Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Electronic Supplementary Information

The short-term reduction of uranium by nanoscale zero-valent iron (nZVI): role of oxide shell, reduction mechanism and the formation of U(V)-carbonate phases

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Table S1. Preparation methods for the fresh, anaerobically-aged and corroded nZVI particles.

Fresh nZVI (fnZVI)	nZVI synthesized using the method described by Crane *et al.* (2011) and then used within a week.
Aged nZVI (anZVI)	Fresh nZVI that were kept in methanol for a period of 3 months in the anaerobic chamber.
Corroded nZVI (cnZVI)	Fresh nZVI that were reacted with identical solutions as in the main experiments (without uranium) for 6 hr (giving a 1:16 U:Fe molar ratio when reacted with uranium) or 24 hr (giving a 1:9 U:Fe molar ratio).

Crane, R. A.; Dickinson, M.; Popescu, I. C.; Scott, T. B. Magnetite and zero-valent iron nanoparticles for the remediation of uranium contaminated environmental water. *Water Res*. 2011, **45** (9), 2931–2942.

Figure S1. Pourbaix diagram for U at the concentrations used in the experiments (210 μM U(VI), 50 mM NaCl, 5.8 mM $NaHCO_3$ and 4 mM $CaCl_2$). The calculations were performed with the computer speciation program JChess with data from Dong W. and Brooks S.C. (2006) Environ. Sci. Technol. 40:4689-4695; Grenthe I., Fuger J., Konings R.J.M., Lemire R.J., Muller A.B., Nguyen-Trung C., Wanner H. (2004) Chemical thermodynamics of uranium. Ed's Wanner H. and Forest I., OECD, p. 715; and Guillaumont R., Fanghänel T., Fuger J., Grenthe I., Neck V., Palmer D.A. and Rand M.H. (2003) Update on the chemical thermodynamics of uranium, neptunium, plutonium, americium and technetium. Chemical Thermodynamics Series, Volume 5. Elsevier.

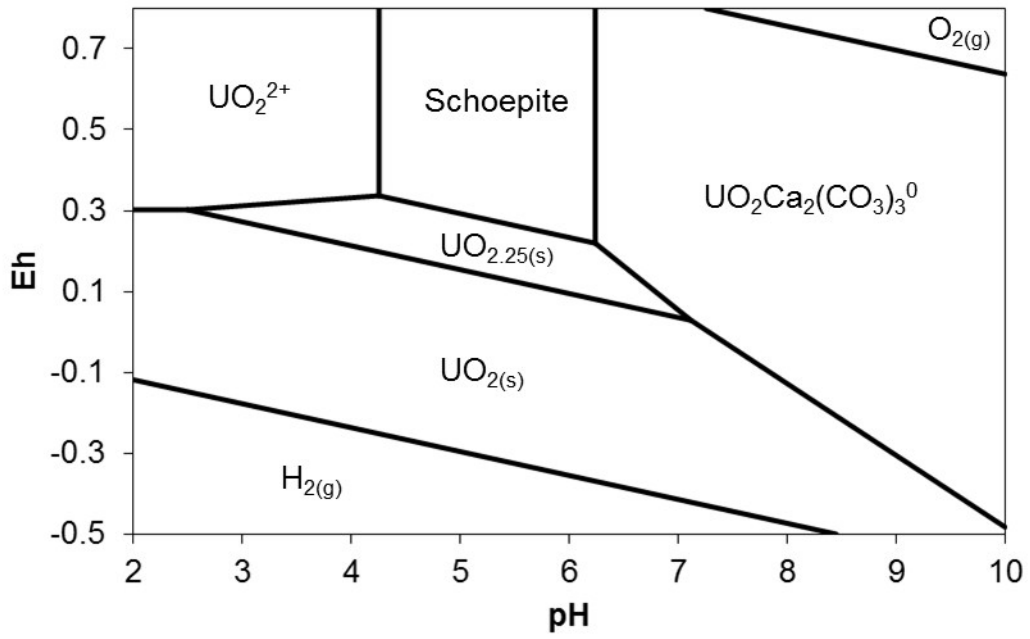

Figure S2. XPS Fe_{2p} region scans of fresh (top), aged (middle) and corroded (bottom) nZVI.

