

Independent Modelling Exercise

Developing a Surface Complexation Model

In this independent project, you will develop a surface complexation model. The exercise is based on a problem we developed in my research group, with details published in the Journal of Chemical Education [1]. The exercise is based on work addressing the removal of toxic arsenic from contaminated drinking and surface waters [2, 3]

Learning Objectives

- Familiarise you with the geochemical code PHREEQC, commonly used in environmental research and consulting, along with the instruction manual.
- Practice writing and running input files and manipulating output files
- Define a conceptual model for the chemical problems we wish to solve, outlining key processes, their sequences, and the required data (equilibrium constants)
- Define the solutions, solid surfaces, and reaction equilibria necessary for your model
- Construct a surface complexation model to predict the adsorption of arsenic on goethite mineral surfaces
- Use the geochemical model developed to conduct experiments determining how changes in pH and ionic strength affect the adsorption and mobility of arsenic in groundwater systems.

Literature - some suggested and some needed

I recommend reading two papers to understand the background of our model exercise.

First, the chapter by Zhu and Anderson on Adsorption Modelling [4]. This paper outlines the adsorption formalism in geochemical modelling and the expression of surface reactants. The same details are in the keynote SURFACE_MASTER_SPECIES description found in the PHREEQC manual's keyword section [5].

Second, read our paper in the Journal of Chemical Education for more details on the exercise background [1]

The critical paper by Dixit and Hering provides essential parameters to characterise your sorbent: surface area, reaction sites, logk values for various equilibrium reactions, etc. [6]. See Tables 1 and 2.

Introduction

Introduction to interface processes and adsorption

Crucial geochemical reactions occur at the fluid-solid interface. A key reaction is the adsorption and desorption of substances onto minerals, regulating the mobility of these toxic elements in groundwater.

Adsorption to a solid surface can occur

- via physisorption – a physical bonding between the sorbent (solid) and sorbate (the adsorbed molecule) due to van der Waals interactions, or
- via chemisorption – the formation of a chemical bond (ionic or covalent) between the sorbent and sorbate.

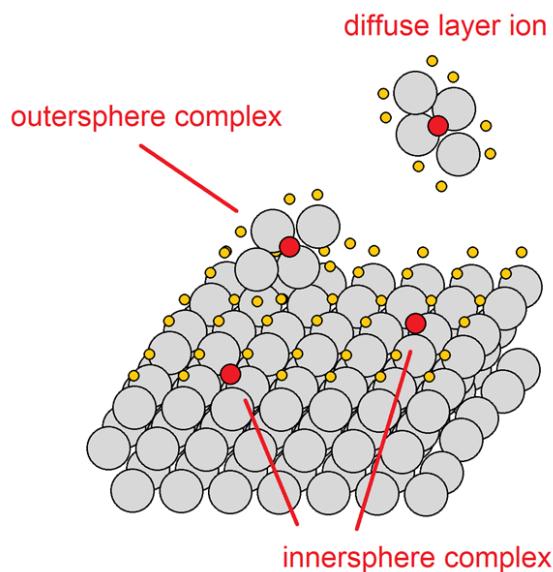


Figure 1: Schematic of innersphere andoutersphere complexes

Chemisorption creates a ‘surface complex’ akin to a metal-ligand complex in solution. When the sorbate retains its solvation sphere (water ligands) and binds electrostatically, it is termed an ‘outer sphere complex.’ When a new covalent bond forms between the sorbate molecule and solid surface, it is termed an ‘*inner sphere complex*.’

Adsorption Isotherms

Scientists and engineers often model adsorption processes using isotherms. These are generally

- the Langmuir model describes monolayer adsorption (where the solid surface is covered by a

single layer of sorbate molecules).

$$q_e = Q_{\max} \cdot \frac{C_e K_L}{1 + C_e K_L} \quad (1)$$

- the Freundlich model addresses non-monolayer adsorption.

$$q_e = K_F C_e^{1/n} \quad (2)$$

- the BET adsorption isotherm describes complex processes, including monolayer physisorption and pore filling.

