

## Supporting Information: Electron Transfer Between Neptunium and Sodium Chlorite in Acidic Chloride Media

Brian T. Arko,<sup>1,2</sup> David Dan,<sup>1</sup> Sara L. Adelman,<sup>1,\*</sup> David B. Kimball,<sup>1,\*</sup> Stosh A. Kozimor,<sup>1,\*</sup> Jenifer C. Shafer,<sup>2,\*</sup>

<sup>1</sup>*Los Alamos National Laboratory, Los Alamos, NM 87545 (U.S.A.)*

<sup>2</sup>*Department of Chemistry, Colorado School of Mines, Golden, CO 80401 (U.S.A.)*

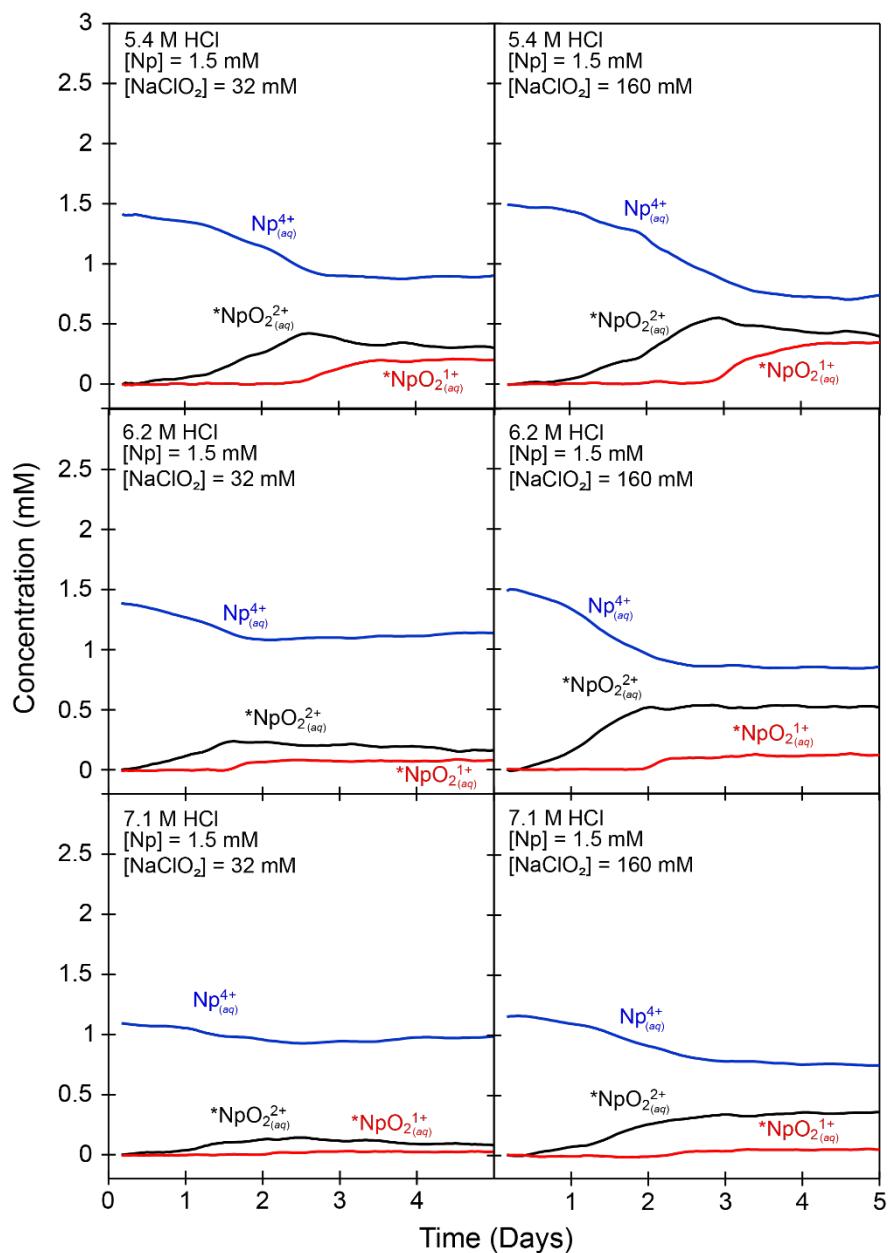
\*Corresponding author; [sadelman@lanl.gov](mailto:sadelman@lanl.gov), [dkimball@lanl.gov](mailto:dkimball@lanl.gov), [stosh@lanl.gov](mailto:stosh@lanl.gov), [jshafer@mines.edu](mailto:jshafer@mines.edu)

