

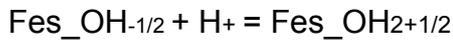
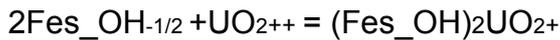
AQUEOUS GEOCHEMISTRY

Practical 3

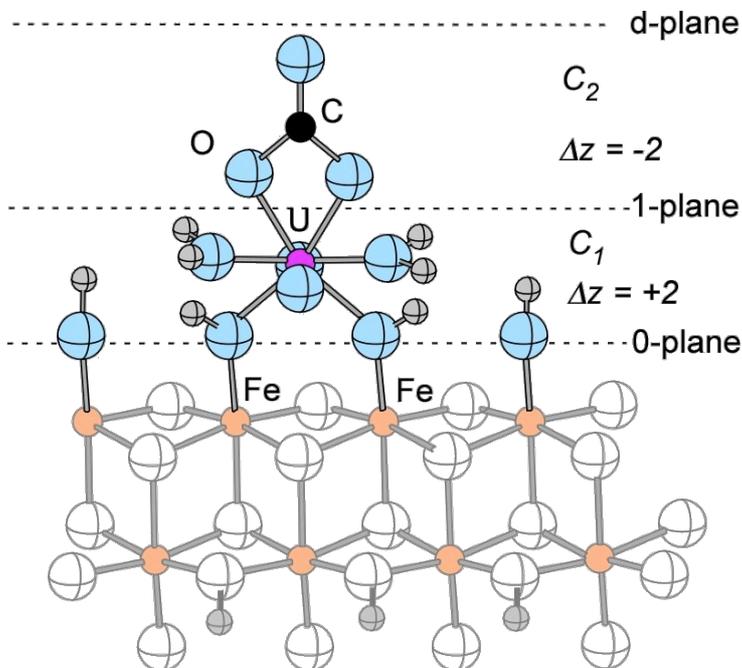
Sorption, Precipitation and Complexation of UO_2^{++} in Soil

Background:

Sherman et al. (2008) developed a surface complexation model for UO_2^{++} sorption to FeOOH . The attached input file allows us to predict sorption as a function of pH, PCO_2 , $[\text{UO}_2]^{++}$ etc. The surface complexation model is based on the reactions:



Here, Fes_OH stands for a surface hydroxyl site (see diagram below). The surface complexation model uses an extended Stern model to treat the electrostatic potential experienced by each complex. For the ternary complex $(\text{Fes_OH})_2\text{UO}_2\text{CO}_3^{-}$, the extended Stern model allows us to distribute the charge between two Stern layers. The charge in each layer is then projected onto the 0-plane and the 1-plane:



We already know equilibrium constants for a variety of aqueous UO_2^{++} complexes that may form and UO_2^{++} minerals that may precipitate out. These are in the `lnl.dat` file. However, we have added some additional complexes in our input file.

Use the attached input file and the `lnl.dat` database to start a series of simulations that enable us to predict the solubility of UO_2^{++} in a soil pore water as a function of relevant chemical variables. Things in particular to explore: what is the effect of P_{CO_2} . What if phosphate and/or carbonate minerals are present? Explain what is going on during each simulation.

Note that the soil has 0.09 g FeOOH (45 m²/g) per kg of soil pore water. What is the sorption capacity of this soil? Calculate a sorption isotherm for U at several pH values. What do these isotherms imply about a K_d model?

After you run some batch simulations, try and set up an advection model to see how the concentration of uranium might change with depth in a soil if there is a source of uranium in cell 1 (e.g., Schoepite dissolving).

TITLE U Sorption on FeOOH

SOLUTION_MASTER_SPECIES

U UO2+2 0.0 U 238.0289
U(6) UO2+2 0.0 238.0290

SOLUTION_SPECIES

UO2+2 = UO2+2
log_k 0

#primary master species for U
#is also secondary master species for U(4)

UO2+2 + H2O = UO2OH+ + H+
log_k -5.20
UO2+2 + 2H2O = UO2(OH)2 + 2H+
log_k -12.15
UO2+2 + 3H2O = UO2(OH)3- + 3H+
log_k -20.25
UO2+2 + 4H2O = UO2(OH)4-2 + 4H+
log_k -32.40
2UO2+2 + 2H2O = (UO2)2(OH)2+2 + 2H+
log_k -5.62
3UO2+2 + 5H2O = (UO2)3(OH)5+ + 5H+
log_k -15.55
UO2+2 + CO3-2 = UO2CO3
log_k 9.94
UO2+2 + 2CO3-2 = UO2(CO3)2-2
log_k 16.61
UO2+2 + 3CO3-2 = UO2(CO3)3-4
log_k 21.56

SURFACE_MASTER_SPECIES

Fes_ Fes_OH-0.5

SURFACE_SPECIES

Fes_OH-0.5 = Fes_OH-0.5
log_k 0.0
-cd_music 0 0 0 0 0

Fes_OH-0.5 + H+ = Fes_OH2+0.5
log_k 9.2
-cd_music 1 0 0 0 0

2Fes_OH-0.5 + UO2+2 = (Fes_OH)2UO2+
log_k 13.8
-cd_music 2 0 0 0 0

```
2Fes_OH-0.5 + UO2+2 + CO3-2 = (Fes_OH)2UO2CO3-
log_k 21.05
-cd_music 2 -2 0 0 0
```

```
PHASES
Fix_H+
H+ = H+
log_k 0.0
END
```

```
# Next, we define a surface with  $4 \times 10^{-5}$  sites/kgw
SURFACE 1
Fes_OH-0.5 4.0E-5 45.3 0.09
-capacitance 0.78 2.0
-cd_music
```

```
SOLUTION 1
units mol/kgw
pH 8.
density 1.0
temp 25.0
Na 0.1
N(5) 0.1 charge
U(6) 1.004E-6 #Explore different total U concs.
```

```
# We can run this for several pH values to get a plot..
```

```
USE solution 1
USE surface 1
EQUILIBRIUM_PHASES 1
Fix_H+ -4.0 HNO3 10.0 #use HNO3 to get below pH 7
CO2(g) -3.5 10000.
Schoepite 0.0 0.0 #allow schoepite to ppt if U is ver
```

```
USE solution 1
USE surface 1
EQUILIBRIUM_PHASES 2
Fix_H+ -8.0 NaOH 10.0 #use NaOH to get pH above 7
CO2(g) -3.5 10000.
Schoepite 0.0 0.0
```

```
USE solution 1
USE surface 1
EQUILIBRIUM_PHASES 3
Fix_H+ -9.0 NaOH 10.0
CO2(g) -3.5 10000.
Schoepite 0.0 0.0
```

```
SELECTED_OUTPUT
-file usorb.txt
```

```
-reset false
-pH true
-total U
-molalities (Fes_OH)2UO2+ (Fes_OH)2UO2CO3-
-equilibrium Schoepite
END
```