These models have *parameters* that define sorbate binding at monolayer coverage and the strength of sorbate-sorbent interaction. Each isotherm model is valid only under specific adsorption conditions; they are insensitive to changes in pH, ionic strength, competitor ions, and other factors that geochemists consider in natural systems.

These models were developed to describe controlled experiments with constant pH, ionic strength, and no competing ions.

- Neither model accounts for changes in environmental conditions during water treatment setup in new locations, groundwater parameter changes due to excessive pumping, or pre-treatment failures.
- For real-life applications, we need models that are sensitive to these parameter changes.

Surface Complexation Models

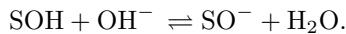
We model the influence of water parameters on adsorption using *Surface Complexation Modelling*. This provides a comprehensive chemical description of the system. We consider sorbate binding to surface hydroxyl sites (S-OH, where S denotes surface) and model adsorption as an equilibrium process.

Each surface complexation reaction is described by a chemical equilibrium equation with an equilibrium constant, log(K). Incorporating logK for various species (e.g., carbonate, which weakly binds to surfaces) enables us to include sensitivity to competitors.

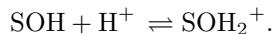
Many sorbates (e.g., HCO_3^- , HAsO_3^{2-} , Na^+ , Cl^- , Pb^{2+} , etc.) are charged, influencing the strength of surface complexation. If the mineral surface is positively charged, positive sorbate ions will be repelled, resulting in weaker binding, whilst negative sorbates will bind more strongly.

The surface charge of minerals arises from the acidity of surface hydroxyl groups (S-OH, where S stands for ‘solid’), which

can deprotonate at high pH, i.e.,



or protonate at low pH, i.e.,



Surface charge

Surface charge results from adsorbed electrolyte ions. Surface charge is typically incorporated into the Surface Complexation Model (SCM). The potential energy is strongest at the surface and diminishes towards the solution, as the surface charge becomes countered by a build-up of electrolyte counter-ions near the solid surface.

This is called the ‘Electrical Double Layer,’ as we have two layers of charge, e.

1. the plane of the solid surface and
2. the region of counter ions with opposite charge to neutralise the charge (see Figure 2).