**Table S1:** Neptunium rate law kinetics in low HCl<sub>(aq)</sub> and LiCl<sub>(aq)</sub> conditions.

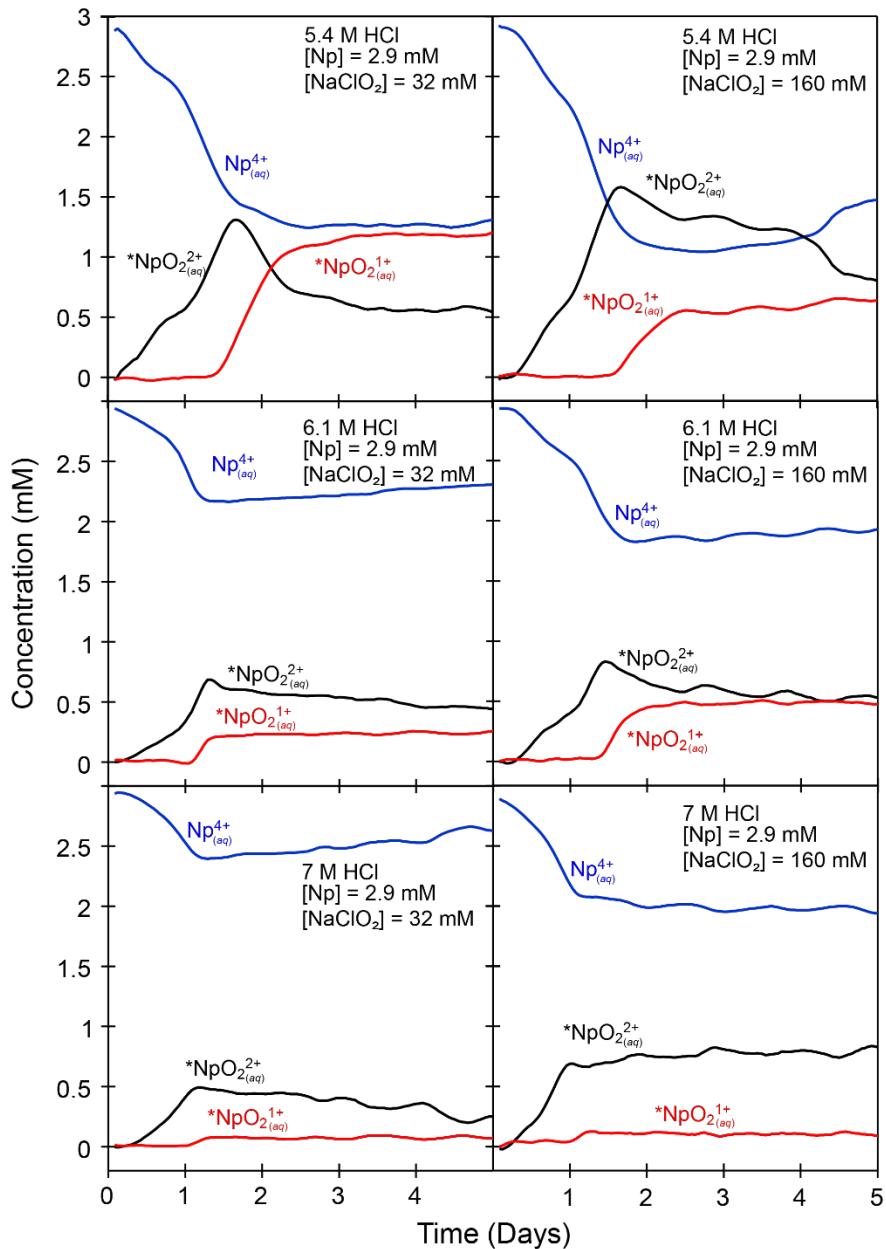
Transition	Rate Law
Np <sup>4+</sup> → NpO <sub>2</sub> <sup>+</sup>	$\frac{dNpO_2^+}{dt} = -\frac{dNp^{4+}}{dt} = (49 \pm 7 \text{ mM} \cdot \text{s}^{-1})[Np^{4+}]^{0.300 \pm 0.008}[NaClO_2]^{0.110 \pm 0.002}$
NpO <sub>2</sub> <sup>+</sup> → NpO <sub>2</sub> <sup>2+</sup>	$\frac{dNpO_2^{2+}}{dt} = -\frac{dNpO_2^+}{dt} = (3 \pm 1 \text{ mM} \cdot \text{d}^{-1})[NpO_2^+]^{0.98 \pm 0.02}[NaClO_2]^{1.71 \pm 0.01}$

