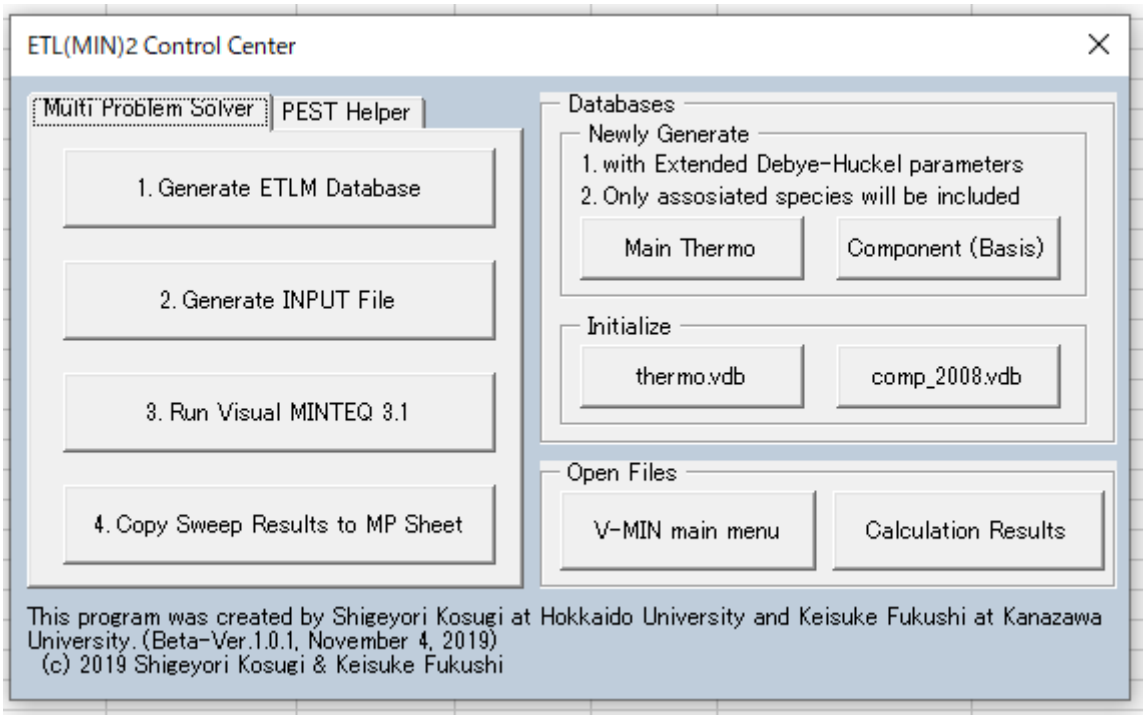
Input conditions for calculations in “Multi Problem List.”

The number must not be “0,” except for pH.

The Component concentrations are for the initial solution concentrations, not equilibrium concentrations.

Input “Fixed Ion. Str.” when “Y” in “Fixed Ionic strength” is selected. Even when “N” is selected (in which case, the ionic strength is calculated from the concentrations of all components), any arbitrary number except for “0” must be entered in the cells. In the presence of CO_2, any arbitrary number except “0” also must be entered in the cells.

4.5. Operation of “Control Center”



4.5.1. Generate new databases (“Databases”)

Generate new database of Thermodynamic and Component from “Main Thermo” and “Component (Basis)” buttons in “Databases→Newly Generate”. Databases with defined file names are created in the “Directory of

Databases," and contain the basis and the related species defined in Aqueous Components (Ch.4.3.2). The species in the database have Extended Debye-Hückel parameters displayed in "Extended Debye-Hückel Parameters for New Databases" (Ch. 4.3.5).

When a database with the same name already exists in the folder, it will be overwritten with the new database.

4.5.2. "Generate ETLM Database"

Button #1, generate ETLM Database in "Directory of Databases".

4.5.3. "Generate INPUT File"

Button #2, generate an INPUT file in "Directory of Databases".

The name of the INPUT file is "minin.VDA".

4.5.4. "Run Visual MINTEQ 3.1"

Button #3, calculate by using Visual MINTEQ 3.1.

The filename of the exe file must be "Mintrun17.exe" in the program folder (Ch.4.3.3). When ETL$(MIN)_2$ is inoperable during the running of "Mintrun17.exe", ETL$(MIN)_2$ must be terminated by entering "Alt+F4".

4.5.5. "Copy Sweep Results to MP Sheet"

Button #4: the calculated results are copied in "Copied Sweep Results" inside the "Multi Problem DATASET".

4.5.6. Other functions on the Control Center

Open File function: open files in Directory of Databases.

Open INPUT File Button

Open INPUT file of "minin.VDA."

Note: the extension of .VDA must be related to Visual MINTEQ 3.1.

Open OUTPUT File Button

Open OUTPUT file of "vmin.out."

