

Supporting Information Cover Sheet

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Table S1. Equilibrium constants for oxalic acid, citric acid, uranium and iron hydrolysis reactions and complexation reactions.

Reaction	log K (I=0)	Reference
<i>U hydrolysis</i>		
$\text{UO}_2^{2+} + \text{H}_2\text{O} = \text{UO}_2\text{OH}^+ + \text{H}^+$	-5.20	1
$\text{UO}_2^{2+} + 2\text{H}_2\text{O} = \text{UO}_2(\text{OH})_2^0 + 2\text{H}^+$	-12.10	1
$2\text{UO}_2^{2+} + 2\text{H}_2\text{O} = (\text{UO}_2)_2(\text{OH})_2^{2+} + 2\text{H}^+$	-5.62	1
$3\text{UO}_2^{2+} + 5\text{H}_2\text{O} = (\text{UO}_2)_3(\text{OH})_5^+ + 5\text{H}^+$	-15.55	1
<i>U citrate complexation</i>		
$\text{UO}_2^{2+} + \text{cit}^{3-} = \text{UO}_2\text{cit}^-$	8.71	2
$2\text{UO}_2^{2+} + 2\text{cit}^{3-} = (\text{UO}_2)_2(\text{cit})_2^{2-}$	21.30	3
<i>U oxalate complexation</i>		
$\text{UO}_2^{2+} + \text{ox}^{2-} = \text{UO}_2\text{ox}$	7.38	4
$\text{UO}_2^{2+} + 2\text{ox}^{2-} = \text{UO}_2(\text{ox})_2^{2-}$	11.7	4
$\text{UO}_2^{2+} + 3\text{ox}^{2-} = \text{UO}_2(\text{ox})_3^{4-}$	13.6	4
<i>Fe hydrolysis</i>		
$\text{Fe}^{3+} + \text{H}_2\text{O} = \text{FeOH}^{2+} + \text{H}^+$	-2.19	5
$\text{Fe}^{3+} + 2\text{H}_2\text{O} = \text{Fe}(\text{OH})^{2+} + 2\text{H}^+$	-5.67	5
$\text{Fe}^{3+} + 3\text{H}_2\text{O} = \text{Fe}(\text{OH})_3 + 3\text{H}^+$	-13.60	5
$\text{Fe}^{3+} + 4\text{H}_2\text{O} = \text{Fe}(\text{OH})_4^- + 3\text{H}^+$	-21.60	5
$2\text{Fe}^{3+} + 2\text{H}_2\text{O} = \text{Fe}_2(\text{OH})_2^{4+} + 2\text{H}^+$	-2.85	5
$3\text{Fe}^{3+} + 4\text{H}_2\text{O} = \text{Fe}_3(\text{OH})_4^{5+} + 4\text{H}^+$	6.29	5
<i>Fe citrate complexation</i>		
$\text{Fe}^{3+} + \text{cit}^{3-} = \text{Fecit}$	13.30	5
$\text{Fe}^{3+} + \text{H}^+ + \text{cit}^{3-} = \text{FeHcit}^+$	14.22	5
$\text{Fe}^{3+} + \text{H}_2\text{O} + \text{cit}^{3-} = \text{FeOHcit}^- + \text{H}^+$	10.40	5
$2\text{Fe}^{3+} + 2\text{H}_2\text{O} + 2\text{cit}^{3-} = \text{Fe}_2(\text{OH})_2(\text{cit})_2^{2-} + 2\text{H}^+$	6.20	3
<i>Fe oxalate complexation</i>		
$\text{Fe}^{3+} + \text{ox}^{2-} = \text{Feox}^-$	7.2	3
<i>Citric acid protolysis</i>		
$\text{H}_3\text{cit} = \text{cit}^{3-} + 3\text{H}^+$	-14.29	5
$\text{H}_2\text{cit}^- = \text{cit}^{3-} + 2\text{H}^+$	-11.16	5
$\text{Hcit}^{2-} = \text{cit}^{3-} + \text{H}^+$	-6.39	5
<i>Oxalic acid protolysis</i>		
$\text{H}_2\text{ox} = \text{ox}^{2-} + 2\text{H}^+$	-5.25	3
$\text{Hox}^- = \text{ox}^{2-} + \text{H}^+$	-4.09	3
<i>Ternary Fe-U-citrate complexation</i>		
$\text{Fe}^{3+} \text{UO}_2^{2+} + \text{cit}^{3-} + \text{H}_2\text{O} = \text{FeUO}_2(\text{OH})\text{cit}^+ + \text{H}^+$	17.10	2
$\text{Fe}^{3+} + \text{UO}_2^{2+} + 2\text{cit}^{3-} + 2\text{H}_2\text{O} =$	20.47	2
$\text{FeUO}_2(\text{OH})_2(\text{cit})_2^{3-} + 2\text{H}^+$		

- OECD/NEA Thermodynamic Database Project (TDB) (accessed March 2005).
<http://www.nea.fr/html/dbtdb/>.

