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Mn removal mechanism from neutral pH mine water coexisting bicarbonate and calcium ions in active treatment

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Heavy metal-rich water generation is recognized as a potential problem at active and abandoned mine sites. To reduce their negative effects on the aqueous environment, the mine water is neutralized with slaked and quick limes; which is called active (chemical) treatment. When the water contains a high amount of manganese (Mn), it is generally precipitated as Mn_3O_4 or MnOOH in an abiotic neutralizing system. These Mn compounds consist of Mn(III) which is formed by oxidation of Mn(II); thus a high alkaline pH condition (pH>10) is required to promote the abiotic Mn(II) oxidation reaction. However, the Mn(II) oxidation reaction could be inhibited by rhodochrosite ($MnCO_3$) formation when a high amount of bicarbonate ion (HCO_3^-) is present in the neutral pH water. In addition, calcite ($CaCO_3$) is formed by adding lime; it could affect the Mn removal behavior by adsorption and/or other precipitate formations such as kutnohorite ($CaMn(CO_3)_2$). In this study, the effects of HCO_3^- and calcite formation on the Mn(II) oxidation and precipitation mechanisms were investigated by a geochemical modeling (PHREEQC) and XRD analysis of precipitates obtained by a neutralizing experiment of simulated drainage samples (initial pH 7.0, Mn: 70 mg/L, HCO_3^-: 1000 mg/L, and Ca: 600 mg/L). The neutralizing experiment revealed that Mn(II) was completely removed at pH 9 in the presence of HCO_3^-, and more effective Mn(II) removal was found at pH 8 in the presence of both HCO_3^- and Ca. The XRD results showed that rhodochrosite was formed in the presence of HCO_3^-, whereas calcite was the only product, and manganese compounds were not found in the presence of Ca. Therefore, this result suggests that Mn(II) was considered to be removed with the crystal growth of calcite instead of rhodochrosite formation when HCO_3^- and Ca coexisted. The results of equilibrium and kinetic calculation by geochemical code indicated that the Mn(II) oxidation rate was reduced (rate constant was 10-times lower) by a formation of Mn(II)–HCO_3^- complexes in the solution. However, ion exchange reactions and/or surface complex formation with calcite could promote successfully the Mn(II) removal in the presence of HCO_3^- and Ca.