Performance of Pilot-Scale Passive Treatment Tests of a Contact Oxidation Manganese-Oxidizing Bacteria for Manganese-Containing Mine Water

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Abstract

The performance of a pilot-scale passive treatment system consisting of a limestone bioreactor and fiber filter material bioreactor in series and employing a contact oxidation method utilizing Mn-oxidation bacteria was evaluated for neutral mine water containing Mn and Zn over approximately one year of operation. In the limestone bioreactor, the maximum Mn removal rate reached 49.7 g/m^3/day under aeration at water temperatures of approximately 20 °C. Even under low water temperatures of around 5 °C, the average Mn removal rate of the system reached 5.65 g/m^3/day at a hydraulic retention time of 3 days in a limestone bioreactor.

Keywords: Passive treatment, Mn-oxidizing bacteria, Contact oxidating process, Mn removal, Zn removal

Introduction

Passive treatment (PT) has been developed as an alternative to active treatment (AT) for mine water due to the lower treatment costs. For example, for the treatment of mine water containing manganese (Mn), AT typically involves adding alkaline reagents to raise the pH above 9, precipitating Mn as an oxide or hydroxide, and then neutralizing by adding acidic reagents (Deepti *et al.*, 2016). In contrast, PT using Mn-oxidizing bacteria (MnOB), which oxidize soluble Mn at circumneutral pH (Bradley *et al.*, 2005), offers a more cost-effective approach.

In Japan, mine water treatment is conducted at approximately 100 abandoned mines to meet the domestic discharge standard. However, the reliance on AT results in high operational costs (Ministry of Economy, Trade and Industry, Japan, 2023). At an abandoned mine in Japan, pilot-scale PT tests using a contact oxidation method utilizing MnOB were performed for neutral mine water containing Mn and zinc (Zn), and the effectiveness of Mn and Zn removal was confirmed (Watanabe *et al.*, 2024, Tum *et al.*, 2024). However, further studies are required to investigate the removal of different concentrations of Mn and Zn.

This study builds upon these findings by evaluating the performance of pilot-scale PT tests at different locations of the same abandoned mine as the above studies for neutral mine water containing higher concentrations of Mn (average 64.1 mg/L) and Zn (average 10.1 mg/L) over an operation period of approximately one year.

Methods

Test site and water profile of the target mine

A pilot-scale PT test was conducted in a test garage in an abandoned mine in a cold Japan region. The annual room temperature

Table 1 Water profile of the target mine.

	pH (-)	Temp. (°C)	Soluble Mn (mg/L)	Soluble Zn (mg/L)	Total Fe (mg/L)	Sulfate (mg/L)
Average	7.18	12.3	64.1	10.1	0.633	370
Maximum	7.79	19.1	78.0	13.0	2.91	441
Minimum	5.83	6.1	53.0	8.0	0.102	300

[1]Temp: temperature; Fe: iron.

ranged from -2 to 30 °C. A portion of the targeted mine water (Table 1) was distributed to a water tank using a pipe in the garage. The system was the same as that in previous reports (Watanabe *et al.*, 2024, Tum *et al.*, 2024) and consisted of two sequential biological processes: a limestone bioreactor (LBR) and a fiber filter material bioreactor (FBR). The system was divided into two parallel test series (X and Y). Mine water first introduced into each LBR (X-1 and Y-1) using an electric pump from the top and the LBR effluents then introduced naturally into each FBR (X-2 and Y-2) from the top.

