Understanding a passive treatment mechanism of manganese and zinc at a legacy mine in northern Japan using geochemical modelling

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Abstract

This study builds upon prior research conducted on a pilot-scale passive treatment (PT) system for manganese (Mn) and zinc (Zn), which operated at circumneutral pH (6.5–7.5) in oxic conditions for 152 days at a legacy mine in northern Japan. The pilot-scale PT successfully removed Mn and Zn, achieving removal efficiencies of 97% and 89%, respectively, with a total hydraulic retention time (HRT) of 6 days (Table 1). However, the optimum HRT has not yet been finalized. Therefore, our objectives are to (1) determine the treatment mechanisms of Mn and Zn in the pilot-scale PT and (2) employ geochemical modeling to comprehensively understand the role of HRT in the long-term implications of passive treatment.

Detailed analyses of sludge in the pilot-scale PT (Fig. 1) were conducted, including X-ray diffraction, X-ray fluorescence, X-ray absorption spectroscopy, and scanning electron microscopy with energy-dispersive X-ray spectroscopy. An inverse kinetic model for the Mn and Zn reactions in the pilot-scale PT, based on field measurements, was constructed to determine kinetic rate constants (k_1), mass transfer coefficients (k_m), and distribution coefficients (K_d). The geochemical model was constructed using Phreeqc and the Wateq4f database coupled with parameter estimation (PEST).

The analytical data highlights that Mn-oxidizing bacteria promote the oxidation of Mn(II) to Mn(IV), resulting in the formation of birnessite (Fig. 2). XANES spectra indicated that up to 90% of Mn(IV) concentrates in sludge as birnessite with a slight concentration of hausmannite (Mn(II,III)). At circumneutral pH, Mn(II) autocatalytic on the birnessite surface is relatively low compared to Mn-oxidizing bacteria catalysis. Thus, Mn-oxidizing bacteria are the main factors in controlling Mn treatment in the pilot-scale passive treatment. For Zn removal, mechanisms include co-precipitation with MnO_2, forming woodruffite, and adsorption on the birnessite surface.

The inverse model of Mn and Zn reaction kinetic transport was obtained following the analytical results. The monitoring data in A-1 successfully obtained k_1, k_m, and K_d, which are suitable for HRT optimization in the pilot study, without the need for additional experiments. The changes in HRT in A-1 (2 days, 0.5 days, and 0.3 days) decreased Mn removal capacity, but Mn remains below the Japanese effluent limit (Mn: 10 mg/L; Zn: 2 mg/L). However, the shorter hydraulic HRT (0.3 days) was not sufficient to treat Zn in the pilot treatment. The geochemical model suggests that an HRT of 0.5 days in A-1 is particularly applicable for achieving optimal removal rates for both Mn (25 mg/L) and Zn (8.9 mg/L) in the pilot-scale PT.

This research addresses the critical need for sustainable AMD treatment in legacy mines and provides valuable insights into efficient Mn and Zn removal through geochemical modeling. It offers essential information for the development of PT strategies and environmental management, particularly for real-scale implementation. The utilization of geochemical modeling contributes to a deeper understanding of these treatment mechanisms and HRT optimization.

Keywords: birnessite, woodruffite, Mn-oxidizing bacteria, circumneutral pH, hydraulic retention time (HRT)

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Table 1 *The average water quality in the treatment system*

	Unit	A-0 (wastewater)	A-1	A-2
Mn	mg/L	19.19	0.72	0.72
Zn	mg/L	6.99	0.35	2.00
pH		6.8	7.1	7.0
OPR	mV	178	161	177
DO	mg/L	7.3	9.2	9.5
EC	µS/cm	1138	1101	1096

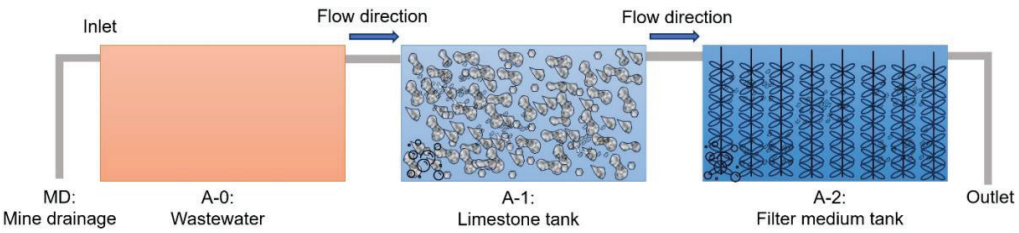

Figure 1 *The schematic illustrates the design of the pilot-scale passive treatment system implemented within the underground tunnel of the legacy mine. The wastewater in A-0 was pumped from the mine drainage (MD) and discharged into A-1 before being directed A-2. Air agitators were installed in A-1 and A-2 to allow oxygen saturation in the treatment plant*

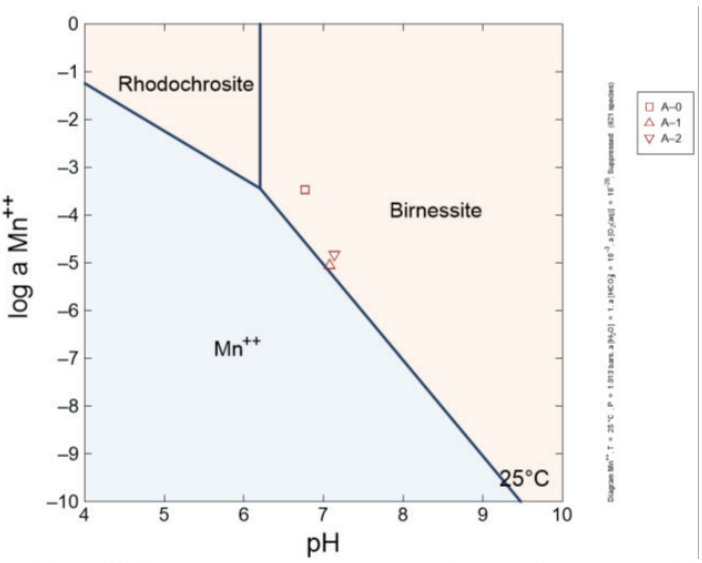

Figure 2 *The solubility of field Mn species in water systems obtained from Act2 module of Geochemical Workbench's*