

### HW 3: Surface complexation Homework assignment and Solution

#### Question 1: extension of example 3.1

If instead we have two types of surface sites on illite surface with the following reactions and parameters, as shown in Table 5. All other conditions remain the same.

- 1) At the specified pH = 8.0, calculate the concentration of surface complexes on the surface sites; what is the pH value after the system reaches equilibrium? What are the dominant surface complex species on solid surface?
- 2) At the specified pH = 4.0, calculate the concentration of surface complexes on the surface sites; what is the pH value after the system reaches equilibrium? What are the dominant surface complex species on solid surface?
- 3) Change pH also to 2.0, 6.0, and 10.0 and run simulations. Combining simulation results from 1) – 3), plot total sorbed Cr(VI) and Na(I) as a function of pH. How does pH change the sorbed concentration of Na(I) and Cr(VI)?
- 4) at the pH of 8.0, run the simulation using the specific surface area of 1, 5, 25, 50 m<sup>2</sup>/g. Combining simulation results from 1), plot total sorbed Cr(VI) and Na(I) as a function of specific surface area. How does specific surface area change the sorbed concentrations for Na(I) and Cr(VI)?

Table 5. Initial conditions, surface complexation reactions and constants <sup>21</sup>

Initial conditions	Value
Temperature	25°C
Solution volume	250 mL
pH	8.0
Total CrO <sub>4</sub> <sup>-</sup>	9.61 × 10 <sup>-5</sup> mol/L
Na <sup>+</sup>	0.01 mol/L
Cl <sup>-</sup>	0.01 mol/L
K <sup>+</sup>	18.5 × 10 <sup>-5</sup> mol/L
Site density ≡ SiOH	1.0 × 10 <sup>-6</sup> mol/m <sup>2</sup>
≡ AlOH	0.1 × 10 <sup>-6</sup> mol/m <sup>2</sup>
Illite specific surface area	15.36 m <sup>2</sup> /g
Illite volume fraction	0.003
Reactions	Log K
≡ SiOH + H <sup>+</sup> ⇌ ≡ SiOH <sub>2</sub> <sup>+</sup>	0.95
≡ SiOH ⇌ ≡ SiO <sup>-</sup> + H <sup>+</sup>	-6.59
≡ SiOH + Na <sup>+</sup> ⇌ ≡ SiONa + H <sup>+</sup>	-6.60
≡ SiOH + CrO <sub>4</sub> <sup>2-</sup> + 2H <sup>+</sup> ⇌ (≡ SiOH <sup>0</sup> - H <sub>2</sub> CrO <sub>4</sub> <sup>0</sup> ) <sup>0</sup>	14.50
≡ AlOH + H <sup>+</sup> ⇌ ≡ AlOH <sub>2</sub> <sup>+</sup>	5.70
≡ AlOH ⇌ ≡ AlO <sup>-</sup> + H <sup>+</sup>	-11.40
≡ AlOH + Na <sup>+</sup> ⇌ ≡ AlONa + H <sup>+</sup>	-9.15
≡ AlOH + Cl <sup>-</sup> + H <sup>+</sup> ⇌ ≡ AlOH <sub>2</sub> Cl	7.90
≡ AlOH + CrO <sub>4</sub> <sup>2-</sup> + H <sup>+</sup> ⇌ (≡ AlOH <sub>2</sub> <sup>+</sup> - CrO <sub>4</sub> <sup>2-</sup> ) <sup>-</sup>	9.42
≡ AlOH + CrO <sub>4</sub> <sup>2-</sup> + 2H <sup>+</sup> ⇌ (≡ AlOH <sub>2</sub> <sup>+</sup> - HCrO <sub>4</sub> <sup>-</sup> ) <sup>0</sup>	16.30

**Solution: Read from the output file \*.out corresponding to \*.in**

1) After the reaction, pH = 7.97

Species	Moles/BulkVolume(m <sup>3</sup> )	Mole Fraction (%)
SiO <sup>-</sup>	1.296E-02	76.6
SiONa	3.948E-03	23.3
SiOH	1.851E-05	0.109
SiOH <sub>2</sub> <sup>+</sup>	6.022E-08	0.000356
(≡SiOH <sup>0-</sup> - H <sub>2</sub> CrO <sub>4</sub> <sup>0</sup> ) <sup>0</sup>	4.041E-08	0.000239
AlOH <sub>2</sub> <sup>+</sup>	5.445E-04	95.1
AlOH <sub>2</sub> Cl	2.241E-05	3.92
AlOH	2.976E-06	0.520
AlONa	1.789E-06	0.313
(AlOH <sub>2</sub> <sup>+</sup> -HCrO <sub>4</sub> <sup>-</sup> ) <sup>0</sup>	4.098E-07	0.0716
(AlOH <sub>2</sub> -CrO <sub>4</sub> <sup>2-</sup> ) <sup>-</sup>	1.475E-07	0.0258
AlO <sup>-</sup>	3.226E-08	0.00564

The dominant species on solid surface is SiO<sup>-</sup>.