Note: the extension of .out should be related to the relevant application such as the text editor.

Database Initialization

thermo.vdb and comp_2008.vdb Buttons

Default databases with the defined names are generated in the "Directory of Databases".

PEST Helper

Optimization of equilibrium constants is conducted by using PEST mode complimented in Visual MINTEQ 3.1.

5. How to do PEST optimizations

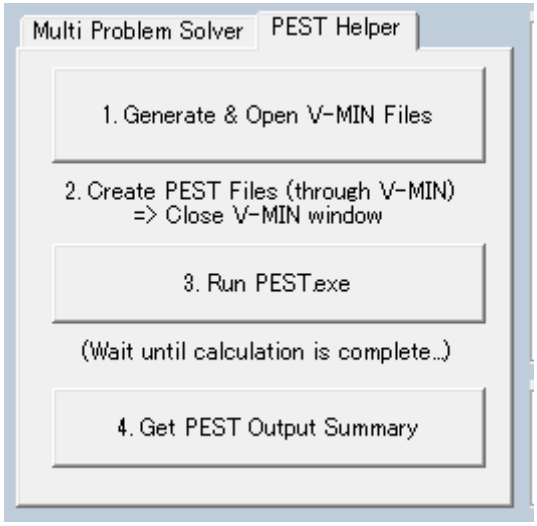
ETL(MIN)$_2$ enables parameter optimizations for equilibrium constants by using the PSET function in Visual MINTEQ 3.1.

5.1. Operation of ETL(MIN)$_2$

Configure the solution conditions of the adsorption data according to 4.4. Fill out "Multi Problem DATASET".
For the optimizations, the extent of adsorption must be expressed as adsorption %.
Input the adsorption % in PEST MEMO. It is defined in Eq. (8).

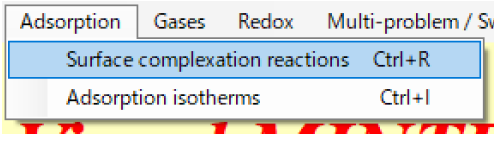
$$\text{adsorption\%} = \frac{\text{Initial conc.} - \text{Equilibrium conc.}}{\text{Intial conc.}} \times 100 \quad (8)$$

The operation is by using "PEST Helper" in Control Center

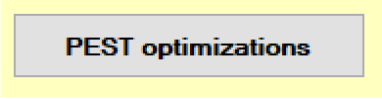


Click "1. Generate & Open V-MIN Files". The database and INPUT file are automatically generated. The screen of Visual MINTEQ is automatically opened. The adsorption % inputed in PEST MEMO is copied in clipboard.

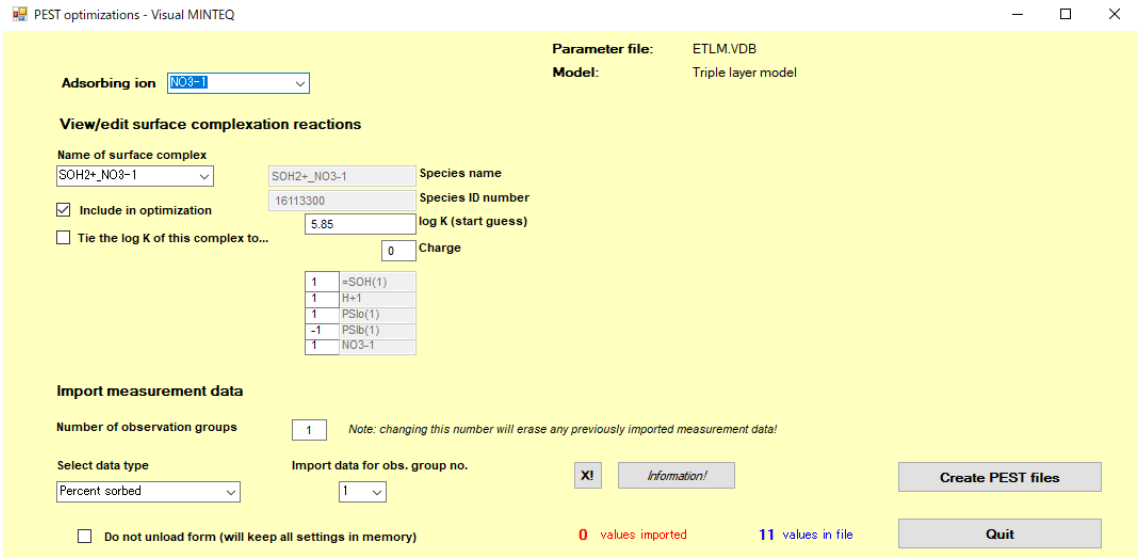
5.2. Operation of Visual MINTEQ



Click "Surface complexation reactions" in the "Adsorption" menu, or input "Ctrl+R" from the keyboard.



Click “PEST optimizations” in the “Surface complexation menu”.



