Improving Fe oxidizing/removal process by limestone addition to rice husk bed on large scale passive treatment test for AMD in Japan

Masataka Kondo[1], Yusei Masaki[2], Kana Hagihara[1], Koki Iguchi[1], Takaya Hamai[2], Yuki Semoto[2], Taro Kamiya[1], Masao Okumura[2], Naoki Sato[2]

[1]Metals Technology Center, Japan Organization for Metals and Energy Security, Furudate 9-3 Kosaka-kozan, Kosaka, Akita, Japan, kondo-masataka@jogmec.go.jp

[2]Metals Environment Management Department, Japan Organization for Metals and Energy Security, Toranomon 2-10-1, Minato-ku, Tokyo, Japan

Abstract

Japan Organization for Metals and Energy Security (JOGMEC) has conducted research on large-scale passive treatment tests for cost reduction. To improve the efficiency of iron (Fe) removal in an Fe oxidation/removal reactor during a large-scale test, limestone was added to the rice husk medium. The weight ratio of the rice husk to limestone mixture was set to 1:4. Consequently, the pH of the effluent increased from 3.0 to 3.2, soluble Fe concentration decreased from 6 to 2 mg/L, and removal rate improved by 10%. This approach reduced the Fe concentration in the influent during the anaerobic process at a later stage, contributing to treatment stability.

Keywords: Passive treatment, Fe removal, rice husk, limestone, AMD

Introduction

In Japan, mine water drainage water treatment is performed at approximately 100 abandoned mine sites by active treatment (mostly using calcium hydroxide). However, a more cost-effective method is required. Therefore, Japan Organization for Metals and Energy Security (JOGMEC) has been conducting research on passive treatment systems. Furthermore, JOGMEC aims to develop a compact treatment process with a short hydraulic retention time (HRT) to expand the scope of mine water treatment facilities. To achieve this, a multi-step passive treatment system, which was initiated in 2020, with a 2 h aerobic iron (Fe) oxidizing/removal and a 25-h anaerobic sulfate-reducing process was conducted (Hayashi et al. 2021) on a large-scale passive treatment test with a water flow rate of 100 L/min. During the Fe oxidation/removal process, acid mine drainage (AMD) was introduced from above the surface into a vertical downflow biochemical reactor and aerated. Ferrous AMD was oxidized to ferric AMD by Fe-oxidizing bacteria and precipitated into the reactor media. From 2021, the reactor was filled with rice husk, which is an agricultural by-product of rice production. In winter, the oxidation of ferrous Fe was sufficient. However, the amount of Fe precipitation decreased at relatively low temperatures. Therefore, the objective of this study was to investigate the effect of limestone addition to the rice husk bed of a biochemical reactor (BCR) on the Fe removal performance.

Methods

Large-scale test site and AMD chemistry

Fig. 1 shows a large-scale passive treatment test system (Location of the study area). The system is surrounded by a 20 m × 40 m fence. The AMD was distributed from an adit to the system through a pipe. The multistep passive treatment system consisted of two Fe-oxidizing/removal biochemical reactors (Fe-A and Fe-B) followed by two sulfate-reducing biochemical reactors (SR-A and SR-B). Fe-A, SR-A, and SR-B were constructed with concrete walls and a floor below the ground surface to maintain at least a 4 °C temperature, as the annual temperature at the test site varied from -10 to 40 °C. Additionally, in 2021, Fe-B was installed in

Figure 1 Large-scale multi-step passive treatment test system (image: Yusei Masaki). Fe-A and Fe-B: Fe-oxidizing/removal biochemical reactors A and B; SR-A and SR-B; sulfate-reducing biochemical reactors A and B. Blue arrow indicates the direction of flow

a steel tank to increase the processing flow rate. The treatment water flow rates of Fe-A and Fe-B were 75 and 25 L/min, respectively, and the blended effluent, totaling 100 L/min, was divided into 50 L/min for SR-A and SR-B. In this study, the treatment results for Fe-B were the main focus. Table 1 shows the water chemistry of the AMD, with the water temperature being 10–17 °C. The pH and soluble Fe, total zinc (Zn), copper (Cu), and cadmium (Cd) concentrations exceeded Japan's domestic discharge standards

Aerobic BCR structures and media conditions

Fig. 2 and Table 2 show the cross-sectional structure and media conditions of Fe-B. The reactor was 2 m wide, 5 m long, and 1.2 m deep