2) After the reaction, pH = 4.92

Species	Moles/BulkVolume(m <sup>3</sup> )	Mole Fraction (%)
SiO <sup>-</sup>	7.042E-04	16.1
SiONa	5.765E-06	0.131
SiOH	3.101E-05	0.707
SiOH <sub>2</sub> <sup>+</sup>	3.109E-06	0.0709
(≡SiOH <sup>0-</sup> - H <sub>2</sub> CrO <sub>4</sub> <sup>0</sup> ) <sup>0</sup>	3.642E-03	83.0
AlOH <sub>2</sub> <sup>+</sup>	8.734E-04	25.9
AlOH <sub>2</sub> Cl	1.338E-03	39.7
AlOH	1.549E-07	0.00459
AlONa	8.116E-11	0.00000241
(AlOH <sub>2</sub> <sup>+</sup> -HCrO <sub>4</sub> <sup>-</sup> ) <sup>0</sup>	1.148E-03	34.0
(AlOH <sub>2</sub> -CrO <sub>4</sub> <sup>2-</sup> ) <sup>-</sup>	1.341E-05	0.398
AlO <sup>-</sup>	5.448E-11	0.00000162

The dominant species on solid surface is (≡SiOH<sup>0-</sup>-H<sub>2</sub>CrO<sub>4</sub><sup>0</sup>)<sup>0</sup>.

3) When pH = 2, 4, 6, 8, and 10,

Species (sorbed)	pH=10	pH=8	pH=6	pH=4	pH=2
Total sorbed Na(I)	1.50E-02	3.95E-03	9.24E-05	5.77E-06	2.66E-08
Total sorbed Cr (VI)	7.49E-10	5.98E-07	4.86E-04	4.80E-03	2.32E-02

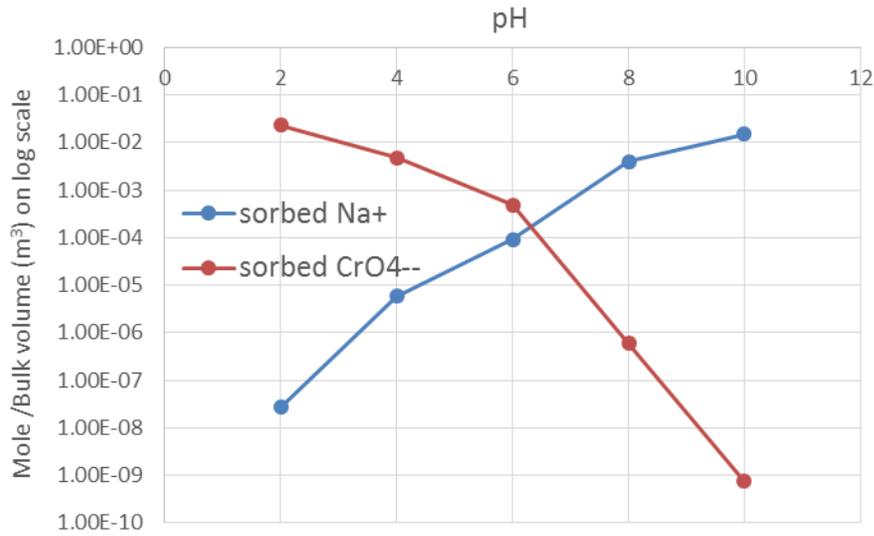
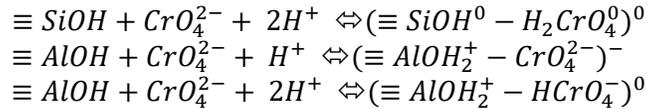


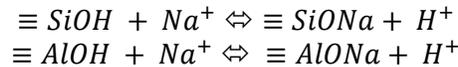
Figure 3. The impact of pH on total sorbed Na(I) and Cr(VI) on surface site.

### Discussion:

The above table and figure show that the increasing pH significantly reduced sorbed Cr(IV) and increased concentration of and Na(I). The sorption of CrO<sub>2</sub><sup>-</sup> on ≡SiOH and ≡AlOH under acidic condition is through the following reactions:



When the pH decreases (with more available H<sup>+</sup> in solution), the concentrations of (≡ SiOH<sup>0</sup> - H<sub>2</sub>CrO<sub>4</sub><sup>0</sup>)<sup>0</sup>, (≡ AlOH<sub>2</sub><sup>+</sup> - CrO<sub>4</sub><sup>2-</sup>)<sup>-</sup>, and (≡ AlOH<sub>2</sub><sup>+</sup> - HCrO<sub>4</sub><sup>-</sup>)<sup>0</sup> increase, resulting in more sorbed CrO<sub>4</sub><sup>2-</sup> on the surface site. The presence of higher H<sup>+</sup> will lead to a higher tendency of reaction toward the left direction as follows:



So the decreased pH (with more available H<sup>+</sup> in the solution) will lead to decrease in sorbed Na(I) on surface sites.

