

Recovery of REEs from acid mine drainage via sorption to MnO₂

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ABSTRACT: High concentrations of critical metals (CM) in acid mine drainage (AMD) has led to research into the potential for their recovery. CM sorption has been investigated in the past, by adding a sorbent solid to AMD, or precipitating Fe/Al oxyhydroxides by raising the pH. We investigated precipitating Mn²⁺ (also present in elevated concentrations) as MnO₂ via oxidation with KMnO₄. Experiments were conducted in a MnSO₄ stock solution and a synthetic AMD (SAMD). In the SAMD, and subsequent field-collected AMD, a staged precipitation process was utilized. In stage 1 Fe and Al are removed by adjusting the pH to 4.25-4.75. In stage 2 KMnO₄ is added to precipitate MnO₂ at low pH, and the pH is adjusted to 4-5.5. We found that MnO₂ was a strong sorbent for REEs, even at acidic pHs in MnSO₄ stock solutions, possibly due to its low pH_{zpc} (pH 2-3). In the presence of excess KMnO₄, REEs were recovered to an even greater extent. However, in SAMD, sorption did not occur until higher pHs (4-5), possibly due to elevated SO₄ concentrations. To reduce the amount of KMnO₄, while improving the effectiveness of MnO₂ as a sorbent, H₂PO₄⁻ and P₂O₇⁴⁻ were added to solution. These ligands made the surface charge of the MnO₂ more negative, thereby increasing our ability to recover REEs at lower pHs. In SAMD, while only precipitating 30% of the Mn²⁺, we were able to recover >80% of REEs by pH 4.2 with P₂O₇⁴⁻ (3.0 mM) being added after MnO₂ precipitation. Also, addition of (NH₄)₂(C₂O₇) and P₂O₇⁴⁻ could selectively desorb HREEs at pH of 8-9.5. In experiments with field-collected AMD three different methods were used: a.) all Mn²⁺ was precipitated in solution and no ligands were added; b.) trials with PO₄ and P₂O₇ in which 20-30% of Mn²⁺ was precipitated; and c.) either a H₂PO₄ or P₂O₇ solution was added after sorption to recover the CMs from the solid. Addition of ligands made MnO₂ more selective for REEs, while reducing unwanted, uneconomic metals from sorbing. The outcome suggests means to produce a solid suitable for further processing that was high in grade.