(12 m³). From the Fe-B bottom, perforated pipes and basalt rock with a 0.1 m thickness (13–20 cm) were installed and filled with rice husk media to a depth of 0.5 m (January 2021 to March 2023). From April 2023, the rice husk bed was changed to a mixture of rice husks and limestone (20–40 cm). The weight ratio of rice husks to limestone was set at 1:4, considering the balance of the clogging speed and pH elevation range from the preliminary test results. AMD was introduced from above the water surface of the reactor as a shower to aerate and increase the dissolved oxygen (DO) in the water, because stoichiometrically 5.8 mg/L DO is required to oxidize approximately 38 mg/L ferrous Fe by Fe-oxidizing bacteria. After oxidation, Fe was removed by trapping the precipitants (mainly

Table 1 AMD[1] water quality between April 2019 to December 2023

	Temp. °C	pH	Fe mg/L	Zn mg/L	Cu mg/L	Cd mg/L	SO_4^{2-} mg/L	DO mg/L
Average	13	3.6	38	17	5	0.06	299	0.1
Min–Max	10–18	3.2–4.0	32–49	13–20	1–10	0.04–0.08	249–339	–
Japan's discharge standards	–	5.8–8.6	10	2	3	0.03	–	–

[1]AMD: acid mining drainage; temp: temperature; Fe: iron; Zn: zinc; Cu: copper; Cd: cadmium; SO_4^{2-}: sulfate ion; DO: dissolved oxygen.
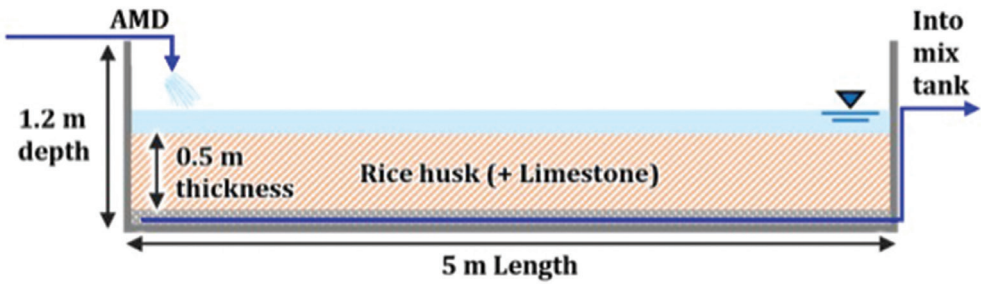
Figure 2 Cross-section structure of Fe-B. Blue arrow indicates the addition of AMD in a shower-like stream, which seeps through the rice husk and limestone layer, and flows into a tank with Fe-A. AMD: acid mine drainage; blue triangle: water level

schwertmannite) in the rice husk media. The Fe-B effluent was mixed with the Fe-A effluent in a mix tank and then fed into the anaerobic process.

Monitoring parameters and Analytical conditions

Temperature, pH, oxidation-reduction potential (ORP, vs. Ag/AgCl) were measured on site using a portable multi-water quality meter (MM-42DP, DKK-TOA Corp., Japan), and dissolved oxygen (DO) using a portable dissolved oxygen meter (HQ1130, Hach Company, CO, USA). The concentrations of ferrous and soluble Fe were measured using the o-phenanthroline method, and Zn, Cu, and Cd were measured using ICP-OES (Agilent 5110 ICP-OES, Agilent Technologies Inc., CA, USA). The sulfate concentrations in the filtrates were determined using ion chromatography (IC; Dionex ICS-6000, Thermofisher Scientific, Waltham, MA, USA).

