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

Grain Boundary Facilitated Dissolution of Nanocrystalline NpO_2(s) from Legacy Waste Processing

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Summary of SI File:

- Pages: 7
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The SI also contains supplementary text.

Table S1. Concentrations of major elements, added as chloride salts, in simulated vadose zone pore water from Savannah River Site used in dissolution experiment.

Element	**Concentration (μg/L)**
Na	1,667
K	513
Ca	1,639
Mg	344
Fe	9.49

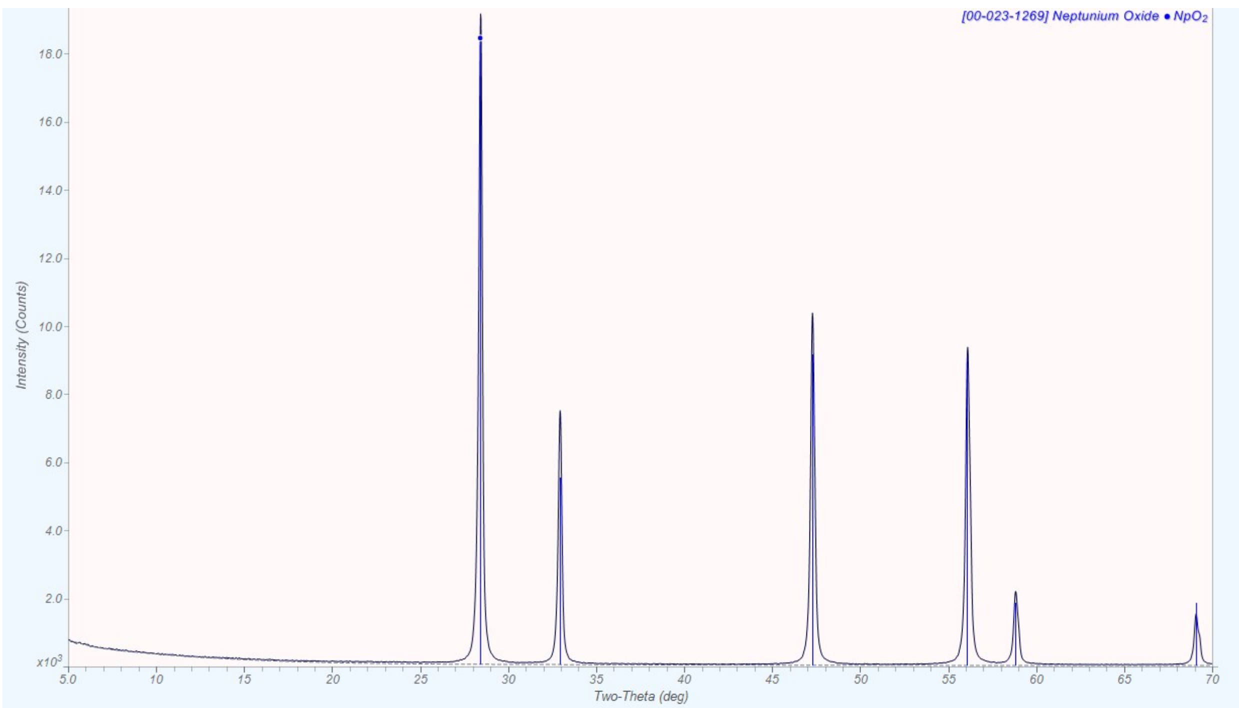

Figure S1. Powder x-ray diffraction pattern of NpO_2(s).