Pilot-scale test

The LBRs (X-1 and Y-1) and FBRs (X-2 and Y-2) in each series (series X and Y) used the same reactor vessel made of fiber-reinforced plastics measuring 1.6 m wide, 0.97 m long, and 0.75 m deep, with a working volume of 630 L. The surface of each reactor was opened to take atmospheric oxygen. A partition wall was installed at the center of each reactor. Water that was introduced from one side of reactor passed under the partition wall and drained from the opposite side of reactor. The LBRs were filled with 800 kg of limestone (20–40 mm) supplied by Okubo Rozai Co., Ltd., Japan, for pH stabilization. The FBRs were suspended in 400 m polypropylene and vinylon fibers (Biocord PP+K-45, TBR Co., Japan) as inorganic carriers to enhance microbial activity. Pilot-scale PT tests were conducted from September 2023 at mine water flow rates of 30 to 650 mL/min, corresponding to hydraulic retention times (HRT) in the LBR of 0.3 to 7 days. Prior to the test, the LBRs and FBRs were filled with mine water, and a suspension of Mn deposits collected from the mine drainage ditch was inoculated as a source of MnOB. The details of the test conditions are presented in Table 2.

Operating conditions for pilot-scale test

The pilot-scale PT tests were performed in two ways during the Mn removal start-up period: continuous-flow operation (series X) and batch operation (series Y). Under continuous-flow operation, an electric pump was used to continuously pump a specified amount of mine water into the LBR and the HRT was set to the HRT in the LBR. Under batch operation, a large electric pump was used to quickly introduce mine water into the LBR, which remained in the LBR and FBR for a certain period, before repeating the cycle. During batch operation, mine water was introduced at twice the effective volume of the LBR to replace the water inside the LBR and FBR. The residence time of the mine water in the LBR after water replacement was considered as the HRT in the batch operation. After the Mn removal start-up, a continuous-flow operation was performed in series X and Y. The water flow was stopped

Table 2 Test contents of series X and Y.

	Series X		Series Y	
	X-1	X-2	Y-1	Y-2
Media	Limestone	Polypropylene and vinylon fibers	Limestone	Polypropylene and vinylon fibers
Working volume (L)	630	630	630	630
Porosity (%)	45	92	45	92
Effective volume (L)	283.5	579.6	283.5	579.6

from June to early July 2024. An air pump was used to provide aeration from the bottom of the LBRs and FBRs to increase the dissolved oxygen for microbial activity, depending on the conditions.

Monitoring parameters and analytical methods

Temperature, pH, oxidation-reduction potential (ORP, vs. Ag/AgCl), and dissolved oxygen (DO) were monitored using a portable multi-water quality meter (MM-42DP, DKK-TOA Corp., Japan). Un-filtered and filtered (pore size of 0.45 µm) water samples were regularly collected to measure the total and soluble concentrations of Mn and Zn using inductively coupled plasma optical emission spectrometry (ICP-OES; Agilent 5110 ICP-OES, Agilent Technologies Inc., USA). The sulfate concentrations and total organic carbon (TOC) in the filtrates were determined using an ion chromatograph (IC; Dionex ICS-6000, Thermo Fisher Scientific Inc.) and TOC analyzer (TOC-L, Shimadzu Corp.), respectively.

Results and Discussion

Mn removal start-up with continuous-flow operation and batch operation

Pilot-scale PT tests were initiated under continuous-flow operation (series X) and batch operation (series Y) at an HRT of 7 days in the LBR to investigate the differences in Mn removal. The soluble Mn concentration in the effluent of X-1 LBR gradually decreased from the beginning of the operation and fell below Japan's domestic discharge standard of 10 mg/L after four weeks. The soluble Mn removal performance in the effluent of Y-1 LBR was higher than that of X-1 LBR from the beginning of the test and the soluble Mn concentration remained below Japan's domestic discharge standard after 3 weeks. Soluble Zn removal followed the same trend in X-1 and Y-1 LBR. It is assumed that the batch operation maintained a stable bacterial community in the LBR compared to the continuous-flow operation, leading to the faster establishment of sufficient microorganisms. Similar results were reported in laboratory tests by