Select “Adsorbing ion” in “PEST optimization.”

For the optimizations, enter the equilibrium constants from “View/edit surface complexation reactions.”

See Visual MINTEQ3.1 manual for the detailed procedure.

Then, input the “Import measurement data.”

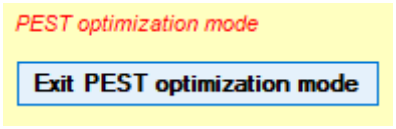
Select and copy all the adsorption % data entered in “Multi Problem DATASET” in Ch. 5.1.

Click “X!” to import values from the clipboard to the PEST files.

Click “Create PEST files” and then click “Quit” “PEST optimization.”

Click “Save and back to main menu” in the “Surface complexations menu.”

The initial screen of Visual MINTEQ should then switch to PEST optimizations mode.



Click “Run” to start PEST optimizations.

After the optimization, “Summary of PEST optimizations” is automatically displayed on screen. The output file (pestopt.rec) of the optimization is generated in the database directory.

Note: During the procedure, the minimum database originated from the default database of Visual MINTEQ is created and used in the PEST calculation. When the database is modified specifically for the optimization, the PEST Helper should be used. After closing the screen of Visual MINTEQ 3.1, click “3. Run PEST.exe” in PEST Helper. After the calculations, click “4. Get PEST Output Summary” the you can see the Summary of PEST optimizations.

6. Theoretical background

6.1. Conversion of equilibrium constants from ETLM to Visual MINTEQ

There are differences in equilibrium constant calculation methodologies between Visual MINTEQ and ETLM. ETL(MIN)$_2$ internally converts the ETLM equilibrium constants to those of Visual MINTEQ.

The two main differences in the calculations are:

1. Definition of standard states of surface species
2. Reference surface hydroxyl group site

In the following section, details of these differences and the associated conversion methodologies are described.

6.1.1. Definition of standard states of surface species

ETLM treats the equilibrium constants (K^{θ}) by using the concentrations α of the surface species based on site-occupancy standard states. In contrast, Visual MINTEQ treats the constants (K^{VM}) by using the concentration X based on 1.0 mol/L hypothetical standard state considering the compensation formula by Venema et al (1996). The relationships between α and X of the surface species are different for sorbent sites (>SOH) and sorbate sites (other than >SOH) (Kobayashi et al. 2020).

The sorbent site (>SOH) for standard states can be expressed after Sverjensky (2003):

$$\alpha_{>\mathrm{SOH}} = \frac{M^{\#}_{>\mathrm{SOH}}}{\left(\frac{N_S}{N_A}\right) A_S C_S} = X_{>\mathrm{SOH}} = 1.0 \tag{9}$$

where $M^{\#}_{>\mathrm{SOH}}$ is the molar concentration (mol-L^{-1}) for the standard state, N_S is the site density (sites m^{-2}), A_S is the specific surface area (m^2-g^{-1}), C_S is the solid concentration (g-L^{-1}), and N_A is Avogadro's number (6.022×10^{23} sites mol^{-1}). The α and X of the sorbent site (>SOH) are both unity for the standard state.

The relationship of sorbate site (other than >SOH; here, consider >SOH$_2^+$ as example) can be expressed according to Sverjensky (2003) as:

$$\alpha_{>\mathrm{SOH}_2^+} = \frac{M^{\ddagger}_{>\mathrm{SOH}_2^+}}{\left(\frac{N^{\ddagger}}{N_A}\right) A^{\ddagger} C^{\ddagger}} = 1.0 \neq X_{>\mathrm{SOH}_2^+} \tag{10}$$

where $M^{\ddagger}_{>\mathrm{SOH2+}}$ is the molar concentration (mol-L^{-1}) in the standard state, $N^{\ddagger}$ is the site density (sites-m^{-2}) in the standard state, $A^{\ddagger}$ is specific surface area (m^2-g^{-1}) in the standard state and $C^{\ddagger}$ is the solid concentration (g-L^{-1}) in the standard state. In the convention of ETLM, $N^{\ddagger}=10\times10^{18}$ sites-m^{-2}, $A^{\ddagger}=10$ m^2-g^{-1}, and $C^{\ddagger}=C_S$. In the standard state, the sorbate site activity is unity while the mole fraction is not unity. Eq. (10) can be expressed in terms of X:

$$\alpha_{>\mathrm{SOH_2^+}} = \frac{M^{\ddagger}_{>\mathrm{SOH_2^+}}}{\left(\frac{N_S}{N_A}\right)A_S C_S} \times \frac{\left(\frac{N_S}{N_A}\right)A_S C_S}{\left(\frac{N^{\ddagger}}{N_A}\right)A^{\ddagger}C^{\ddagger}} = X_{>\mathrm{SOH_2^+}}\left(\frac{N_S A_S}{N^{\ddagger}A^{\ddagger}}\right) \tag{11}$$

Generally, the molar concentrations of surface species are low (10^{-5}–10^{-3} M). In addition, the mole fractions of sorbate sites are usually <0.1. Therefore, Eqs. (9) and (11) can be applicable regardless of the standard state.