2. Kantar, C.; Gillow, J.B.; Harper-Arabie; R., Honeyman, B.D.; Francis, A.J. 2005. Determination of stability constants of U(VI)-Fe(III)-citrate complexes. *Env. Sci. Technol.* 39: 2161-2168
3. Smith, R.M., ; Martell, A.E. *NIST Critical Stability Constants of Metal Complexes Database*; NIST Standard Reference Database 46; U.S. Department of Commerce: Gaithersburg, MD, 1993.
4. Ferri, D.; Iuliano, M.; Manfredi, C.; Vasca, Ermanno; Caruso, T.; Clemente, M.; Fontanella, C.; Dioxouranium(VI) oxalate complexes. *J. Chem. Soc., Dalton Trans.* 2000, 3460-3466.
5. Field, T.B.; McCourt, J.L.; McBryde, W.A.E. Composition and stability of iron and copper citrate complexes in aqueous-solution. *Can. J. Chem.* 1974, 52, 3119-3124.

Speciation modeling was performed using PHREEQCi 2.8 (Parkhurst and Appelo, 1999) and the MINTEQ database edited to include the reactions and constants listed in Table S1.

Parkhurst, D.L.; Appelo, C.J. *User's Guide to PHREEQC (Version 2)- A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations*. Water-Resources Investigations Report 99-4259: United States Geological Survey, Denver, 1999.

Figure S1 shows results of the speciation modeling for the following conditions: I=0.1 M, Fe(III)=0.7 mM, U(VI)=0.4 mM, oxalic acid = 0.18 mM, citric acid = 0.90 mM.

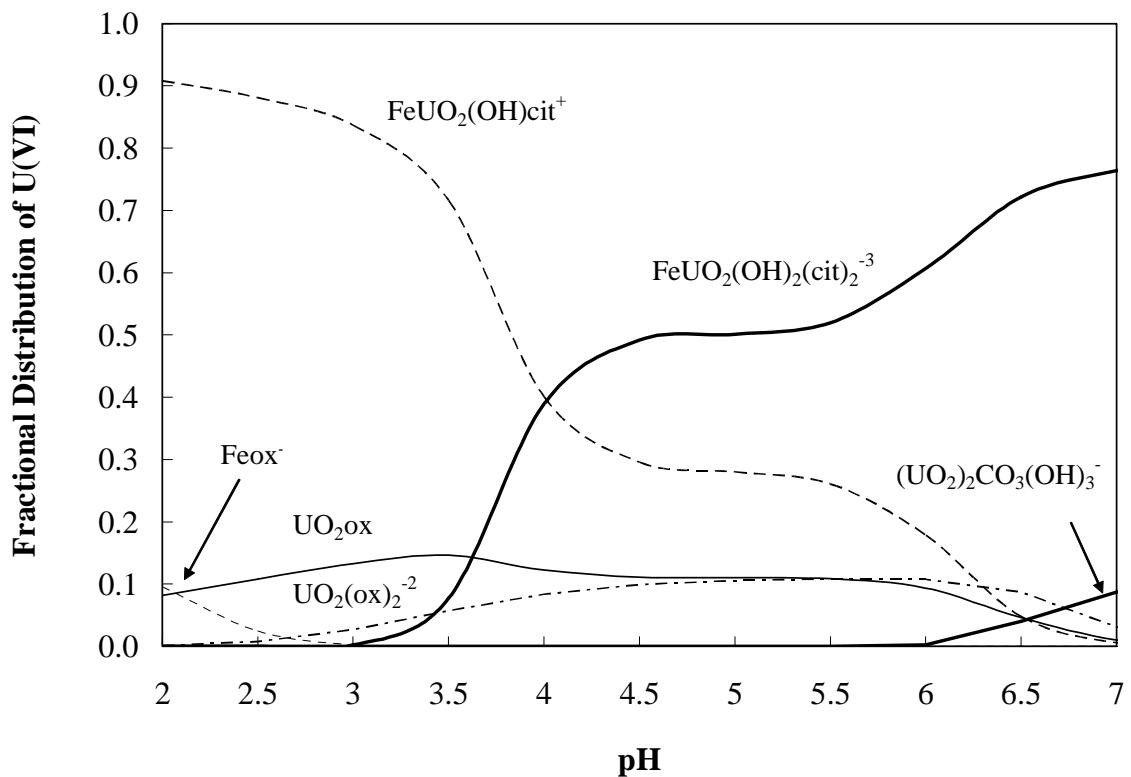


Figure S1. Distribution of solution-phase U(VI) species in equilibrium with air ($P_{\text{CO}_2}=10^{-3.5}$ atm) in the U(VI)-Fe(III)-ox-cit solution as a function of pH including the mixed metal complexes.