Results and Discussion

Treatment performance of Fe-B before and after limestone addition

Fig. 3 demonstrates the changes in temperature, pH, ORP, DO, soluble Fe, ferrous concentration, and Fe removal efficiency. The temperature changes of Fe-B influent and effluent between 2021–2023 was between 10 to 18 °C and 7 to 18 °C, respectively. The HRT of the reactor was 2 h, and the water temperature decreased during winter due to the lower temperature. There was no effect on the water temperature upon the addition of limestone from April 2023. The average pH of Fe-B effluent before and after the addition of limestone was 3.0 and 3.2, respectively. In the Fe oxidizing/removal reactor, Fe precipitates were found to mainly form schwertmannite (Masaki et al. 2021), meeting the formation conditions of less than pH 4. The average ORP in the Fe-B effluent was 545 mV before and 490 mV after the addition of limestone. The increase in the average ORP of the influent from 324 mV was due to Fe oxidation, which increased the ferric/ferrous ratio. After the addition of limestone, the ORP decreased as limestone increased the pH, both the ferric concentration and ferric/ferrous ratio decreased. The value of DO in the surface water of Fe-B was maintained at > 5.8 mg/L, which is the stoichiometrically required concentration to oxidize 38 mg/L of Fe. The DO in the surface water was

Table 2 Media conditions of Fe-B

Period	January 2021–March 2023	April 2023–
Media	Rice husk	Mixture of Rice husk and Limestone
Thickness (m)	0.5	0.5
Total media volume (m3)	5	5
Weight of Rice husk (t)	0.6	0.56
Weight of Limestone (t)	0	2.2

affected by water temperature and tended to be low in the summer and high in winter. The soluble Fe concentration in the effluent ranged between 3.9 to 14.9 mg/L (average 6.1 mg/L) before and 1.1 to 3.9 mg/L (average 2.4 mg/L) after limestone addition. Both average concentrations were lower than Japan's domestic discharge standard (10 mg/L); however, the removal rate of soluble Fe increased by an average of 10 %. The ferrous Fe concentration did not change substantially after the addition of limestone, as it had an average of 2.0 and 1.6 mg/L, respectively. Before the addition of limestone, ferric ions were not partially precipitated and were not removed in winter (October to March), whereas after the addition of limestone, the difference in concentration between soluble Fe and ferrous Fe almost disappeared, indicating that ferric ions were removed more efficiently. The average Fe removal efficiency in the effluent of Fe-B was 109 g Fe/day/m^2 (218 g Fe/day/m^3) before and 127 g Fe/day/m^2 (253 g Fe/day/m^3) after the addition of limestone. The Fe removal efficiency increased by 9% with the addition of limestone, indicating that an increase in pH increased the amount of Fe precipitates and the removal efficiency.

Treatment performance of anaerobic processes focused on Fe removal

In the later stage of the Fe oxidation/removal process, metal ions other than Fe (Zn, Cu, and Cd) were precipitated and removed mainly as sulfides. Fig. 4 shows the changes in the pH and soluble Fe, Total Zn, Total Cu concentrations of the AMD, influent, and effluent of SR-A and SR-B. The influent was a mixture of effluents from Fe-A and Fe-B. Since April 2023, only 25 L/min from Fe-B has been acquired from the addition of limestone and since July 2023, whereas, all 100 L/min from both Fe-A and Fe-B have been from the limestone addition conditions. The average effluent pH of SR-A and SR-B was approximately 7.0, from 2021 to 2023. It is assumed that there was enough limestone in the anaerobic reactors to raise the pH, and it was not affected by the effluent in the aerobic reactors. The concentration of soluble Fe in the influent of the anaerobic reactor averaged 7 mg/L between January