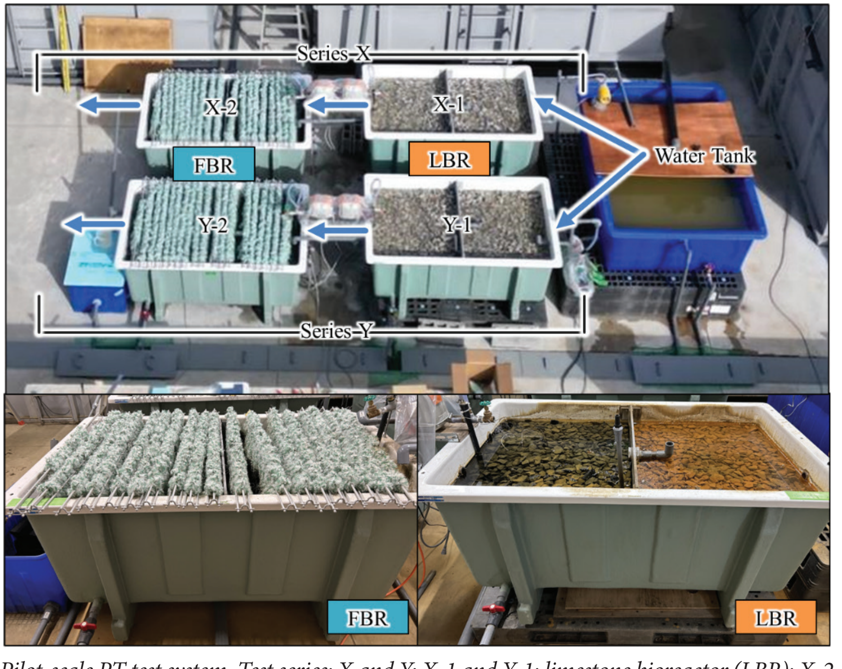

Figure 1 Pilot-scale PT test system. Test series: X and Y; X-1 and Y-1: limestone bioreactor (LBR); X-2 and Y-2: fiber filter materials bioreactor (FBR).

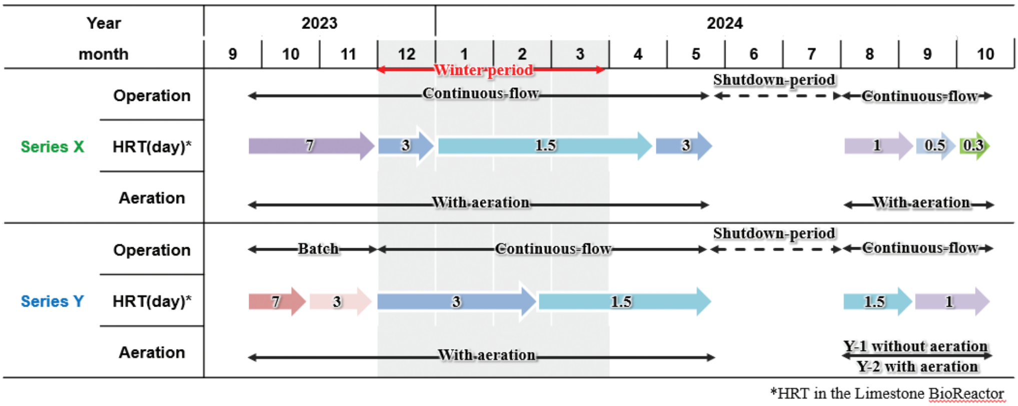

Figure 2 *Changes under the operating conditions in series X and Y.*

Obey *et al.* (2024), suggesting that batch operation was effective for fast Mn removal start-up, even on a pilot scale. As the test progressed, the limestone surfaces of X-1 and Y-1 LBR gradually became covered with blackish deposits. It is estimated that MnOB acclimated in each LBR over time; soluble Mn was oxidized and deposited as Mn oxides, such as birnessite (δ-MnO_2); and Zn was adsorbed on the surface of the Mn oxides or coprecipitated Mn oxides containing Zn, such as woodruffite ($ZnMn_3O_7 \cdot H_2O$), as reported by Watanabe *et al.* (2024) and Tum *et al.* (2024).