**Table S2:** Neptunium rate law kinetics in high Cl<sub>(aq)</sub> (>9 M LiCl) conditions.

Transition	Rate Law
Np <sup>4+</sup> → NpO <sub>2</sub> <sup>2+</sup> (LiCl)	$\frac{dNpO_2^{2+}}{dt} = -\frac{dNp^{4+}}{dt} = (0.24 \pm 0.09 \text{ mM} \cdot \text{min})[Np^{4+}]^{4.11 \pm 0.09}[NaClO_2]^{0.50 \pm 0.07}$



**Figure S1:** 1.5 mM Np<sup>4+(aq)</sup> 25°C in various concentrations of HCl<sub>(aq)</sub> reacted with different concentrations of NaClO<sub>2(aq)</sub>. \*signifies estimated concentrations of NpO<sub>2+(aq)</sub> and NpO<sub>22+(aq)</sub> using molar extinction coefficients from a previous report.<sup>52</sup>



**Figure S2:** 2.9 mM  $\text{Np}^{4+}_{(aq)}$  25°C in various concentrations of  $\text{HCl}_{(aq)}$  reacted with different concentrations of  $\text{NaClO}_2_{(aq)}$ . \*Signifies estimated concentrations of  $\text{NpO}_2^+_{(aq)}$  and  $\text{NpO}_2^{2+}_{(aq)}$  using molar extinction coefficients from a previous report.<sup>52</sup>

Example calculation of rate constant determination shown in Table S1 and Table S2.

$$\frac{\text{Initial Rate}_a}{\text{Initial Rate}_b} = \frac{k[Np]_a^x[NaClO_2]^y}{k[Np]_b^x[NaClO_2]^y}$$

$$\frac{\text{Initial Rate}_a}{\text{Initial Rate}_b} = \frac{k[Np]_a^x[NaClO_2]^y_a}{k[Np]_b^x[NaClO_2]^y_b}$$

$$\frac{\text{Initial Rate}_a}{\text{Initial Rate}_b} = \frac{[NaClO_2]^y_a}{[NaClO_2]^y_b}$$

$$\ln\left(\frac{\text{Initial Rate}_a}{\text{Initial Rate}_b}\right) = \ln\left(\frac{[NaClO_2]_a}{[NaClO_2]_b}\right)^y$$

$$y = \frac{\ln\left(\frac{\text{Initial Rate}_a}{\text{Initial Rate}_b}\right)}{\ln\left(\frac{[NaClO_2]_a}{[NaClO_2]_b}\right)}$$