2021 and March 2023. The concentrations in the effluents of SR-A and SR-B increased in winter, reaching maximum of 9 and 8 mg/L, respectively. Among the metals contained in the effluent, Cu, Cd, Zn, and Fe had the highest solubility as sulfides, where Fe is the least likely to precipitate as sulfides. Therefore, the Fe concentration in the effluent was almost 0 mg/L in summer (April–September) when the amount of sulfate reduction was sufficient. However, in winter (October–March), the Fe concentration in the effluent increased because it did not precipitate in the SR reactor, as the amount of sulfate reduction decreased at low temperatures (Masaki et al. 2023). Furthermore, it is possible that as the amount of reduced sulfate becomes inadequate, as metal ions such as Zn may undergo ion exchange reactions with Fe sulfides, resulting in the re-leaching of Fe. From July 2023, after the addition of limestone to both Fe-A and Fe-B, the average influent concentration decreased to 3 mg/L. The soluble Fe concentrations in the effluents of SR-A and SR-B were less than 1 mg/L because of the decrease in the Fe concentration of the influent. This is well below Japan's domestic discharge standard of 10 mg/L, indicating that stable treatment is possible. Soluble Fe concentrations have remained at nearly 0 mg/L since October 2023, and the results for the winter season after January 2024 will be reported in a presentation. Metals other than Fe (Zn, Cu, and Cd) were treated regardless of changes in the Fe oxidation/removal reactor conditions. The concentrations in the influents of anaerobic reactors before and after limestone addition in aerobic reactors (July 2023) were 16.8 and 16.5 mg/L for total Zn, 4.7 and 4.2 mg/L for total Cu and both 0.06 mg/L for total Cd. These metal concentrations did not change substantially. The spikes in the Zn concentrations in the effluents of SR-A and SR-B in winter were mainly affected by the nutrient conditions of anaerobic reactors. For the last 3 years (January 2021 to December 2023), the concentrations in the effluent of SR-A and SR-B were 0.5 and 0.6 mg/L for total Zn (except spikes in winter) and 0.01 and 0.03 mg/L for Cu, respectively. The concentrations in the effluent of SR-A and SR-B for Cd were below detection limits. These concentrations
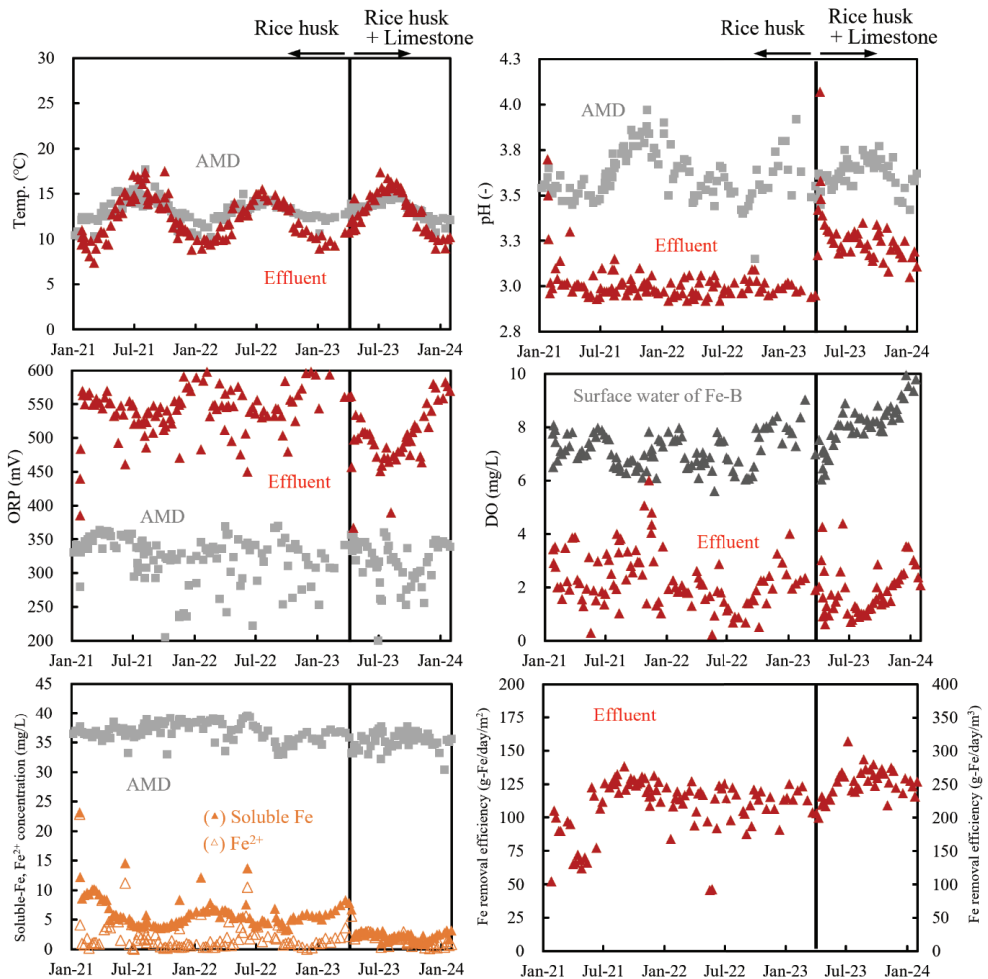
Figure 3 Changes in temperature, pH, ORP, DO, concentrations of soluble and ferrous Fe, Fe removal efficiency, and effluent of Fe-B. Grey squares: AMD; red triangles: effluent; dark grey triangles: surface water of Fe-B. Bottom left figure, orange triangle: soluble Fe; orange-bordered triangle: Fe^{2+}. AMD: acid mine drainage; ORP: oxidation-reduction potential; DO: dissolved oxygen

were below Japan's domestic discharge standards.