Treatment performance of series X and Y in winter periods

From December 2023 to March 2024, after the Mn removal start-up, water was introduced under continuous-flow operation in series X and Y. From December 2023 to March 2024, series X operated at an HRT of 1.5 days in the X-1 LBR from January 2024 to March 2024, whereas series Y operated at an HRT of 3 days in the Y-1 LBR from December 2023 to February 2024. The water temperature in each period ranged from 2.3 to 6.3 °C (average 4.8 °C) and 1.9 to 6.5 °C (average 4.0 °C) in the effluent of X-1 LBR and X-2 FBR and 1.9 to 6.4 °C (average 4.7 °C) and 6.3 to 0.4 °C (average 3.6 °C) in the effluent of Y-1 LBR and Y-2 FBR, corresponding to changes in room temperature. During the operation of series X during the winter period at an HRT of 1.5 days in the X-1 LBR, the soluble Mn in the effluent of the X-2 FBR remained below 10 mg/L in the early period but dramatically increased after 3 months. This was presumably due to a decrease in microbial activity at lower water temperatures compared to the PT tests in the non-winter periods described below. The maximum Mn removal rate in series X during this period was 9.3 g/m3/day. For series Y during the winter period at an HRT of 3 days in the LBR, the soluble Mn in the effluent of the Y-2 FBR remained below 10 mg/L, with an average Mn removal rate of 5.65 g/m3/day. This suggests that the PT system can function well for the Mn removal below Japan's domestic discharge standard by setting an appropriate Mn loading rate, even under conditions with average water temperatures below 5 °C. The treatment performance of soluble Zn in series X and Y showed the same trend as that of soluble Mn.

Treatment performance of LBR in non-winter periods

Following the water shutdown period from June to early July 2024, the pilot-scale PT tests were resumed in series X and Y from August to October 2024 to investigate the maximum Mn removal rate of the LBR with aeration at an HRT of the X-1 LBR from 0.3 to 1 day and without aeration at an HRT of the Y-1 LBR from 1 to 1.5 days. The water temperatures in the effluent of X-1 and Y-1 LBRs in this period ranged from 18.4 to 21.9 °C and 19.2 to 22.9 °C, respectively, corresponding to changes in room temperature. For X-1 LBR with aeration, the Mn removal rate remained stable up to an Mn loading rate of approximately 30.0 g/m^3/day. However, at higher Mn loading rates, the Mn removal rate gradually decreased. Within the tested HRT of X-1 LBR, a maximum Mn removal rate of 49.7 g/m^3/day was obtained when the Mn loading rate was 94.4 g/m^3/day. Based on the correlation between the Mn removal rate and Mn loading rate, the maximum Mn removal rate for the LBR with aeration is expected to be approximately 50.0 g/m3/day. However, for the Y-1 LBR without aeration, the Mn removal rate increased with the Mn loading rate within the tested HRT, with a maximum Mn removal rate of 27.7 g/m^3/day. Since no noticeable decline in Mn removal was observed relative to the Mn loading rate at HRT in the Y-1 LBR from 1 to 1.5 days, an improved Mn removal rate can be expected in the LBR without aeration. The trends showed that the LBR with or without aeration in this system achieved high Mn removal rates up to Mn loading rates of about 30.0 g/m^3/day under water temperatures of approximately 20 °C.

