Thermodynamic Constraints of Biogenic UO₂ oxidation by Fe(III)-(hydr)oxides: Implications for Uranium Bioremediation Matthew Ginder-Vogel¹, Craig Criddle², and Scott Fendorf¹ 1. Department of Geological and Environmental Sciences: 2. Department of Civil and Environmental Engineering

Introduction

The stability of authigenic uraninite is critical for determining the viability of uranium remediation via in-situ biological uranium precipitation and for discerning natural uranium cycling. While uraninite, a commonly precipitated biogenic U(IV) phase, has an estimated solubility product of 10⁻⁸ to 10⁻¹², it can be rapidly oxidized and remobilized by a variety of common environmental constituents. In addition to molecular oxygen, for example, Mn-oxides rapidly and extensively oxidize UO₂ in the absence of biological activity (3). Nitrate, a common co-contaminant with uranium not only impedes biological uranium reduction, but induces U(IV) oxidation through the production of reactive intermediates (i.e. NO_2^{-1} , NO, and N_2O) in denitrification.

Under common groundwater conditions, the redox couples for U(IV)/U(VI) and Fe(III)-oxide/Fe(II) occur at similar potentials, and small changes in aqueous chemistry can result in the thermodynamic favorability of UO₂ oxidation by Fe(III)oxides (below). Recent work appears to confirm that Fe(III)-oxide minerals play a role in the oxidation of biogenic U(IV). Senko et al. observed oxidation of biogenic U(IV) and concomitant release of Fe(II) in the presence of Fe(III)-oxide minerals, which were produced by nitrate dependent oxidation of Fe(II). Additionally, Fe(III)-oxide minerals have been implicated in U(IV) oxidation under sulfate-reducing and methanogenic conditions (10). However, the evidence for abiotic U(IV) oxidation by Fe(III)-oxides is not conclusive. Interpretation of abiotic U(IV) oxidation experiments may be convoluted by several factors, including, but not limited to: high carbonate concentrations, actively metabolizing microbes, Mn(IV) doping in Fe(III) oxides, remnant microbial, and nitrate reduction intermediates (NO₂, N₂O, and NO). In order to determine conditions under which UO_{2(biogenic)} may be oxidized by common Feoxides, we experimentally examine the abiotic oxidation of biogenic UO₂ by various environmentally relevant ferric iron phases and present a detailed thermodynamic analysis of Fe(III)-oxide promoted U(IV) oxidation.

Representative Fe(III)/Fe(II) and U(VI)/U(IV) Redox Couples

(\ (\	H OX [U(VI)]	Red	Ox [Fe(II)] =	Red 5 x 10 ⁻⁷ M	Ox [Fe(II)]	Red = 10 ⁻⁵ M	р£
0.05	— UO ₂ ²⁺ —	— UO ₂					
0.0			Fe(OH) ₃	– – - Fe ²+			- 0
-0.05	$ UO_2CO_3$	UO2					
-0.1	$UO_{2}(CO_{3})_{3}^{+}$ $(UO_{2})_{2}CO_{3}(OH)_{3}^{-}$ $CaUO_{2}(CO_{3})_{3}^{-2}$ $UO_{2}(CO_{3})_{2}^{-2}$				Fe(OH)₃—	— Fe ²⁺	
-0.15	-	α — μο	(-FeOOH	Fe ²⁺			-2.5
-0.2			Fe ₂ O ₃	– – - Fe ²+ (x-FeOOH—	— Fe ²⁺	
-0.25							
-0.3					Fe_2O_3 —	— Fe ²⁺	

with 3 x 10⁻³ M HCO₃, 10⁻⁶ M U(VI), 10⁻³ M Ca²⁺, and either 5 x 10⁻⁷ or 1 x 10⁻⁵ M Fe(II)

