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Supporting information for

Electrochemical deposition for the separation and recovery of metals

using carbon nanotube-enabled filters

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Figure S1. Blank carbon nanotube filter encapsulated in polyvinyl alcohol. Custom made by NanoTech Labs (Yadkinville, NC).



Deaerated System

Figure S2. Schematic of the deaerated system. Step 1: 500 mL of test solution was purged with nitrogen at 200 mL min⁻¹ in a 500 mL Erlenmeyer flask with an aeration stone for 90 min before the experiment to ensure no oxygen was present. Step 2: 5 mL min⁻¹ Eu was delivered to the filter while a constant flow of N₂ was pushed into the vacated headspace at 5 mL min⁻¹ to maintain neutral pressure and an oxygen-free environment for the duration of the experiment.



Figure S3. Arsenic recovery as a function of voltage and pH. Arsenic was unrecovered across the entire range tested, presumably due to the high solubility of the oxide (assuming the same mechanism of recovery as described in the main text for other tested metals; see Figure 5; S9).



Figure S4. X-ray photoelectron spectra for (a) Sc, (b) Eu, (c) Cu, (d) Ga, and (e) Nd at pH extrema (i.e., where one might expect a chance in the speciation of metal recovered). Cu was recovered as Cu₂O at the low pHs and CuO at the high pHs, consistent with the proposed mechanism of water splitting and oxygen reduction as the main metal-trapping mechanism at high pH and competition between Cu reduction and O₂ reduction at the low pHs due to their similar reduction potentials, 0.13 V_{Ag/AgCl} and 0.19 V_{Ag/AgCl}, respectively.¹ Sc, Eu, Ga, and Nd were recovered as Sc₂O₃, Eu₂O₃, Ga₂O₃, and Nd₂O₃, respectively, consistent with the mechanism of water splitting and oxygen reduction (Figure 5), which is enhanced at high pH.

Table S1. X-ray photoelectron binding energies for each sample and reference spectra used to identify metal speciation. The reported binding energies correspond to the spectra in Figure S4. Identification was confirmed with other spectral lines for Ga, Sc, Nd, and Eu and peak shape for Cu.^{2, 3}

XPS Binding Energies									
Element	pH 4 (eV)	pH 8/10 (eV)	Reference (eV) ²						
Ga 2p 3/2	1119.1	1118.8	Ga ₂ O ₃ , 1119.0						
Cu 2p 3/2	933.8	935.4	Cu ₂ O, 932.8; CuO, 934.2						
Sc 2p 3/2	403.0	403.2	Sc ₂ O ₃ , 403.4						
Nd 3d 5/2	984.3	983.7	Nd ₂ O ₃ , 983.1						
Eu 3d 5/2	1135.6	1134.9	Eu ₂ O ₃ , 1135.6						



Figure S5. Voltage experiment scanning electron micrographs for (a) Cu, (b) Sc (c) Eu (d) Nd (e) Ga. All five metals had increasing recovery as the voltage increased, and voltage is noted in the upper right corner of each image. Cu showed metal crystals at 1.5 V and 2.0 V (tested 0.1-2.0 V), while Sc, Eu, Nd, and Ga deposited in large platelets across all voltages (1.0-3.0 V).

Ionization Energies (kJ/mol)									
Transition	Eu	Nd	Ga	Sc	As	Cu			
$M \rightarrow M^+ + e^-$	547.1	533.1	578.8	633.1	947	745.5			
$M^+ \rightarrow M^{2+} + e^-$	1085	1040	1979.3	1235	1798	1957.9			
$M^{2+} \rightarrow M^{3+} + e^{-}$	2404	2130	2963	2388.6	2735	3555			
$M^{3+} \rightarrow M^{4+} + e^{-}$	4120	3900	6180	7090.6	4837	5536			
$M^{2+} + 2e^- \rightarrow M$						2703.4			
$M^{3+} + 3e^- \rightarrow M$	4036.1	3703.1	5521.1	4256.7	5480				

Table S2. Ionization energies for Eu, Nd, Ga, Sc, As, and Cu.⁴



Figure S6. Scanning electron micrographs as a function of pH for (a) Cu, (b) Sc (c) Eu (d) Nd (e) Ga. The Cu crystals changed morphology as the pH changed, consistent with the XPS data (Figure S5). Sc, Eu, Nd, and Ga deposited as metal platelets at all pHs. Note that all five metals had increasing recovery over pH ranges were metal hydroxide species dominate the system (see Stability Diagrams, Figure S9), consistent with metal hydroxide intermediates and an oxygen-mediated trapping mechanism.



Figure S7. (a) Molar flux and (b) mass flux across the flow rate range 1-5 mL/min.



Figure S8. Scanning electron micrographs as a function of flowrate for (a) Cu, (b) Sc, and (c) Eu. Cu crystallinity showed a sensitivity to flow rate with near perfect crystals at lower flow rates, growing less crystalline as the flow rate increased, as would be expected. In contrast, Sc and Eu did not show any sensitivity. The limited sensitivity of recovery to flow rate suggested that the redox kinetics were not severely limiting in this recovery process over the range tested (i.e., the reduction, precipitation, and collection process was fast or approximately equivalent to the rate of bulk mass transport past the filter).



Figure S9. Stability diagrams for (a) Cu, (b) Ga, (c) Nd, (d) Sc, (e) Eu, and (f) As. Adapted from Brown et al., Cheng et al., Ames et al., and Smedley et al.⁵⁻⁸ These solubility profiles agree with the proposed mechanism, where the collection of metal oxide minerals proceeds through metal hydroxide intermediates, corresponding to increased metal recovery at the pH(s) where the metal hydroxide species dominate.

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