Conclusions

Pilot-scale PT tests were conducted to treat mine water containing Mn and Zn in an abandoned mine in a cold district in Japan using a contact oxidation method utilizing MnOB. The Mn removal start-up phase in the LBR of the system required approximately four weeks under continuous-flow operation and three weeks under batch operation. Soluble Zn removal followed the same trend as Mn removal. It is estimated that the batch operation maintained a stable bacterial community in the LBR compared to the continuous-flow operation, leading to the faster establishment of sufficient microorganisms. Even at an average water temperature below 5 °C in the winter period, a maximum Mn removal rate of 9.3 g/m^3/day was obtained, with an Mn removal rate of 5.65 g/m^3/day. The results suggest that the system can remove Mn to levels under

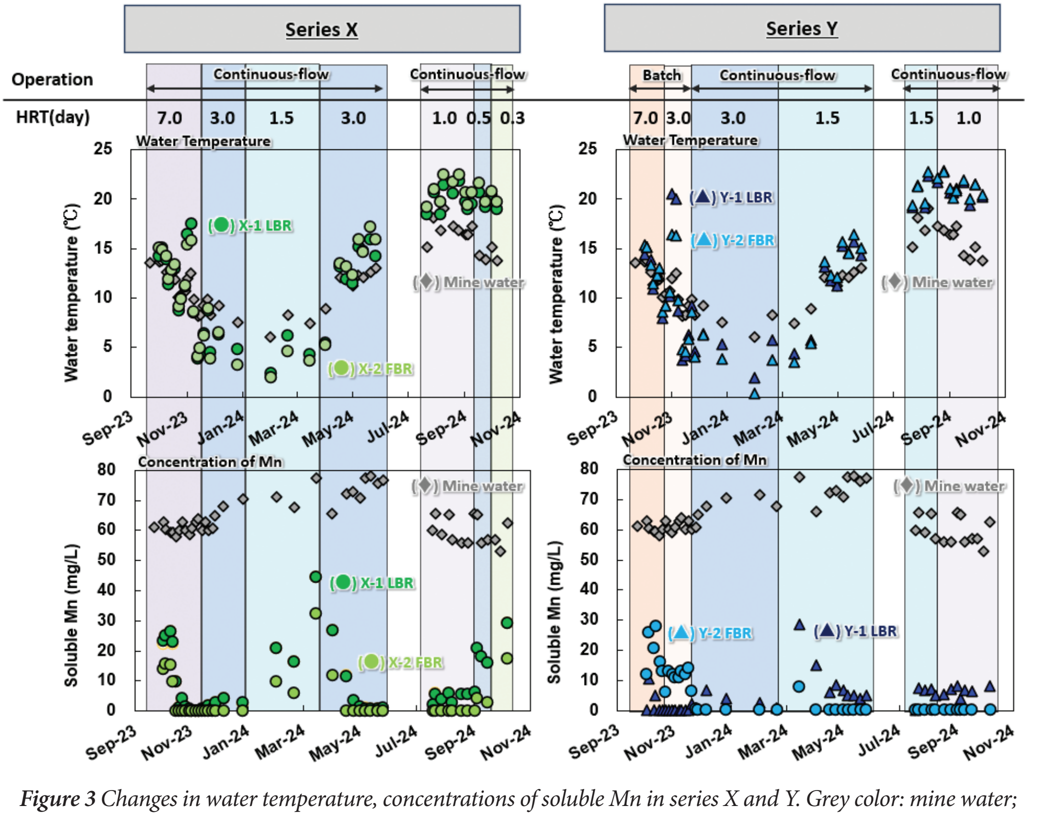

Figure 3 Changes in water temperature, concentrations of soluble Mn in series X and Y. Grey color: mine water; green color: X-1 LBR; light green color: X-2 FBR; blue color: Y-1 LBR; Light blue color: Y-2 FBR.

Japan's domestic discharge standards by setting an appropriate Mn loading rate. During the non-winter periods, at an average water temperature of approximately 20 °C, the Mn removal rate in the LBR increased with the Mn loading rate until approximately 30.0 g/m^3/day regardless of aeration. With aeration, the Mn removal rate gradually decreased in the LBR at higher Mn loading rates. The results showed that, regardless of aeration, the LBR in the system achieves high Mn removal rates up to Mn loading rates of about 30.0 g/m^3/day under water temperatures of 20 °C. Future PT tests will investigate the maximum Mn loading rate in FBR and evaluate the long-term treatability and maintainability of the system.

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