Ovidation Deastion	۸G°-	ΔG° ,
Oxidation Reaction	(kJ/mol)	(kJ/mol)
$Fe(OH)_2 + 0.5 UO_2 + 3 H^+ + Fe^{2+} + 0.5 UO_2^{2+} + 3H_2O$	-60.08	59.72
$Fe(OH)_2 + 0.5 UO_2 + 2.5 H^+ + 0.5 HCO_2^- + 0.5 UO_2CO_2 + Fe^{2+} + 3H_2O_2$	-58 97	40.86
$\frac{Fe(OH)_2 + 0.5 UO_2 + 2 H^+ + HCO_2^- + 0.5 UO_2(CO_2)_2^2 + Fe^{2+} + 3H_2O_2}{Fe(OH)_2 + 0.5 UO_2 + 2 H^+ + HCO_2^- + 0.5 UO_2(CO_2)_2^2 + Fe^{2+} + 3H_2O_2}$	-48.53	31.34
$\frac{Fe(OH)_{2} + 0.5 UO_{2} + 1.5 H^{+} + 1.5 HCO_{2}^{-} + 0.5 UO_{2}(CO_{2})_{2}^{4-} + Fe^{2+} + 3 H_{2}O_{2}}{Fe(OH)_{2} + 0.5 UO_{2} + 1.5 H^{+} + 1.5 HCO_{2}^{-} + 0.5 UO_{2}(CO_{2})_{2}^{4-} + Fe^{2+} + 3 H_{2}O_{2}}$	-33.98	25.92
1000000000000000000000000000000000000	-58 40	1 50
$\frac{10001}{1000000000000000000000000000000$	-44 02	15.88
1000000000000000000000000000000000000	-44 14	35.72
$\frac{10001}{5} + \frac{1000}{5} + $	-48 58	71.22
$\frac{10001 + 0.5002 + 511 + 002}{\text{FeOOH} + 0.51002 + 2.5H^{+} + 0.5HCO2^{-} + 1002CO2 + Fe^{2+} + 2H_{2}O}$	-40.30	52.36
$\frac{100011 + 0.5002 + 2.511 + 0.51003 + 002003 + 10 + 21120}{100000000000000000000000000000000$	-47.40	12.50
$\frac{1}{10001 + 0.5 \text{ UO}_2 + 2 \text{ II} + 1 \text{ IICO}_3 + 002(003)_2 + 100 + 21120}{10001 + 15 \text{ UO}_2 + 15 \text{ H}^2 + 15 \text{ H}^2 + 100 (000)^{4^2} + \text{E}_2^{2^2} + \text{H}_2^{2^2} + \text{H}_2^{2^2} + 100000000000000000000000000000000000$	-37.03	37 42
$\frac{1}{10001} + 0.5 U_{2} + 1.5 H^{+} + 1.5 HCO_{3}^{-} + 0.5 C_{2}^{-} U_{2}^{-} U_{2$	-22.48	12.00
$\frac{1}{10001} + 0.5 UO_2 + 1.5 UO_3 + 1.5 UO_3 + Ca^{-2} + 0.5 Ca^{-2} +$	-40.90	13.00
$\frac{\text{FeOOH} + 0.5 \text{ UO}_2 + 1.5 \text{ H} + 1.5 \text{ HCO}_3 + 0.5 \text{ Ca}}{\text{FeOOH} + 0.5 \text{ UO}_2 + 1.5 \text{ H} + 1.5 \text{ HCO}_3 + 0.5 \text{ Ca}} = 0.25 \text{ (UO}_2 + 1.5 \text{ H}_2 + 1$	-32.32	27.38
$\frac{\text{FeOOH} + 0.5 \text{ UO}_2 + 2 \text{ H} + 0.25 \text{ HCO}_3 0.25 (\text{UO}_2)_2 \text{CO}_3 (\text{OH})_3 + \text{Fe}^2 + 5/4 \text{ H}_2 \text{O}}{2}$	-32.64	47.22
$\frac{0.5 \text{ Fe}_2 \text{O}_3 + 0.5 \text{ UO}_2 + 3 \text{ H}^2 + \text{Fe}^2 + 0.5 \text{ UO}_2^2 + 1.5 \text{ H}_2 \text{O}}{24}$	-39.82	/9.97
$0.5 \text{ Fe}_2\text{O}_3 + 0.5 \text{ UO}_2 + 2.5 \text{ H}^+ + 0.5 \text{ HCO}_3^- + \text{Fe}^2^+ + 1.5 \text{ H}_2\text{O} + 0.5 \text{ UO}_2\text{CO}_3$	-38.72	61.11
$0.5 \text{ Fe}_2\text{O}_3 + 0.5 \text{ UO}_2 + 2 \text{ H}^+ + 1 \text{ HCO}_3^- + \text{ Fe}^{2+} + 1.5 \text{ H}_2\text{O} + 0.5 \text{ UO}_2(\text{CO}_3)_2^{2-}$	-28.28	51.58
$0.5 \text{ Fe}_2\text{O}_3 + 0.5 \text{ UO}_2 + 1.5 \text{ H}^+ + 1.5 \text{ HCO}_3^- + \text{ Fe}^{2+} + 1.5 \text{ H}_2\text{O} + 0.5 \text{ UO}_2(\text{CO}_3)_3^{4-}$	-13.73	46.16
$0.5 \text{ Fe}_2\text{O}_3 + 0.5 \text{ UO}_2 + 1.5 \text{ H}^+ + 1.5 \text{ HCO}_3^- + 0.5 \text{ Ca}^{2+} + \text{Fe}^{2+} + 1.5 \text{ H}_2\text{O} + 0.5 \text{ Ca}_2\text{UO}_2(\text{CO}_3)_3$	-38.15	21.75
$0.5 \text{ Fe}_2\text{O}_3 + 0.5 \text{ UO}_2 + 1.5 \text{ H}^+ + 1.5 \text{ HCO}_3^- + 0.5 \text{ Ca}^{2+} + \text{Fe}^{2+} + 1.5 \text{ H}_2\text{O} + 0.5 \text{ CaUO}_2(\text{CO}_3)_3^{2-}$	-23.77	36.13
$0.5 \text{ Fe}_2\text{O}_3 + 0.5 \text{ UO}_2 + 2 \text{ H}^+ + 0.25 \text{ HCO}_3^- + 0.25 (\text{UO}_2)_2\text{CO}_3(\text{OH})_3^- + \text{Fe}^{2+} + 0.75 \text{ H}_2\text{O}$	-23.89	55.97