6.1.2. Reference surface hydroxyl group site

ETLM can change the reference surface hydroxyls depending on the (elementary) surface reactions. In contrast, Visual MINTEQ describes all the surface reactions by using >SOH (i.e., basis of surface hydroxyls). The different conventions with regard to the type of surface hydroxyl results in differences in equilibrium constant values.

The general surface complexation reactions adopted in ETLM can be expressed as:

$$a > \mathrm{SOH_2^+} + b > \mathrm{SOH} + \mathrm{c} > \mathrm{SO^-} + d\mathrm{H^+} + e\mathrm{H_2O} + \sum_i f_i\,[\mathrm{Comp.}]_i = [\mathrm{PRODUCTS}] \tag{12}$$

The stoichiometry coefficients of the surface hydroxyls (*a, b, c*) depend on the elementary reactions. Generally, the reference site for surface complexation with cations is $>SO^-$, while that for anions is $>SOH_2^+$.

In contrast, the reference surface site for Visual MINTEQ is solely >SOH because it is the basis. Therefore, the above reaction equation can be rewritten as:

$$(a+b+c) > \mathrm{SOH} + (a-c+d)\mathrm{H^+} + e\mathrm{H_2O} + \sum_i f_i\,[\mathrm{Comp.}]_i = [\mathrm{PRODUCTS}] \tag{13}$$

The mass action expressions of Eq. (12) in ETLM and Eq. (13) can be expressed as Eqs. (14) and (16), respectively:

$$K^{\theta}_{[\mathrm{PRODUCTS}]} = \frac{a_{[\mathrm{PRODUCTS}]}}{\left(a_{>\mathrm{SOH_2^+}}\right)^a (a_{>\mathrm{SOH}})^b (a_{>\mathrm{SO^-}})^c (a_{\mathrm{H^+}})^d \left(a_{\mathrm{H_2O}}\right)^e \prod_i \left(a_{[\mathrm{Comp.}]_i}\right)^{f_i}} 10^{\frac{F(\Delta\psi_{\mathrm{r}})}{2.303RT}} \tag{14}$$

$${}^{*}K^{\theta}_{[\mathrm{PRODUCTS}]} = \frac{a_{[\mathrm{PRODUCTS}]}}{(a_{>\mathrm{SOH}})^{a+b+c} (a_{\mathrm{H^+}})^{a-c+d} \left(a_{\mathrm{H_2O}}\right)^e \prod_i \left(a_{[\mathrm{Comp.}]_i}\right)^{f_i}} 10^{\frac{F(\Delta\psi_{\mathrm{r}})}{2.303RT}} \tag{15}$$

$$K^{VM}_{[\mathrm{PRODUCTS}]} = \frac{X_{[\mathrm{PRODUCTS}]}}{(X_{>\mathrm{SOH}})^{a+b+c} (a_{\mathrm{H^+}})^{a-c+d} \left(a_{\mathrm{H_2O}}\right)^e \prod_i \left(a_{[\mathrm{Comp.}]_i}\right)^{f_i}} 10^{\frac{F(\Delta\psi_{\mathrm{r}})}{2.303RT}} \tag{16}$$

where the equilibrium constant with the superscript * in Eq. (15) is with respect to >SOH surface sites in the ETLM. Another version of the definition is that of equilibrium constants with respect to the molar concentration *M* of surface sites (hypothetical 1.0-M standard state). The standard state is used in classic geochemical codes such as GEOSURF (Sahai & Sverjensky, 1998). The equilibrium constants are expressed as K^0 with superscript "0." The corresponding equilibrium constants to Eqs. (14) and (15) are:

$$K^0_{[\mathrm{PRODUCTS}]} = \frac{M_{[\mathrm{PRODUCTS}]}}{\left(M_{>\mathrm{SOH_2^+}}\right)^a (M_{>\mathrm{SOH}})^b (M_{>\mathrm{SO^-}})^c (a_{\mathrm{H^+}})^d \left(a_{\mathrm{H_2O}}\right)^e \prod_i \left(a_{[\mathrm{Comp.}]_i}\right)^{f_i}} 10^{\frac{F(\Delta\psi_r)}{2.303RT}} \quad (17)$$

$${}^*K^0_{[\mathrm{PRODUCTS}]} = \frac{M_{[\mathrm{PRODUCTS}]}}{(M_{>\mathrm{SOH}})^{a+b+c} (a_{\mathrm{H^+}})^{a-c+d} \left(a_{\mathrm{H_2O}}\right)^e \prod_i \left(a_{[\mathrm{Comp.}]_i}\right)^{f_i}} 10^{\frac{F(\Delta\psi_r)}{2.303RT}} \quad (18)$$