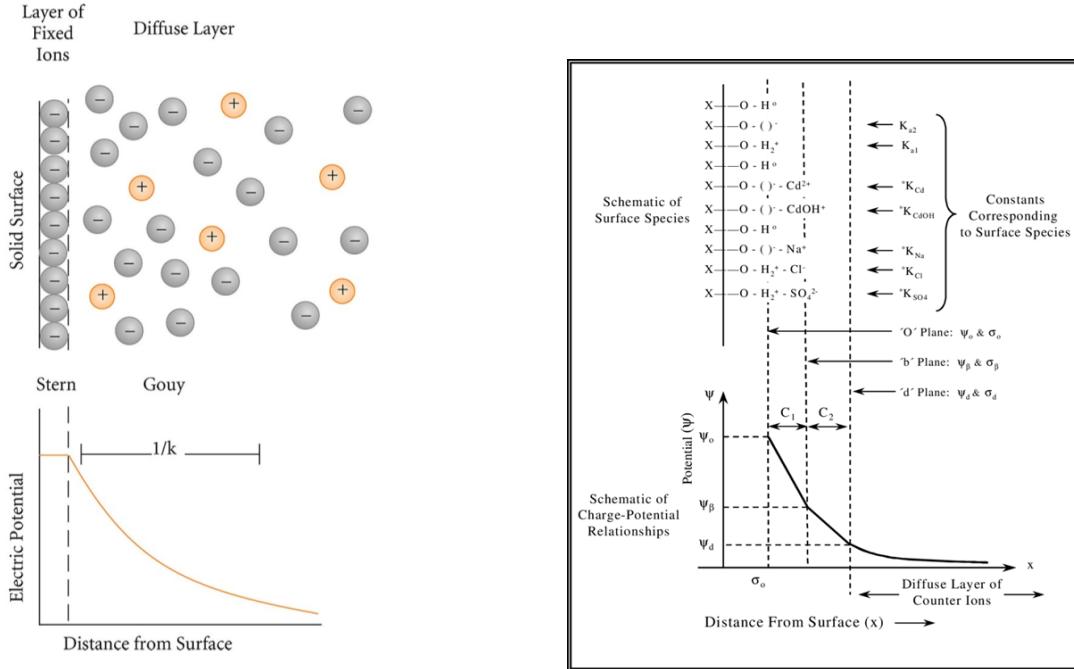


Figure 2: Schematic and formalism used in surface models to describe the charge at the surface

The double layer affects the thermodynamic (or intrinsic) equilibrium constant. We express this as

$$K_{\text{app}} = K_{\text{int}} \exp \left(\frac{\Delta Z F \Psi}{RT} \right) \quad (3)$$

where ΔZ denotes the change in surface charge from sorption reactions, and Ψ is the surface potential in volts.

The exponential term, known as the electrostatic or coulombic correction factor, serves as an activity coefficient for the long-range effects of charged surface groups

The concept of MASTER_SPECIES

PHREEQC has ‘master species’ and ‘species.’ Each species is a type of chemical or molecule, while master species serve as building blocks for each molecule.

Considering the ‘master species’ CO_3^{2-} and H^+ , we can combine these blocks in four ways to create four distinct ‘species’

1. H^+
2. CO_3^{2-}
3. HCO_3^-
4. H_2CO_3

Defining the equilibrium constants for each species from its master species generates our chemical speciation problem.

Using PHREEQC, we could calculate changes in carbonate speciation based on pH and other water quality parameters of interest. (See Tutorial on Solubility and Speciation).

PHREEQC incorporates solid surfaces and precipitation/dissolution reactions. Here, we have SURFACE_SPECIES, which are our surface complexes formed from our SURFACE_MASTER_SPECIES and SOLUTION_SPECIES.

Our Geochemical Problem

The aim of this exercise is to set a surface complexation model for arsenic adsorption on iron oxides. To this end, we develop a conceptual framework using surface complexation theory.

1. First, we quantify the aqueous acid–base speciation of arsenic acid across pH 3–9 to determine dominant arsenate species as a function of pH.
2. Second, we characterize the protonation and deprotonation behavior of surface hydroxyl groups on iron oxides to determine surface charge development and the point of zero charge.
3. Finally, we couple aqueous arsenate speciation with surface site equilibria to simulate adsorption via surface complexation reactions.

This modular approach allows mechanistic interpretation of pH-dependent adsorption behavior and provides a transparent pathway for model calibration and validation.

Conceptual Model

Figure 3 is a sketch of the conceptual model I developed. We aim to set a surface complexation model for arsenic adsorption on iron oxide. To this end, I break the problem into four steps as described above.

First, I investigate the speciation of arsenic in aqueous solution, i.e., which chemical species dominates at each pH. This is fundamentally an acid base reaction, and I need to outline the deprotonation steps of arsenic acid. (H_3AsO_4). I conduct this for one pH, i.e., pH 7, and then for a range of pH values from 3 to 9. (Experiments 1 and 2)

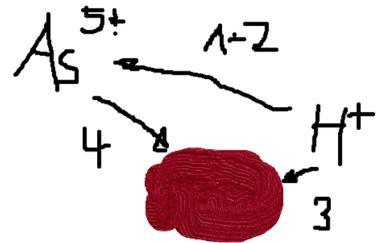


Figure 3: Conceptual model underlying my SCM model

Second, I investigate the acid base reaction of iron oxides with protons in solution, again in the form of equilibrium reactions. This enables me to calculate and identify the range of my sorbent surface in both positive and negative cases and to calculate the overall surface charge Q.