Table S2. XPS fitting parameters

Sample	FWHM			G/L	Tail
	$4f_{7/2}$	$4f_{5/2}$	Satellite		
Initial	1.75	1.75	1.30	60.00	1
Dissolved	1.75	1.75	1.30	60.00	1
Np(IV) control	1.75	1.75	1.30	60.00	1
Np(V) control	1.75	1.75	1.30	60.00	1

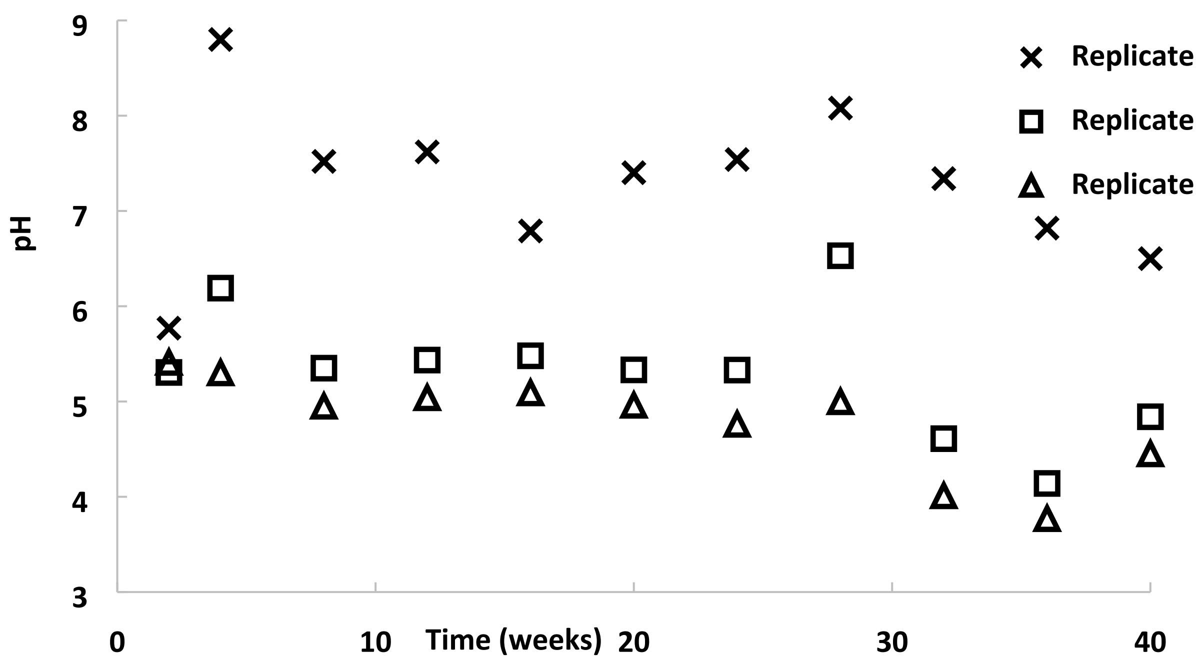

Figure S2. pH measurements as a function of time for 3 dissolution replicates.

Table S3. Raw averaged (3 replicates) aqueous phase Np concentration data used in Figure 1

Sampling time (weeks)	Average Unfiltered Np Concentration ($x10^{-6}$ M)	Standard Deviation ($x10^{-6}$ M)	Average Filtered Np Concentration ($x10^{-6}$ M)	Standard Deviation ($x10^{-6}$ M)	Average Filterable Fraction of Np
0.003	0.34	0.03	0.28	0.03	0.18
0.006	0.39	0.02	0.34	0.02	0.12
0.018	0.57	0.11	0.45	0.03	0.22
0.036	0.76	0.12	0.68	0.08	0.11
0.149	1.14	0.05	1.04	0.15	0.09
0.298	1.34	0.17	1.10	0.18	0.18
0.446	1.55	0.19	1.32	0.17	0.14
1.024	1.91	0.19	1.59	0.22	0.17
2.024	2.34	0.17	1.91	0.12	0.18
4.006	2.79	0.42	2.68	0.34	0.04
8.036	3.96	0.19	2.92	0.34	0.26
12.02	4.62	0.53	3.49	0.44	0.25
16.02	4.52	0.01	3.87	0.38	0.14
20.02	4.80	0.04	4.37	0.11	0.09
24.02	5.51	0.05	4.51	0.22	0.18
28.02	4.16	0.93	3.05	0.26	0.07
32.02	6.02	1.18	3.97	1.02	0.34
36.02	5.07	0.04	4.49	0.23	0.12
40.00	5.13	0.08	4.77	0.11	0.07