6.1.3. Conversion of equilibrium constants

The protonation and deprotonation reactions of surface hydroxyls can be expressed in ETLM (Sverjensky 2005):

$$> \mathrm{SOH} + \mathrm{H^+} => \mathrm{SOH_2^+} \quad (19)$$

$$> \mathrm{SO^-} + \mathrm{H^+} => \mathrm{SOH} \quad (20)$$

The corresponding mass action expressions based on the site-occupancy of the standard state are:

$$K_1^\theta = \frac{a_{>\mathrm{SOH_2^+}}}{a_{>\mathrm{SOH}} a_{\mathrm{H^+}}} 10^{\frac{F\psi_0}{2.303RT}} \quad (21)$$

$$K_2^\theta = \frac{a_{>\mathrm{SOH}}}{a_{>\mathrm{SO^-}} a_{\mathrm{H^+}}} 10^{\frac{F\psi_0}{2.303RT}} \quad (22)$$

where F is the Faraday constant (9.649×10^4 C-mol^{-1}), R is the gas constant (8.314 J-K^{-1}-mol^{-1}) and T is the absolute temperature (K).

The equilibrium constants $K_1{}^\theta$ and $K_2{}^\theta$ can be calculated by using $\mathrm{pH_{ZPC}}$ and $\Delta\mathrm{p}K_n{}^\theta$ (see Sverjensky 2005):

$$\log K_1^\theta = \mathrm{pH_{ZPC}} - \frac{\Delta\mathrm{p}K_n^\theta}{2} \quad (23)$$

$$\log K_2^\theta = \mathrm{pH_{ZPC}} + \frac{\Delta\mathrm{p}K_n^\theta}{2} \quad (24)$$

The reference surface hydroxyl site in Visual MINTEQ is >SOH (Ch. 6.1.2). The relationship between the Visual MINTEQ and ETLM equilibrium constants can be expressed by considering the relationship between the surface activity and the mole fraction:

$$> \mathrm{SOH} + \mathrm{H^+} => \mathrm{SOH_2^+} \quad (25)$$

$$\log K_1^{VM} = \log\left(\frac{X_{>\mathrm{SOH_2^+}}}{X_{>\mathrm{SOH}} \alpha_{\mathrm{H^+}}} 10^{\frac{F\psi_0}{2.303RT}}\right) = \log\left\{\frac{\alpha_{>\mathrm{SOH_2^+}}}{\alpha_{>\mathrm{SOH}} \alpha_{\mathrm{H^+}}} \left(\frac{N^\ddagger A^\ddagger}{N_S A_S}\right) 10^{\frac{F\psi_0}{2.303RT}}\right\}$$

$$= \log K_1^\theta + \log\left(\frac{N^\ddagger A^\ddagger}{N_S A_S}\right) \quad (26)$$

$$> \mathrm{SOH} => \mathrm{SO^-} + \mathrm{H^+} \tag{27}$$

$$\log K_2^{VM} = \log\left(\frac{X_{>\mathrm{SO^-}}\alpha_{\mathrm{H^+}}}{X_{>\mathrm{SOH}}} 10^{\frac{-F\psi_0}{2.303RT}}\right) = \log\left\{\frac{\alpha_{>\mathrm{SO^-}}\alpha_{\mathrm{H^+}}}{\alpha_{>\mathrm{SOH}}}\left(\frac{N^{\ddagger}A^{\ddagger}}{N_S A_S}\right) 10^{\frac{-F\psi_0}{2.303RT}}\right\}$$

$$= -\log K_2^{\theta} + \log\left(\frac{N^{\ddagger}A^{\ddagger}}{N_S A_S}\right) \tag{28}$$

The PSI factor ($\Delta\psi_r$) in the ETLM reactions are different from those of Visual MINTEQ. Therefore, the PSI factors in the "INTERFACE for ETLM" sheet must be based on the equation in Visual MINTEQ, **i.e., relative to >SOH** (see Ch. 6.2).

The surface complexation reactions of electrolyte cations M^+ and anions L^- in ETLM can be expressed as:

$$> \mathrm{SO^-} + \mathrm{M^+} => \mathrm{SO^-\_M^+} \tag{29}$$

$$> \mathrm{SOH_2^+} + \mathrm{L^-} => \mathrm{SOH_2^+\_L^-} \tag{30}$$

The mass action expressions are given by (Sverjensky, 2005):

$$K_{\mathrm{M^+}}^{\theta} = \frac{a_{>\mathrm{SO^-\_M^+}}}{a_{>\mathrm{SO^-}} a_{\mathrm{M^+}}} 10^{\frac{F\psi_\beta}{2.303RT}} \tag{31}$$

$$K_{\mathrm{L^-}}^{\theta} = \frac{a_{>\mathrm{SOH_2^+\_L^-}}}{a_{>\mathrm{SOH_2^+}} a_{\mathrm{L^-}}} 10^{\frac{-F\psi_\beta}{2.303RT}} \tag{32}$$

