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Mn removal rate from simulated mine drainage by formation of rhodochrosite and calcite solid solution

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Dissolved divalent manganese ($Mn(II)_{aq}$) is often contained at high concentrations (~350 mg/L) in mine drainage waters. $Mn(II)_{aq}$ exhibits chronic toxicity to the nervous and respiratory systems of living organisms; therefore, its efficient removal is required to meet increasingly stringent discharge standards. Oxidation of $Mn(II)_{aq}$ to Mn(III) and Mn(IV), leading to the formation of insoluble Mn oxides and oxyhydroxides is a primary removal pathway. In addition, the formation, carbonate formation, such as rhodochrosite ($MnCO_3$), is also the effective removal process because it does not require oxidation to higher valence states. This study focused on neutral to alkaline mine drainages, which often contain high concentrations of bicarbonate (HCO_3^-) and calcium ions (Ca^{2+}) ranging from several hundred to thousand mg/L. Under these conditions, $CaCO_3$ and $Ca_{1-x}Mn_xCO_3$ can formed upon addition of alkaline reagent, and these reactions may influence the $Mn(II)_{aq}$ removal rate. Simulated mine drainage containing $Mn(II)_{aq}$ (80 mg/L) was reacted at pH 6–10 for 60–180 min. Complete removal of $Mn(II)_{aq}$ was achieved at pH 9 in the absence of HCO_3^- and Ca^{2+}, accompanied by the formation of hausmannnite (Mn_3O_4), whereas complete removal occurred at pH 8.5 in the presence of those ions, associated with calcite formation. Kinetic analysis using PHREEQC indicated HCO_3^- decreased the $Mn(II)_{aq}$ oxidation rate by suppressing the formation of reactive Mn hydroxyl species through Mn-CO_3 complexation. Nevertheless, the overall $Mn(II)_{aq}$ removal rate was significantly enhanced via coprecipitation with calcite. FE-STEM and Mn K-edge EXAFS analyses revealed that Mn was immobilized through the formation of a heterogeneous solid solution. These findings demonstrate that Mn removal in HCO_3^- and Ca^{2+} containing mine drainage governed by kinetic coupling between calcite precipitation and Mn incorporation, rather than thermodynamic stability alone.