

Geochemical evaluation in mine drainage treatment using manganese neutralization sludge for effective waste functionalization

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Japanese abandoned mines have been releasing a large quantity of drainage with a high concentration of manganese (Mn) above the effluent standard (10 mg dm^{-3}), which requires the appropriate treatment for a long time. Since the conventional neutralization process produces a huge quantity of unwanted Mn-sludge as a byproduct, a novel approach has been sought from an economic viewpoint. In this study, we thus assessed the applicability of this Mn-sludge to Mn removal from mine drainage for its effective utilization as an environmental material. Mineral characterization found that the Mn content in the sludge was 14.9 wt% with the composition of 83.2 mol% of γ -MnOOH and 16.8 mol% of δ -MnO₂; the latter is known to be effective in removing heavy metals such as Mn, cadmium (Cd), zinc (Zn). The results of the metal removal test showed that the addition of a sufficient amount of Mn-sludge achieved the successful removal of Mn ($\approx 100\%$) from the solution at pH 8, which was a much milder condition than the conventional neutralization process. To clarify the Mn removal mechanism by the sludge, geochemical modeling using PHREEQC was carried out. Calculation with the conventional model, where only autocatalytic Mn oxidation and adsorption by δ -MnO₂ are considered, significantly deviated from the experimental results at pH < 8. This suggested that the consideration of only δ -MnO₂ was insufficient to explain the whole mechanism of Mn removal by the Mn sludge. We thus developed the novel model incorporating the Mn surface complexation induced by γ -MnOOH: a major component in the Mn sludge. The novel model successfully reproduced the experimental results, which implied that not only δ -MnO₂ but also γ -MnOOH plays an important role in the Mn removal from drainage when Mn-sludge is used. Our research demonstrated that the Mn sludge generated via Mn drainage neutralization, normally disposed of as waste, is useful to be reused as an Mn removal material.