The relationship between the Visual MINTEQ and ETLM equilibrium constants can be expressed as:

$$> \mathrm{SOH} + \mathrm{M^+} => \mathrm{SO^-\_M^+} + \mathrm{H^+} \tag{33}$$

$$\log K_{\mathrm{M^+}}^{VM} = \left\{\frac{X_{>\mathrm{SO^-\_M^+}}\alpha_{\mathrm{H^+}}}{X_{>\mathrm{SOH}}\alpha_{\mathrm{M^+}}} 10^{\frac{F(-\psi_0+\psi_\beta)}{2.303RT}}\right\} = \log\left\{\frac{a_{>\mathrm{SO^-\_M^+}}}{a_{>\mathrm{SO^-}} a_{\mathrm{M^+}}} \frac{a_{>\mathrm{SO^-}} a_{\mathrm{H^+}}}{a_{>\mathrm{SOH}}}\left(\frac{N^{\ddagger}A^{\ddagger}}{N_S A_S}\right) 10^{\frac{F(-\psi_0+\psi_\beta)}{2.303RT}}\right\}$$

$$= \log K_{\mathrm{M^+}}^{\theta} - \log K_2^{\theta} + \log\left(\frac{N^{\ddagger}A^{\ddagger}}{N_S A_S}\right) \tag{34}$$

$$> \mathrm{SOH} + \mathrm{L^-} + \mathrm{H^+} => \mathrm{SOH_2^+\_L^-} \tag{35}$$

$$\log K_{\mathrm{L^-}}^{VM} = \left(\frac{X_{>\mathrm{SOH_2^+\_L^-}}}{X_{>\mathrm{SOH}}\alpha_{\mathrm{L^-}}\alpha_{\mathrm{H^+}}} 10^{\frac{F(\psi_0-\psi_\beta)}{2.303RT}}\right) = \log\left(\frac{a_{>\mathrm{SOH_2^+\_L^-}}}{a_{>\mathrm{SOH_2^+}} a_{\mathrm{L^-}}} \frac{a_{>\mathrm{SOH_2^+}}}{a_{>\mathrm{SOH}} a_{\mathrm{H^+}}}\left(\frac{N^{\ddagger}A^{\ddagger}}{N_S A_S}\right) 10^{\frac{F(\psi_0-\psi_\beta)}{2.303RT}}\right)$$

$$= \log K_{\mathrm{L^-}}^{\theta} + \log K_1^{\theta} + \log\left(\frac{N^{\ddagger}A^{\ddagger}}{N_S A_S}\right) \tag{36}$$

If the conversion equations for the generalized surface complexation reactions [Eqs. (12) and (13)] are considered, the conversion of the ETLM equilibrium constants to Visual MINTEQ [Eq. (14) to Eq. (16)] can be performed by

using $\log K_1^{\theta}$ and $\log K_2^{\theta}$.

$$\log K^{VM}_{[\mathrm{PRODUCTS}]} = \log K^{\theta}_{[\mathrm{PRODUCTS}]} + a\log K_1^{\theta} - c\log K_2^{\theta} + \log\left(\frac{N^{\ddagger}A^{\ddagger}}{N_S A_S}\right) \quad (37)$$

When considering Eq. (15), the equilibrium constants $^*K^{\theta}$, K^{θ}, and K^{VM} can be mutually related by using the following equations:

$$\log K^{VM}_{[\mathrm{PRODUCTS}]} = \log {}^*K^{\theta}_{[\mathrm{PRODUCTS}]} + \log\left(\frac{N^{\ddagger}A^{\ddagger}}{N_S A_S}\right) \quad (38)$$

$$\log {}^*K^{\theta}_{[\mathrm{PRODUCTS}]} = \log K^{\theta}_{[\mathrm{PRODUCTS}]} + a\log K_1^{\theta} - c\log K_2^{\theta} \quad (39)$$

$^*K^{\theta}$ and K^{VM} can be related to $^*K^0$ for the hypothetical 1.0-M standard states by using

$$\log {}^*K^{\theta}_{[\mathrm{PRODUCTS}]} = \log {}^*K^{0}_{[\mathrm{PRODUCTS}]} + \log\frac{(N_S A_S)^{a+b+c}}{N^{\ddagger}A^{\ddagger}} + \log\left(\frac{C_S}{N_A}\right)^{a+b+c-1} \quad (40)$$

$$\log K^{VM}_{[\mathrm{PRODUCTS}]} = \log {}^*K^{0}_{[\mathrm{PRODUCTS}]} + \log\left(\frac{N_S A_S C_S}{N_A}\right)^{a+b+c-1} \quad (41)$$

Although ETL(MIN)$_2$ does not use the equilibrium constants $^*K^0$ based on the hypothetical 1.0-M standard states, a number of previous studies with GEOSURF used the $^*K^0$. There are some misunderstandings with regard to the definition and conversion equations of the equilibrium constants $^*K^0$ to the K^{θ} (see below).