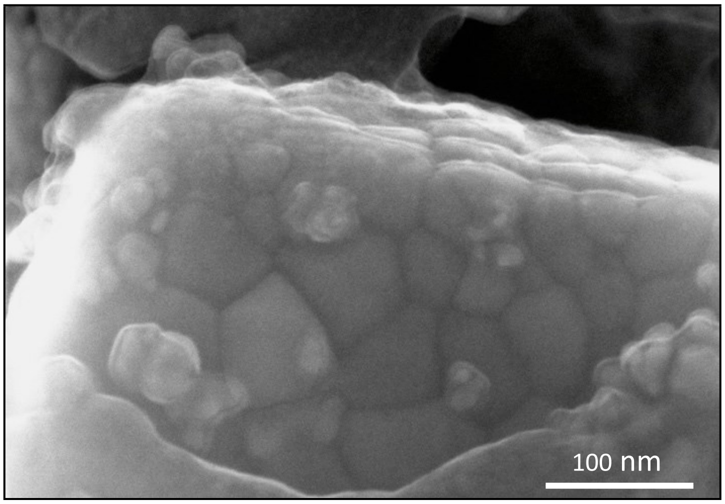

Figure S3. Scanning transmission electron microscope images of $NpO_2(s)$ after 12 weeks of dissolution.

Table S4. XPS satellite distances for measured Np solids.

Sample	Distance to Satellites $\Delta_{sat.}$ (eV)			
	1A	1B	2A	2B
Initial	6.74	6.68	6.81	6.86
	0.47	*0.27*	*0.16*	*0.34*
Dissolved	6.34	6.41	6.40	6.58
	0.25	*0.64*	*0.51*	*0.47*
Np(IV) control	6.51	7.04	6.53	7.13
	0.10	*0.06*	*0.09*	*0.04*
Np(V) control	10.26	10.61	8.37	10.90
	0.21	*0.50*	*0.55*	*2.64*

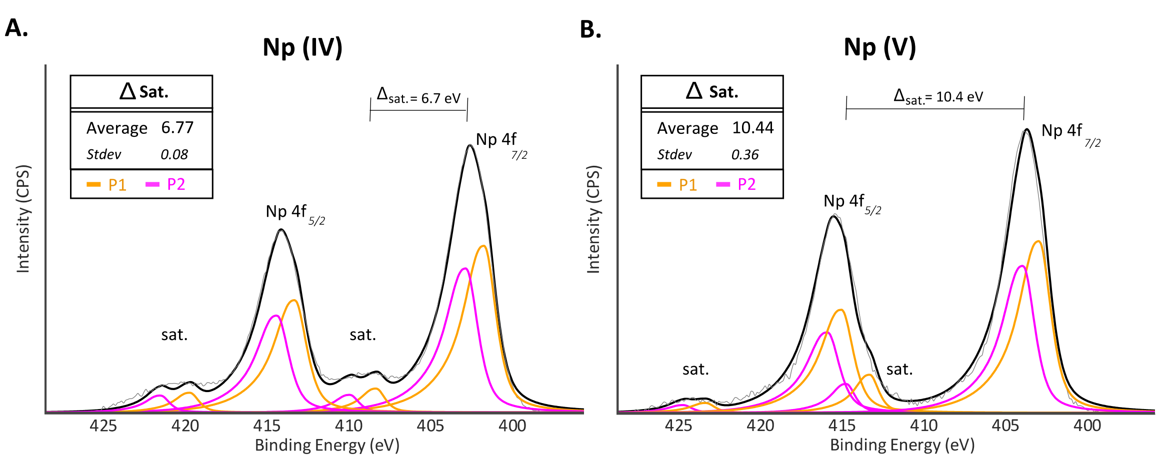

Figure S4. XPS spectra of Np(IV) and Np(V) control samples.