Finally, I combine the codes from steps 1 and 2 to investigate arsenic adsorption on iron oxide, controlled by arsenic speciation in solution and the surface charge of iron oxide.

Here are the steps again

1. Arsenic speciation at certain pH
2. Arsenic speciation over pH range
3. Surface acidity
4. Arsenic adsorption

Conducting Experiments, Writing the Codes, and Processing the Data

For each exercise, save your input and output files with a unique name to facilitate error backtracking.

The materials we need is

1. PHREEQC Manual
2. PHREEQC programme (access via software hub or downloaded)
3. These lecture notes
4. The Dix and Hering paper from Web of Science or Git Hub [6] to get the parameters needed for our model (Tables 1 and 2).
5. INPUT FILE from GitHub to verify your coding accuracy.

Constructing the Surface Complexation Model

Step 1: A Simple Aqueous System

First, we want to investigate the Arsenic species present at a certain pH.

1. Change the PHREEQC database to llnl.dat. To do this, go to Options > Set Default Database and click “...” to browse
2. First, we consider only the aqueous environment (no goethite, no surface complexation). You will need to define your solution master species
 - (a) Add the keyword block **SOLUTION_MASTER_SPECIES**
 - (b) On the next line, define the As(V) master species by entering
 $\text{As}(+5)$ H_2AsO_4^- 0.0 As 74.92
 - (c) Finish the block with a new line stating END
3. Next, define the different solution species formed by the sequential protonation of the arsenate anion
 - (a) Start the keyword block by typing **SOLUTION_SPECIES**
 - (b) Type the reaction formula for the first protonation
 $\text{AsO}_4^{3-} + \text{H}^+ \rightleftharpoons \text{HAsO}_4^{2-}$
 - (c) On the line below, define the equilibrium constant for this reaction by typing
logk 11.60
You find the values in Table 1 and 2 in the Dixit and Herring paper.
 - (d) On the next lines, add other possible species by writing reactions for the arsenate anion plus two and three protons, using the equilibrium constants from the literature [6]
 - (e) END this keyword block
4. Now that you have defined the possible chemical species and the equilibrium constants that govern their balance, you need to define the aqueous system and its conditions
 - (a) Create a new solution with the ID of “1” by typing **SOLUTION 1**
 - (b) Define the pH as 5 as follows pH 7.0
 - (c) Add 0.1 M of chloride by typing
Cl 0.1 mol/kgw
 - (d) Add the same amount of sodium (it’s important to ensure charge balance by having equivalent concentrations of cations and anions).
 - (e) Add 100 ppb (ug/L) arsenate as follows
 $\text{As}(+5)$ 100 ug/kgw
 - (f) END the solution block
5. Now run your first model
 - (a) Click RUN and Start

- (b) You will see an Output file open (and also saved to your folder)
 - (c) Which is the most prominent arsenic species under these conditions? What are the concentrations of each species?

6. Try changing the pH from 7 to 3 and then to 11, running the model again each time.

 - (a) How does the speciation of arsenic change with pH?
 - (b) What do we see, and how can we explain the pH dependence of arsenic speciation?

Step 2: pH dependence of Arsenic speciation

Now we want to look how arsenic speciation changes with pH.

- (d) Enter the name for the first species, e.g. AsO₄-3
 - (e) For the x-values drag around the pH data (column G for me)
 - (f) For the y-values select the data under the column labelled “m_ASO₄-3”
 - (g) Repeat for each species
 - (h) Add axis titles and a legend to your figure
 - (i) Save the spreadsheet with a new name so that we don’t accidentally overwrite it
8. You will have to close the output spreadsheet each time you want to run the model again (PHREEQC won’t overwrite the output file)

Step 3: Surface Acidity of Goethite

We now examine the protonation and deprotonation of the Goethite surface Groups. (S-OH) that extend into the solution.