* Eq. (40) in Sverjensky (2003) and the following papers did not consider the presence of N_A [e.g., equation (57) in Sverjensky 2003]. In addition, the N_S units in the relevant papers used sites-nm^{-2} instead of sites-m^{-2} (original definition). These mistreatments led to incorrect K^{θ} values calculated from the $^*K^0$ using hypothetical 1.0-M standard states for reactions with multi-dentate (other than monodentate reactions) surface complexation reactions (e.g., Sverjensky, 2006; Sverjensky & Fukushi, 2006a; Sverjensky & Fukushi, 2006b; Fukushi & Sverjensky, 2007a; Fukushi & Sverjensky, 2007b; Nagata & Fukushi, 2010; Kanematsu *et al*., 2010; Usiyama & Fukushi, 2016; Kitadai *et al*., 2018). The correction equation for the old equilibrium constants for the n-dentate reactions with respect to those for ETL(MIN)$_2$ can given by:

$$\log K^{\theta}_{\mathrm{ETL(MIN)2}} = \log K^{\theta}_{old} - (n-1) \times 5.78 \quad (42)$$

The database of the surface complexation reactions in ETL(MIN)$_2$ lists the values after the corrections.

6.2. PSI factor calculation

The PSI factor ($\Delta\psi_r$) in ETL(MIN)$_2$ must be determined according to the following reaction, which has a reference surface hydroxyl site >SOH:

$$(a+b+c) > \mathrm{SOH} + (a-c+d)\mathrm{H^+} + e\mathrm{H_2O} + \sum_i f_i\,[\mathrm{Comp.}]_i = [\mathrm{PRODUCTS}] \qquad (13)$$

The general configuration of the PSI factor in ETLM can be summarized:

- Protonation or deprotonation of the surface hydroxyl occurs at the 0-plane, i.e., the adsorption of $n\mathrm{H^+}$ results in a $+n\psi_0$ PSI factor, while the desorption of $n\mathrm{H^+}$ results in $-n\psi_0$.
- Outer spherically adsorbed cations and anions are coordinated at the β-plane; i.e., the adsorption of the ions results in a $nz_i\psi_\beta$ PSI factor, where n and z_i respectively represent the stoichiometric coefficient and the valence of the ith ion.
- Inner spherically adsorbed cations (metals) are coordinated at the 0-plane (Usiyama and Fukushi, 2016). The adsorption of metals results in a $+nz_i\psi_0$ PSI factor, where n and z_i respectively represent the stoichiometric coefficient and valence of the ith metal.
- Inner-spherically adsorbed anions are coordinated at the β-plane, as are the outer spherically adsorbed anions. In contrast, the adsorption of the inner spherically adsorbed anions is accompanied with the desorption of water (dipole) from the surface hydroxyls (Sverjensky and Fukushi, 2006). The desorption of n water dipoles results in a $-n\times(\psi_0 - \psi_\beta)$ PSI factor.

  Eqs. (43) and (44) are examples of the configuration of PSI factors of the bidentate-binuclear inner-sphere arsenate adsorptions (Fukushi and Sverjensky, 2007a).

$$2 > \mathrm{SOH} + 2\mathrm{H^+} + \mathrm{AsO_4^{-3}} = (> \mathrm{SO})_2\mathrm{AsO_2^-} + 2\mathrm{H_2O}$$
$$\Delta\psi_\mathrm{r} = 2\psi_0 - 3\psi_\beta - 2(\psi_0 - \psi_\beta) = -\psi_\beta \qquad (43)$$

$$2 > \mathrm{SOH} + 2\mathrm{H^+} + \mathrm{HAsO_4^{-2}} = (> \mathrm{SO})_2\mathrm{AsOOH} + 2\mathrm{H_2O}$$
$$\Delta\psi_\mathrm{r} = 2\psi_0 - 2\psi_\beta - 2(\psi_0 - \psi_\beta) = 0 \qquad (44)$$