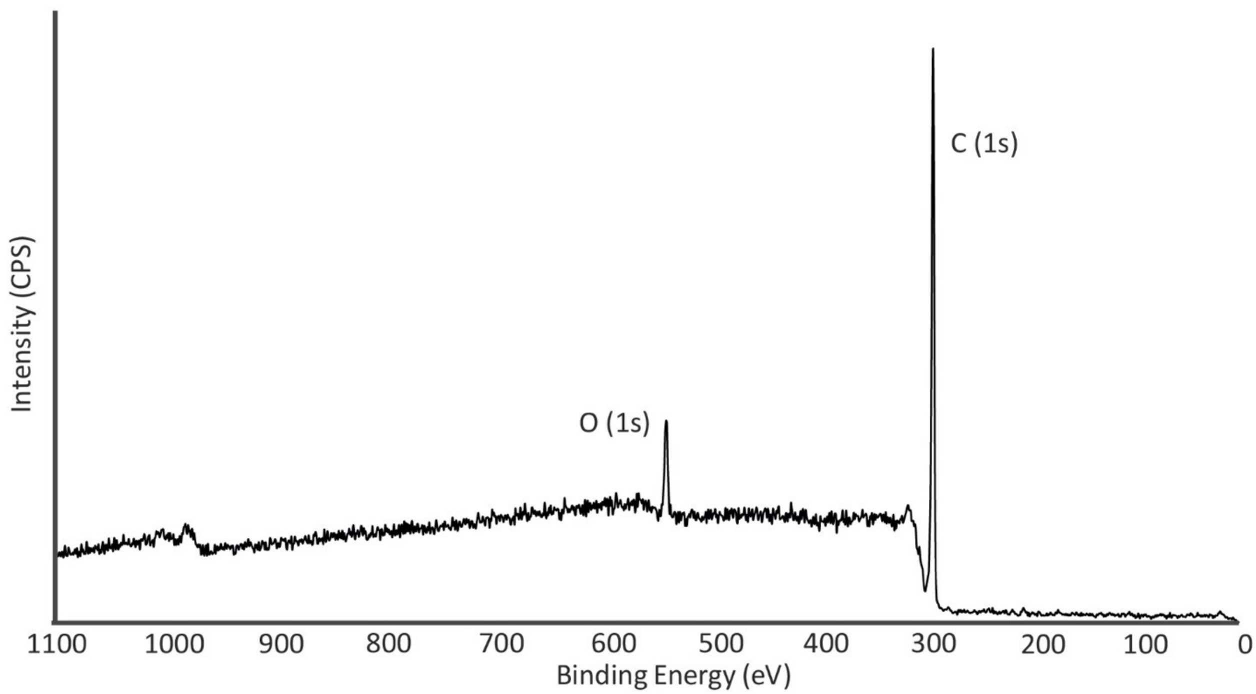

Figure S5. Representative XPS survey spectra. Survey spectra were collected for multiple regions to verify that there was no contamination. At this step size (0.8eV), pass energy, and XY scale, the Np 4f signal is not clearly observable because of the small NpO_2(s) sample mass compared to embedding resin. Survey scans demonstrate sample is predominantly Carbon and Oxygen as expected based on the adhesive used to support the Np sample.