					-	
Iron Oxide	[HCO ₃ ⁻] (mM)	Fe(II)_{aq} (μM)	Fe(II) extracted (mmoles mmole ⁻¹ Fe _{total})	U(VI) (µmoles mmole⁻¹ Fe _{total})	Predominant U(VI) Species	G _{reaction} (kJ/mole)
Ferrihydrite	3	6	141.8	2.1	64.2% UO₂(CO₃)₂²⁻ 19.4% UO ₂ (CO ₃) ₃ ⁴⁻ 10.5% UO ₂ CO _{3(aq)} 6.0% (UO ₂) ₂ CO ₃ (OH) ₃	-0.6 1.2 1.7 1.3
Goethite	3	ND	3.6	1.5	$\begin{array}{c} 64.9\% \text{ UO}_2(\text{CO}_3)_2^{2^-} \\ 19.6\% \text{ UO}_2(\text{CO}_3)_3^{4^-} \\ 10.6\% \text{ UO}_2\text{CO}_{3(\text{aq})} \\ 4.6\% (\text{UO}_2)_2\text{CO}_3(\text{OH})_3 \end{array}$	NA
Hematite	3	ND	ND	0.5	66.9% UO ₂ (CO ₃) ₂ ²⁻ 19.6% UO ₂ (CO ₃) ₃ ⁴⁻ 11.0% UO ₂ CO _{3(aq)} 1.6% (UO ₂) ₂ CO ₃ (OH) ₃	NA

Geochemical Condition				
Iron Oxide	[HCO₃⁻] (mM)	Fe(II) aq (μΜ)	Fe(II) extrac (mmoles mmo Fe _{total})	
Ferrihydrite	3	6	141.8	
Ferrihydrite	10	6.8	223.7	
Ferrihydrite	50	22.8	326.5	
Ferrihydrite	100	24.7	342.5	





[Fe(II)_{aq}] (μΜ)	[U(VI)_{aq}] (μΜ)	Notes	Reference
NA	2.5	Day 399 - Prior to EtOH addition	Wu et al., Environ. Sci. Technol. 200_, In Review.
NA	1.5	Day 401 - Beginning of EtOH addition	Wu et al., Environ. Sci. Technol. 200_, In Review.
NA	2.9	Day 404 - Conclusion of EtOH addition	Wu et al., Environ. Sci. Technol. 200_, In Review.
0-500	1-5	Test 40 Well FW034	Istok et al., Environ. Sci. Technol. 2004, 38, 468-475.
100	0.2-1	Well M-13	Anderson et al., Appl. Environ. Microb. 2003, 69, 5884-5891.
0	~100	Soluble Fe(II) is negligible after NO2- addition	Senko et al., Environ. Sci. Technol. 2005, 39, 2529-2536.
NA	60	Soluble U(VI) at 20 d Figure 3	Sani et al., Environ. Sci. Technol. 2005, 39, 2059-2066.
NA	0.1	Day 107 of Figure 1	Wan et al., Environ. Sci. Technol. 2005, 39, 6162-6169.
0.42	1.4	Day 346 of Figure 1 - Steady State	Wan et al., Environ. Sci. Technol. 2005, 39, 6162-6169.