1. Next, we want to introduce the goethite mineral to the model. We will first look at the surface acidity – the protonation and deprotonation of S-OH surface hydroxyl groups. These are the active sites where arsenic will bind.
2. Below your SOLUTION_SPECIES keyword block start the key word block SURFACE_MASTER_SPECIES
3. Below this define the surface master species S-OH by typing
Surf_Surf_OH
4. This component will be used to build our surface complexes.
5. Next start the SURFACE_SPECIES keyword block
 - (a) Considering surface acidity, we have three possibilities for the surface hydroxyl
 - i. Remaining unchanged as S-OH (or Surf_OH)
 - ii. Becoming protonated as SOH₂⁺ (or Surf_OH+2)
 - iii. Becoming deprotonated as S-O⁻ (or Surf_O-)
 - (b) Type in the formulae for each reaction, similar to the aqueous reactions. Additionally, add the log_k values using the acidity constants from the literature
 - i. Note that we need to define S-OH with a log(K) value of zero. Thus, one of your equations will read
Surf_OH = Surf_OH
log_k 0.0
6. Now we have our surface acidity reactions we need to create the surface, just like we previously created our solutions
 - (a) Start the keyword block SURFACE 1

- (b) State that we will define the concentration of surface hydroxyls in terms of ‘site density’ which takes the units ‘sites nm⁻²’, by typing-sites DENSITY. We could alternatively define our surface hydroxyls as ‘mol/L’
- (c) Define the surface by typing
- ```
Surf_OH <density> <surface area> <concentration>
where site density (sites nm-2), surface area (m2g-1) and solid concentration (g L-1) are all found in the literature
```
- (d) END the block
7. What we do next is mix the surface with the solution and see what speciation we get once we reach equilibrium. We only need one solution to do this, so you can delete all solutions except for SOLUTION 1, which should be at pH 1
- (a) Change the arsenic concentration to zero, since we will just look at surface acidity
8. We can use the PHASES keywords to mix the surface and solution, buffering to a specific pH
- (a) Underneath the END of SOLUTION 1 add the following
- ```
PHASES
Fix_H+
H+ = H+
log k 0.0
END
```
9. Then we will mix the solution and the surface as follows
- ```
USE SURFACE 1
USE SOLUTION 1
EQUILIBRIUM_PHASES 1
Fix_H+ -3.0 NaOH 11.0
END
```
- (a) This is a ‘pseudo-phase’ adding sodium hydroxide until we reach the pH needed
- i. Here we want pH 3 so we set Fix\_H+ to -3.0 (minus pH ...)
10. Copy and paste the input data from step 7, and now change the -3.0 to -3.5
- (a) This will increase the pH to 3.5
- (b) Repeat this until we have the whole pH range from 3 to 11 in 0.5 step intervals
11. Change the SELECTED\_OUTPUT –molalities to the species we want to look at (Surf\_OH Surf\_OH<sub>2</sub><sup>+</sup> Surf\_O<sup>-</sup>)
12. Run the simulation
13. Add a new column and call it Q (which stands for surface charge). To determine Q we can simply take the concentration of SOH<sub>2</sub><sup>+</sup> and subtract SO<sup>-</sup>. Do this.
14. Plot Q, [SOH], [SOH<sub>2</sub><sup>+</sup>] and [SO<sup>-</sup>] as a function of pH
15. How does surface charge change as a function of pH? Can you explain this?

