Geochemical Redox Fractionation of Rare Earth Elements in Acid Mine Drainage Treatment Solids: Implications for Recovery

Colleen L. Hoffman ^{1,2}; Benjamin C. Hedin³; Mengling Y. Stuckman¹; Christina L. Lopano¹

¹National Energy Technology Laboratory, 626 Cochran Mill Road, P.O. Box 10940, Pittsburgh, PA

15236-0940, USA

² NETL Support Contractor, 626 Cochran Mill Road, P.O. Box 10940, Pittsburgh, PA 15236-0940, USA ³Hedin Environmental, Inc., 4607 Library Road Suite 220#1009, Bethel Park, PA, 15102, USA

Author Email: colleen.hoffman@netl.doe.gov

Acid mine drainage (AMD) treatment solids are a promising unconventional resource for domestic rare earth element (REE) recovery. AMD is produced from the weathering of sulfide minerals in coal or other mining formations^{1,2} during water-rocks reactions between acidic streams and surrounding rocks³. Passive remediation systems within Pennsylvania – where the low-pH, metal-laden AMD were treated passively through limestone beds – have been shown to generate 18,000 tons/yr of AMD treatment solids containing up to 2,000 mg/kg REEs^{4,5,6}. However, given the heterogeneity of AMD treatment solids, REE distribution and binding mechanisms within different mineral hosting phases are poorly understood. This study explores how the redox conditions during the AMD treatment process will impact REE distribution and hosting phases in these solids by investigating cerium (Ce) oxidation, Ce and manganese (Mn) speciation, and REE distributions of four geochemically diverse AMD solids (two Al-rich, a Ca,Mn-rich, and an Al,Fe,Mn-rich solids) via bulk X-ray Absorption Near Edge Spectroscopy (XANES), micro-XANES, and micro-X-ray fluoresces. Three Ce-sorbed synthetic minerals (boehmite, ferrihydrite, and birnessite) that represent the endmembers in AMD soils were also explored via bulk XANES. Briefly, synthetic birnessite showed the highest Ce loading (7.55mmol/g) with dominant Ce(IV) species (94.4 ± 0.4%) compared to the other synthetic endmembers. Within the AMD solids explored, Ce oxidation was highest on Mn-rich and Al/Mnrich hotspots (65-83% Ce(IV)). Conversely, Al-rich solids and hotspots were dominated by Ce(III). Mn speciation was predominantly Mn(IV) within the Mn-rich solid, while Mn is more reduced (e.g. Mn(II), Mn(III), and Mn(IV)) in the other solids. The cooccurrence of highly oxidized Ce(IV) with oxidized Mn(IV) spots/samples is due to Ce and Mn being co-precipitated and oxidized as Ce(IV)sorbed birnessite minerals within the AMD passive treatment conditions. These results can be used to investigate mechanisms of Ce oxidation and REE fractionation to inform REE recovery from AMD solids.

References

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