7. References

- Criscenti, L. J.; Sverjensky, D. A. The Role of Electrolyte Anions (ClO_4-, NO3- , and Cl-) in Divalent Metal (M2+) Adsorption on Oxide and Hydroxide Surfaces in Salt Solutions. *Am. J. Sci.* **1999**, *299*, 828–899.
- Fukushi, K. and Sverjensky, D. A. A predictive model (ETLM) for arsenate adsorption and surface speciation on oxides consistent with spectroscopic and theoretical molecular evidence. *Geochim. Cosmochim*. *Acta.* **2007**(a), *71*, 3717–3745.
- Fukushi, K.; Sverjensky, D. A. A Surface Complexation Model for Sulfate and Selenate on Iron Oxides Consistent with Spectroscopic and Theoretical Molecular Evidence. *Geochim. Cosmochim. Acta.* **2007**(b), *71* (1), 1−24.
- Fukushi, K.; Aoyama, K.; Yang, C.; Kitadai, N.; Nakashima, S. Surface complexation modeling for sulfate adsorption on ferrihydrite consistent with in situ infrared spectroscopic observations. *Applied Geochemistry*. **2013**, *36*, 92–103.
- Gustafsson, J. P. Visual MINTEQ Version 3.1. Stockholm, Sweden **2018**.
- Helgeson, H. C.; Kirkham, D. H.; Flowers, G. C. Theoretical Prediction of the Thermodynamic Behavior of Aqueous Electrolytes at High Pressures and Temperatures: IV. Calculation of Activity Coefficients, Osmotic Coefficients, and Apparent Molal and Standard and Relative Partial Molal Properties to 600 ˚. *Am. J. Sci.* **1981**, *281* (10), 1249–1516.
- Kanematsu, M.; Young, T. M.; Fukushi, K.; Green, P. G.; Darby, J. L. Extended triple layer modeling of arsenate and phosphate adsorption on a goethite-based granular porous adsorbent. *Environmental science & technology*. **2010**, *44*, 3388–3394.
- Kitadai, N.; Nishiuchi, K; Tanaka, M. A comprehensive predictive model for sulfate adsorption on oxide minerals. *Geochim. Cosmochim. Acta*. **2018**, *238*, 150−168.
- Kobayashi, Y.; Fukushi, K.; Kosugi, S. A Robust Model for Prediction of U(VI) Adsorption onto Ferrihydrite Consistent with Spectroscopic Observations. *Environ. Sci. Technol.* **2020**, *54*, 2304-2313.
- Nagata, T.; Fukushi, K.; Takahashi, Y. Prediction of Iodide Adsorption on Oxides by Surface Complexation Modeling with Spectroscopic Confirmation. *J. Colloid Interface Sci.* **2009**, *332* (2).
- Nagata, T.; Fukushi, K. Prediction of iodate adsorption and surface speciation on oxides by surface complexation modeling. *Geochim. Cosmochim. Acta.* **2010**, *74*, 6000–6013.
- Sahai, N.; Sverjensky, D. A. Evaluation of internally consistent parameters for the triple-layer model by the systematic analysis of oxide surface titration data. *Geochim. Cosmochim. Acta* **1997**, *61* (14) 2801−2826.
- Sahai, N.; Sverjensky, D. A. GEOSURF: a computer program for modeling adsorption on mineral surfaces from aqueous solution. *Computers and Geosciences.* **1998**, *24* (9), 853–873.
- Sverjensky, D. A. Interpretation and prediction of triple-layer model capacitances and the structure of the oxide-electrolyte-water interface. *Geochim. Cosmochim. Acta*. **2001**, *65*(21), 3643−3655.
- Sverjensky, D. A. Standard States for the Activities of Mineral Surface Sites and Species. *Geochim. Cosmochim. Acta.* **2003**, *67* (1), 17–28.
- Sverjensky, D. A. Prediction of Surface Charge on Oxides in Salt Solutions: Revisions for 1:1 (M+L-)

Electrolytes. *Geochim. Cosmochim. Acta.* **2005**, *69* (2), 225–257.

- Sverjensky, D. A. Prediction of the speciation of alkaline earths adsorbed on mineral surfaces in salt solutions. *Geochim. Cosmochim. Acta*. **2006**, *70*, 2427−2453.
- Sverjensky, D. A.; Fukushi, K. A predictive model (ETLM) for As (III) adsorption and surface speciation on oxides consistent with spectroscopic data. *Geochim. Cosmochim. Acta*. **2006**(a), *70*, 3778−3802.
- Sverjensky, D. A.; Fukushi, K. Anion Adsorption on Oxide Surfaces: Inclusion of the Water Dipole in Modeling the Electrostatics of Ligand Exchange. *Environmental Science & Technology*. **2006**(b), *40*, 263–271.
- Sverjensky, D. A.; Sahai, N. Theoretical prediction of single-site surface-protonation equilibrium constants for oxides and silicates in water. *Geochim. Cosmochim. Acta*. **1996**, *60*(20), 3773−3797.
- Usiyama, T.; Fukushi, K. Predictive Model for Pb(II) Adsorption on Soil Minerals (Oxides and Low-Crystalline Aluminum Silicate) Consistent with Spectroscopic Evidence. *Geochim. Cosmochim. Acta* **2016**, *190*, 134–155.
- Venema, P.; Hiemstra, T.; van Riemsdijk, W.H. Multisite cadmium adsorption on goethite. *J. Colloid Interface Sci.* **1996**, *183*, 515-527.