*Step 4: Surface Complexation of As(V) over goethite*

1. We have now successfully performed (1) arsenic speciation in aqueous solution, and (2) looked at the surface charge of goethite
2. Next, we will add in the arsenic surface complexation reactions to complete our model
  - (a) In the SURFACE\_SPECIES keyword block define your possible surface complexation reactions between S-OH and arsenic, adding in the equilibrium constants from the literature
    - i. Your first entry will be
$$\text{Surf\_OH} + \text{AsO}_4^{3-} + 3\text{H}^+ = \text{Surf\_H}_2\text{AsO}_4 + \text{H}_2\text{O}$$
 $\log_k 31.00$
    - ii. Add all three possible complexes
  - (b) Set the concentration of arsenic to 100 uM, just like in the literature paper
    - i. You could also change the ionic strength from 0.1 to 0.01 M if you want to match the paper more closely
  - (c) Change the species to be printed into the output file, by going to the SELECTED\_OUTPUT keyword block and changing the -molalities
    - i. You will probably want to print each of the different aqueous arsenic species, and each of the arsenic surface complexes
  - (d) Run the model, and in your output, spreadsheet add a new column, labelling it as ‘Total adsorbed Arsenic’
    - i. This column needs to be the sum of the concentrations of each arsenic surface complex
  - (e) Plot the total adsorbed arsenic, as well as each individual surface complex species, as a function of pH
  - (f) What is the trend in total adsorption with pH? How can you explain this? (Think about the surface charge of goethite as a function of pH, and the charge of the aqueous arsenic species)
  - (g) At which pH do we see each individual surface complex appear? Can you ex-plain this?

*Further Experiments - Application of the Surface Complexation Model*

1. Sea water is approximately 0.7 M NaCl. What happens to our surface complexation model as we move from 0.1 M NaCl to 0.7 M NaCl?
  - (a) a. Run the model at a range of different ionic strengths, collecting all the results and plotting together
  - (b) b. Describe what we see and explain this where possible
2. Next let’s look at a ‘break through’ curve. If we construct a philtre system to remove arsenic from drinking water by adsorbing it to goethite, we need to determine how much arsenic can be removed before the material becomes saturated and needs replacement.

- (a) Change the concentration of goethite to 10 g/l
  - (b) Change the ionic strength to 0.01 M
  - (c) We will now need to copy and paste the solution keyword block, changing the amount of arsenic in each solution
  - (d) I used 0, 0.1, 1, 10, 20, 30, 50, 75, 100, 150, 200, 300, 400 and 600 ppm (mg/kgw) As(V)
  - (e) Now you will need to ‘USE’ your SURFACE 1 and a solution, then run EQUILIBRIUM\_PHASES, with the pH fixed to a specific value (I used pH 7)
    - i. So change the number of solution in each of your equilibrium phases blocks
  - (f) Run the model, and there are two ways of plotting the data
    - i. As(V) (aq) as a function of total As(V) added (this is a breakthrough curve)
    - ii. As(V) (adsorbed) (mg arsenic per gram sorbent) versus As(V) (aq) (this is an ‘adsorption isotherm’)
    - iii. Try plotting the data in both ways, you will have to normalise your data to one gram per solid (you are using 10 g/l)
3. Change the ionic strength of your solutions to investigate the effect of salinity.
- (a) Simply change the concentration of Na and Cl and run the model again. Each time you run the model, add the output data as a new curve to your graph.
  - (b) How does salinity affect the breakthrough curve and adsorption isotherm? Is this good or bad for arsenic remediation (cleaning up drinking water)?
4. Calculate the pH adsorption-edge for As(III). How does this compare with the As(V) adsorption edge? Can we explain this in terms of surface charge and the charge of the aqueous arsenic species?

## References

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3. Bullen, J. C. *et al.* Improved accuracy in multicomponent surface complexation models using surface-sensitive analytical techniques: Adsorption of arsenic onto a TiO<sub>2</sub>/Fe<sub>2</sub>O<sub>3</sub> multifunctional sorbent. *Journal of Colloid and Interface Science* **580**, 834–849 (2020).
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6. Dixit, S. & Hering, J. G. Comparison of arsenic(V) and arsenic(III) sorption onto iron oxide minerals: Implications for arsenic mobility. *Environmental Science and Technology* **37**. Cited by: 2155; All Open Access; Green Accepted Open Access; Green Open Access, 4182–4189. <https://www.scopus.com/inward/record.uri?eid=2-s2.0-0042691310&doi=10.1021%2Fes030309t&partnerID=40&md5=c31f2da5df6a2543cdd5e54db2fb9577> (2003).