Conclusions

The improvement in Fe removal performance in a large-scale passive treatment test by the addition of limestone to rice husk media of an aerobic reactor was investigated. The limestone to rice husk (weight ratio of 4:1) increased the pH of the effluent in the BCR from 3.0 to 3.2, and almost all the ferric ions were removed by precipitation. The pH was maintained below 4, which is in the precipitation range of schwertmannite.

The concentration of soluble Fe in the Fe-B effluent decreased from 6 mg/L to an average of 2 mg/L. The concentration of soluble Fe in the effluent of the anaerobic reactor was up to 9 mg/L before the addition of limestone to the aerobic reactors; however, after the addition of limestone, the concentration remained below 1 mg/L until December 2023, which is well below Japan's domestic discharge standard. Zn, Cu, and Cd were treated stably regardless of changes in the Fe oxidizing/removal reactor conditions. For the last 3 years (January 2021 to December 2023), the concentrations in the effluent of SR-A
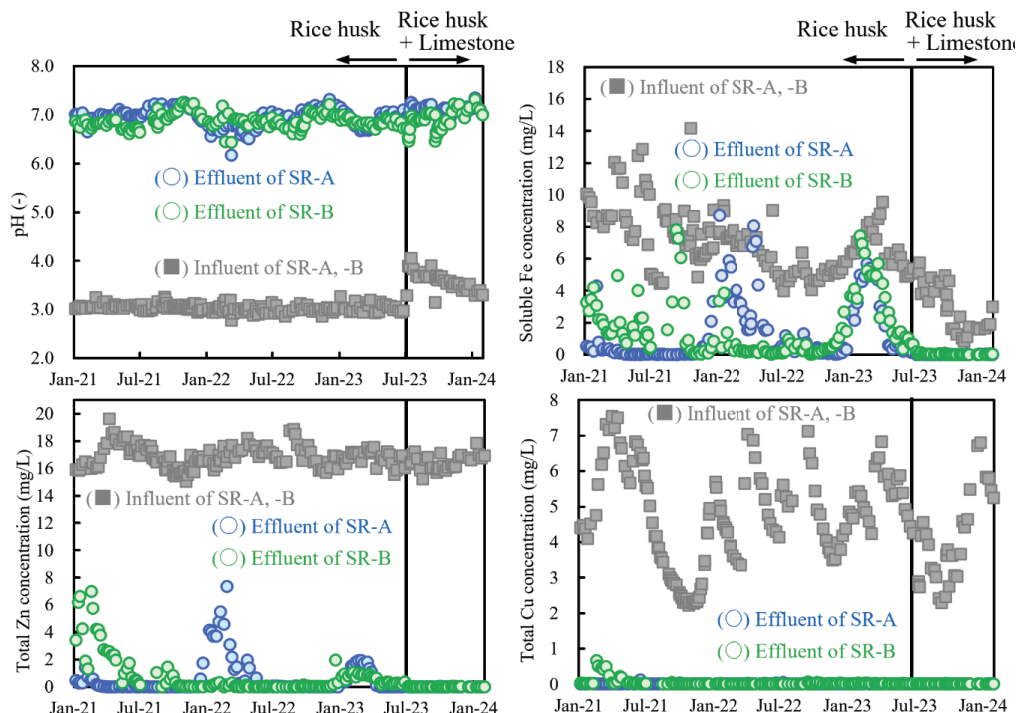
Figure 4 Changes in pH, soluble Fe, Total Zn and Cu concentration of AMD, mixture of Fe-A and Fe-B (influent of anaerobic process), effluent of SR-A and SR-B. Blue circle: effluent of SR-A; green circle: effluent of SR-B; grey square: influent of SR-A, -B. SR-: sulfate reducing bioreactor

and SR-B were 0.5 and 0.6 mg/L for total Zn (except the spikes in winter) and 0.01 and 0.03 mg/L for Cu, respectively. The concentrations in the effluent of SR-A and SR-B for Cd were below detection limits. Long-term treatability and maintainability should be tested in future large-scale studies.

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