<u>Complete solutions for differential equations used in kinetic fitting:</u>

Overall Reaction:

$$NpO_2 + xH_2O \overset{k1}{\rightarrow} NpO_2 \cdot xH_2O \overset{k2}{\rightarrow} (NpO_2)^{+}_{(aq)} + xH_2O$$

assume reactions are non-reversible and that no other reactions occur

Set of Differential Equations:

$$\frac{d[NpO_2]}{dt} = -k_1[NpO_2]$$

$$\frac{d[NpO_2 \cdot xH_2O]}{dt} = k_1[NpO_2] - k_2[NpO_2 \cdot xH_2O]$$

$$\frac{d[(NpO_2)^+_{(aq)}]}{dt} = k_2[NpO_2 \cdot xH_2O]$$

Initial Conditions:

$[NpO_2]_0 = 1.84 * 10^{-5}\, mol \;\; @\, t = 0$
$[NpO_2 \cdot xH_2O]_0 = 5.55 * 10^{-8}\, mol\, @\, t = 0$
$[(NpO_2)^+_{(aq)}]_0 = \; 6.70 * 10^{-9} \;\; @\, t = 0$
$Np_{TOT} = NpO_2 + NpO_2 \cdot xH_2O + (NpO_2)^+_{(aq)}$

Solve for [NpO$_2$]:

$$\frac{d[NpO_2]}{dt} = - k_1[NpO_2]$$

$$\int \frac{d[NpO_2]}{[NpO_2]} = \int - k_1 dt$$

$$\ln (NpO_2) = - k_1 t - C$$

$$[NpO_2] = Ce^{-k_1 t}$$

$$[NpO_2] = [NpO_2]_0 e^{-k_1 t}$$

Solve for [$NpO_2 \cdot xH_2O$]:

$$\frac{d[NpO_2 \cdot xH_2O]}{dt} = k_1[NpO_2] - k_2[NpO_2 \cdot xH_2O]$$

$$\frac{d[NpO_2 \cdot xH_2O]}{dt} = [NpO_2]_0 e^{-k_1 t} - k_2[NpO_2 \cdot xH_2O]$$

$$d([NpO_2 \cdot xH_2O]) \; = [NpO_2]_0 e^{-k_1 t}(dt) - k_2[NpO_2 \cdot xH_2O](dt)$$

$$d([NpO_2 \cdot xH_2O]) + \; k_2[NpO_2 \cdot xH_2O](dt) = [NpO_2]_0 e^{-k_1 t}(dt)$$

$$e^{k_2 t}\left(d([NpO_2 \cdot xH_2O]) + \; k_2[NpO_2 \cdot xH_2O](dt)\right) = e^{k_2 t}([NpO_2]_0 e^{-k_1 t}(dt))$$

$$\int d\left([NpO_2 \cdot xH_2O]e^{k_2 t}\right) = \int ([NpO_2]_0 k_1 e^{(k_2 - k_1)t}(dt))$$

$$[NpO_2 \cdot xH_2O]e^{k_2 t} - [NpO_2 \cdot xH_2O]_0 = \frac{[NpO_2]_0 k_1 e^{(k_2 - k_1)t}}{k_2 - k_1} - \frac{[NpO_2]_0 k_1}{k_2 - k_1}$$

$$[NpO_2 \cdot xH_2O]e^{k_2 t} = \frac{[NpO_2]_0 k_1 e^{(k_2 - k_1)t}}{k_2 - k_1} - \frac{[NpO_2]_0 k_1}{k_2 - k_1} + [NpO_2 \cdot xH_2O]_0$$

$$[NpO_2 \cdot xH_2O] = \frac{[NpO_2]_0 k_1}{k_2 - k_1}\left(\frac{e^{(k_2 - k_1)t}}{e^{k_2 t}} - \frac{1}{e^{k_2 t}}\right) + [NpO_2 \cdot xH_2O]_0 e^{-k_2 t}$$

$$[NpO_2 \cdot xH_2O] = \frac{[NpO_2]_0 k_1}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right) + [NpO_2 \cdot xH_2O]_0 e^{-k_2 t}$$

Solve for [$(NpO_2)^+_{(aq)}$]:

$$(NpO_2)^+_{(aq)} = Np_{TOT} - (NpO_2 + NpO_2 \cdot xH_2O)$$