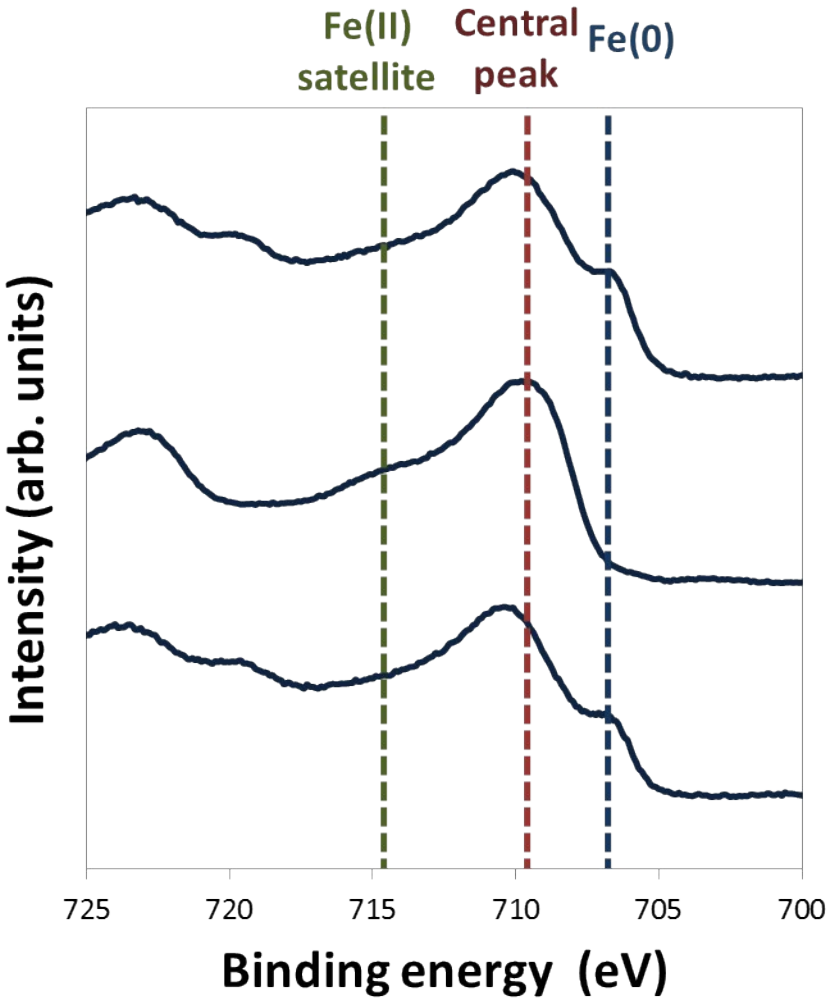

Figure S3. Uranium L_{III}-edge XANES spectra of fresh (fnZVI), aged (anZVI) and corroded (cnZVI) samples, relative to the U(IV) uraninite and U(VI) uranyl nitrate references. Samples shown are for 1:21 U:Fe molar ratios (1:16 for cnZVI).

