Electronic Supplementary Information

Complexation of $UO_2(CO_3)_3{}^{4-}$ with Mg^{2+} at Varying Temperatures and

Its Effect on U(VI) Speciation in Groundwater and Seawater

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Details in U(VI) speciation

U(VI) speciation in Mg^{2+}-rich groundwater condition at 25 °C and 70 °C

Geochemical calculation was conducted by Phreeqc version 3[1] with NEA thermodynamic database[2] for Phreeqc (version 1 released in November 2018, https://www.oecd-nea.org/dbtdb/tdbdata/). Analytical expressions based on isoelectric reactions[3] for ternary $Ca-UO_2-CO_3$ U(VI) species and carbonato U(VI) species were added or revised to obtain temperature-dependent formation constants for the calculation. The analytical expression for magnesite ($MgCO_3$) was taken from Phreeqc database 'sit.dat' based on ThermoChimie TDB[4] (www.thermochimie-tdb.com). The coefficients are listed in Table S1.

$$\log K(T) = A_1 + A_2 \cdot T + \frac{A_3}{T} + A_4 \cdot \log T + \frac{A_5}{T^2}$$
Analytical expression:

Table S1. Analytical expression for temperature-dependent formation constant

$x \cdot Mg^{2+} + y \cdot UO_2^{2+} + z \cdot CO_3^{2-} \leftrightarrow Mg_x(UO_2)_y(CO_3)_z^{2x+2y-2z}$					
(xyz)	A_1	A_2	A_3	A_4	A_5
(011)	444.5811999	8.39388E-02	-28047.08816	-1.57793E+02	2.20870E+06
(012)	453.6162869	8.39388E-02	-28752.23886	-1.57793E+02	2.20870E+06
(013)	448.7377297	8.39388E-02	-25738.37253	-1.57793E+02	2.20870E+06
(113)	887.5214104	1.67878E-01	-53780.23735	-3.15586E+02	4.41739E+06
Magnesite (nat)	-1.31654E+1	0	1.26875E+3	0	0

Simulation of U(VI) extraction from seawater

Simulation of U(VI) complexations with glutarimidedioxime[5] and glutardiamidoxime[6] in seawater was calculated by Visual MINTEQ ver 3.1.[7] Chemical thermodynamic data except for ternary $Mg/Ca-UO_2-CO_3$ and U(VI)-ligands complexations were obtained from NEA TDB.[2] Formation constants of most U(VI) species at 0.5 M NaCl was calculated based on specific ion theory (SIT).[8] Ion interaction coefficients for SIT were taken from NEA TDB[2], preferentially.

Ion interaction coefficients for Mg/Ca-UO_2-CO_3 was taken from PSI Nagra TDB[9] as described in this work. For the minor U(VI) species whose coefficients were not selected in TDB, Davies equation[10] was applied to obtain the formation constants at 0.5 M ionic strength. The data of U(VI)-ligands were used as determined at 0.5 M NaCl in previous works. Complexations of glutarimidedioxime with Mg^{2+} and Ca^{2+} were also considered in this simulation based on the data in previous work.[11]

The temperature effect on ion interaction coefficients was assumed to be negligible. In case seven U(VI) species (UO_2CO_3(aq), $UO_2(CO_3)_2^{2-}$, $UO_2(CO_3)_3^{4-}$, $(UO_2)_3(CO_3)_6^{6-}$, $CaUO_2(CO_3)_3^{2-}$, $Ca_2UO_2(CO_3)_3$(aq), and $MgUO_2(CO_3)_3^{2-}$), the temperature-dependent formation constants were obtained based on isoelectric reactions[3] as suggested in previous[12] and this work. The corrected formation constants are summarized in Table S2.

Table S2. Formation constants at 10, 25, and 40 C for U(VI) simulation.

Reaction	log β' @ I = 0.5 M NaCl		
	25 °C	10 °C	40 °C
$UO_2^{2+} + CO_3^{2-} \leftrightarrow UO_2(CO_3)$(aq)	8.60	8.62	8.63
$UO_2^{2+} + 2CO_3^{2-} \leftrightarrow UO_2(CO_3)_3^{2-}$	15.24	15.14	15.39
$UO_2^{2+} + 3CO_3^{2-} \leftrightarrow UO_2(CO_3)_3^{4-}$	21.83	22.23	21.53
$3UO_2^{2+} + 6CO_3^{2-} \leftrightarrow (UO_2)_3(CO_3)_6^{6-}$	53.89	54.59	53.46
$Ca^{2+} + UO_2^{2+} + 3CO_3^{2-} \leftrightarrow$ $CaUO_2(CO_3)_3^{2-}$	24.31	24.83	23.96
$2Ca^{2+} + UO_2^{2+} + 3CO_3^{2-} \leftrightarrow$ $Ca_2UO_2(CO_3)_3$(aq)	26.42	26.51	26.05
$Mg^{2+} + UO_2^{2+} + 3CO_3^{2-} \leftrightarrow$ $MgUO_2(CO_3)_3^{2-}$	23.33	23.79	23.02

Using the default setting of MINTEQ,[7] van't Hoff equation was applied to obtain formation constants of the U(VI) species whose molar reaction enthalpy has been selected in NEA TDB.[2] For the minor U(VI) species whose enthalpy data has not been reported yet, the temperature effect was assumed to be negligible.

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