Goldschmidt 2026 Abstract
https://doi.org/10.46427/gold2026.38272

Critical Metals Recovery from Acid Mine Drainage: Three-Stage Selective Precipitation with pH Adjustment and Ozonation

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The Penn State Center for Critical Minerals has created a pilot-scale, three-stage treatment process with a flow rate of approximately 37.8 m3/min to convert acid mine drainage (AMD), a low-pH, metal- and sulfate-rich waste from legacy mines, into separate product streams mainly containing iron, aluminum, or specific critical metals. The process includes staged pH adjustment, intermediate solid-liquid separation, and oxidation steps to enrich critical metals such as Co, Ni, Zn, and rare-earth elements (REE).

In **Stage 1**, sodium carbonate is added to increase the pH of AMD to approximately 4 ($Na_2CO_3 + 2H^+ \rightarrow 2Na^+ + CO_2 + H_2O$), which aids hydrolysis and the formation of an iron oxyhydroxide that is then removed by filtration ($Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3(s) + 3H^+$). When ferrous iron is present, vigorous aeration or H_2O_2 may be used to quickly convert Fe^{2+} to Fe^{3+}.

In **Stage 2**, the filtrate is further neutralized with Na_2CO_3 to a pH of about 5 to selectively remove an aluminum-rich precipitate ($Al^{3+} + 3H_2O \rightarrow Al(OH)_3(s) + 3H^+$). This step produces a filtrate depleted of Fe and Al, while still containing the bulk of targeted critical metals.

In **Stage 3**, the filtrate from Stage 2 is treated with Na_2CO_3 to maintain a pH of approximately 7, while ozone is added to produce a “collector” precipitate that captures targeted critical metals. Ozone oxidizes Mn^{2+} to form Mn(IV) oxide/oxyhydroxide ($Mn^{2+} + O_3 + H_2O \rightarrow MnO_2(s) + O_2 + 2H^+$), and any residual Fe^{2+} is similarly oxidized and hydrolyzed to $Fe(OH)_3(s)$. At neutral pH, the newly formed Mn/Fe oxyhydroxides adsorb and co-precipitate critical metals (Co^{2+}, Ni^{2+}, Zn^{2+}, REE^{3+}).

Pilot-scale results and product characterization show the potential for AMD valorization and domestic recovery of critical metals. Geochemical modeling of the stage-wise treatment process using PHREEQC demonstrates the effects and importance of aqueous system variables, such as the kinetics of Fe and Mn oxidation and the removal of metals by adsorption and/or precipitation, on critical metal recovery. This modeling helps define the operational range (robust pH/alkalinity/oxidation envelopes) for the Penn State three-stage process and its possible application across different AMD chemistries.