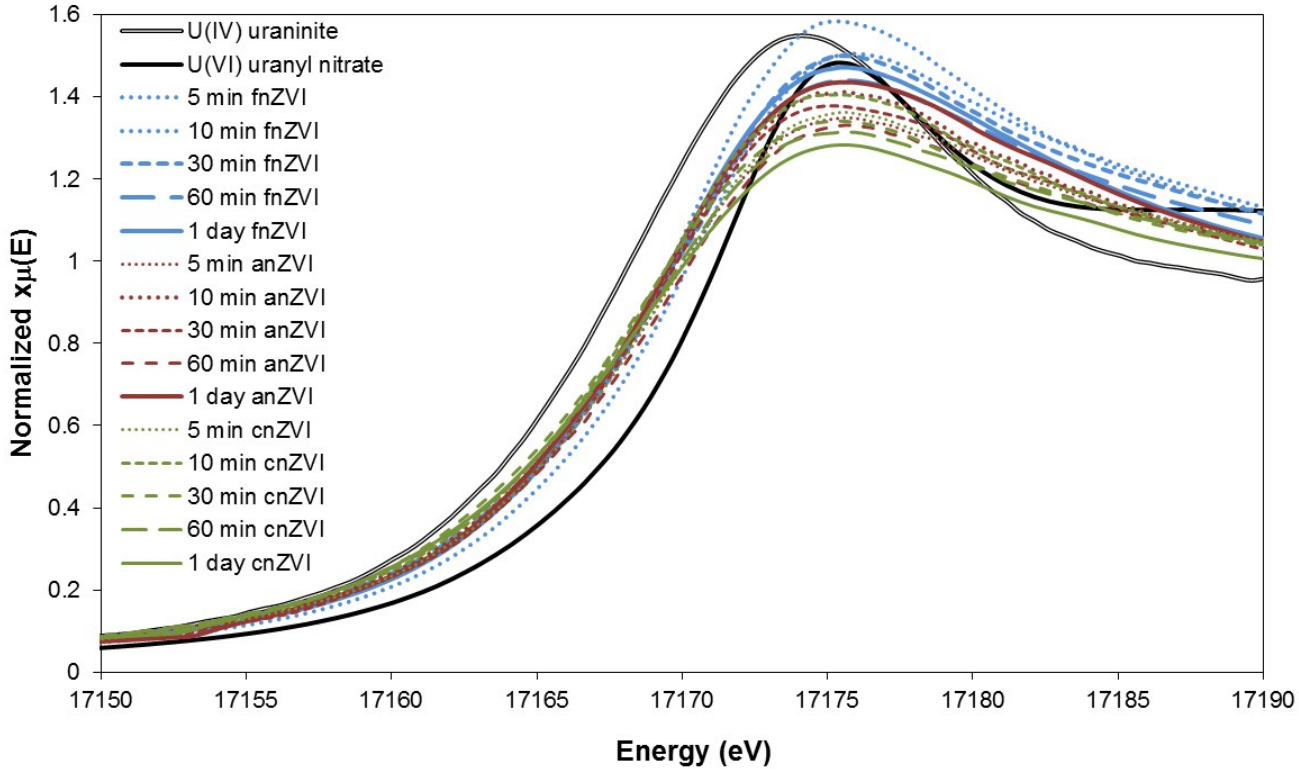

Table S3. Uranium L_{III}-edge 1st derivative positions of fresh, aged and corroded nZVI samples relative to the U(IV) uraninite and U(VI) uranyl nitrate references.

Time	**nZVI U L_{III}-edge 1st derivative position (eV)**		
	Fresh	**Aged**	**Corroded**
U(VI) reference	**17172.4**		
5 min	17172	17170.6	17170.8
10 min	17171.7	17170.4	17170.5
30 min	17171.4	17170.4	17170.3
60 min	17171.0	17170.4	17170.1
1 day	17170.3	17169.8	17169.8
U(IV) reference	**17169.3**		

Table S4. Modelling parameters used to obtain the results shown in Table 1 of the main manuscript. [a] fixed during fitting.

Reaction time	Path	ΔE (eV)	CN	R (Å)	σ^2 (10^{-3} Å^2)
5 min	U-O_{ax}	ΔE	2 x CN1	ΔR1	$\sigma^2$1
	U-O_{eq}		(6 x CN1) + (8 x (1-CN1))	ΔR2	$\sigma^2$2
	U-C		CN2	ΔR3	$\sigma^2$3
1 hour	U-O	ΔE	2 x CN1	ΔR1	$\sigma^2$1
	U-O		8 x (1-CN1)	ΔR2	$\sigma^2$1
	U-O		6 x CN1	ΔR3	$\sigma^2$1
	U-C		CN2	ΔR4	$\sigma^2$2
1 day	U-O	ΔE	2 x CN1	ΔR1	$\sigma^2$1
	U-O		8 x (1-CN1)	ΔR2	$\sigma^2$1
	U-O		6 x CN1	ΔR3	$\sigma^2$1
	U-C		CN2	ΔR4	$\sigma^2$2
Uraninite	U(IV)-O	ΔE	8.0[a]	ΔR1	$\sigma^2$1
	U(IV)-U(IV)		12[a]	ΔR2	$\sigma^2$1