4) At pH = 8, specific surface area (SSA) of 1, 5, 25, 50 m<sup>2</sup>/g

Species (sorbed)	SSA=1	SSA=5	SSA=25	SSA=50
Total sorbed Na(I)	2.47E-04	1.26E-03	6.49E-03	1.31E-02
Total sobed Cr(VI)	4.31E-08	2.06E-07	9.48E-07	1.84E-06

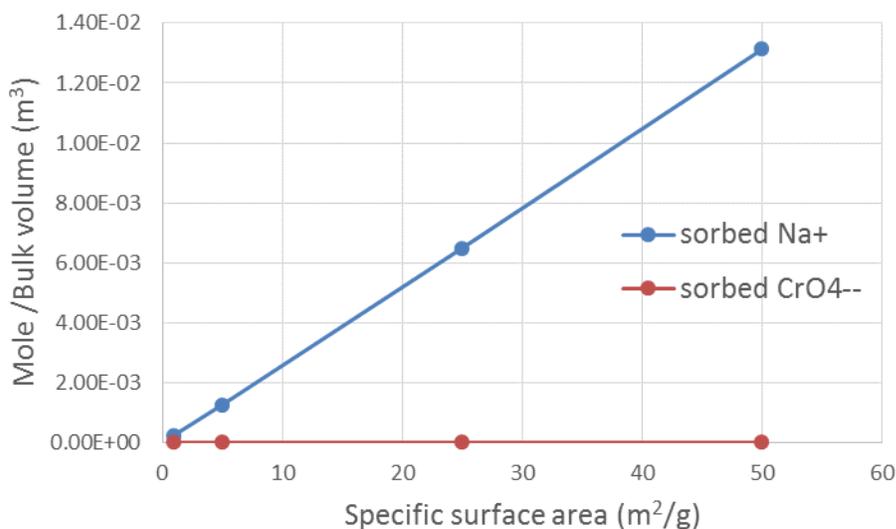


Figure 4. The impact of specific surface area on total sorbed Na(I) and Cr(VI) on surface site. The increasing specific surface area results in linear increase in both sorbed Na(I) and Cr(VI). The blue line shows this trend. Please note that the red line represents sorbed Cr(VI), which is in the range of  $10^{-6}$  to  $10^{-8}$  mol/m<sup>3</sup>. So the linear increase for red line does not visually appear in the above figure.

#### Discussions:

The increasing specific surface area results in linear increase in both total sorbed Na(I) and Cr(VI) on surface site. This is because larger SSA means more surface sites and available  $\equiv SiOH$  and  $\equiv AlOH$ , which will adsorb more Na(I) and Cr(VI) from solution as specific surface area increases.

#### Question 2 (optional):

Set up a batch experiment model for  $AsO_4^{3-}$  sorption on  $Fe(OH)_3$  and run to understand how the sorbed concentration is affected by important parameters. The initial conditions and parameters are shown in Table 6.

- 1) Effect of initial pH on the adsorption amount of  $AsO_4^{3-}$ ,  $PO_4^{3-}$  and  $Na^+$  by setting initial pH at 2, 4, 6, 7, 8 and 10, respectively. Plot the sorption amount of the three ions as a function of pH. Describe the comparison and explain your observations.
- 2) Effect of  $Na^+$  concentration on the adsorption amount of  $AsO_4^{3-}$ ,  $PO_4^{3-}$  and  $Na^+$  by setting the  $Na^+$  conc. at  $10^{-4}$ ,  $10^{-3}$ ,  $10^{-2}$ ,  $10^{-1}$  and 1 mol/L, respectively. Plot the sorption amount of the three ions as a function of  $Na^+$  conc. Describe the comparison and explain your observations.
- 3) Effect of equilibrium constant on the adsorption amount of  $AsO_4^{3-}$ ,  $PO_4^{3-}$  and  $Na^+$  by setting the LogK for  $AsO_4^{3-}$  surface complexation reaction at 15.6, 16.6, 17.6, respectively. Plot the sorption amount of the three ions as a function of LogK. Describe the observations and explain why.

Table 6. Initial conditions, surface complexation reactions and constants <sup>50, 51</sup>

Initial conditions	Value
Temperature	25°C
pH	7.0
AsO <sub>4</sub> <sup>3-</sup>	0.005 mol/L
Na <sup>+</sup>	0.001 mol/L
Fe <sup>+++</sup>	0

PO4---	0.001 mol/L
<b>Site density</b> $\equiv$ FeOH	$1.0 \times 10^{-6}$ mol/m <sup>2</sup>
Specific surface area	50 m <sup>2</sup> /g
Fe(OH)3 volume fraction	0.2
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<b>Reactions</b>	<b>Log K</b>
$\equiv FeOH + H^+ \rightleftharpoons \equiv FeOH_2^+$	5.10
$\equiv FeOH \rightleftharpoons \equiv FeO^- + H^+$	-10.70
$\equiv FeOH + Na^+ \rightleftharpoons \equiv FeO - Na + H^+$	-9.00
$\equiv FeOH + AsO_4^{3-} + H^+ \rightleftharpoons (\equiv FeOAsO_3)^{2-} + H_2O$	16.6
$\equiv FeOH + PO_4^{3-} + H^+ \rightleftharpoons (\equiv FeOPO_3)^{2-} + H_2O$	16.9
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