A compact Passive Treatment Process for AMD Using Rice Husk and Rice Bran

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Abstract

An energy and cost saving biological passive treatment system for acid mine drainage (AMD) developed by Japan Oil, Gas and Metals National Corporation (JOGMEC) is a vertical flow anaerobic process that utilizes sulfate-reducing bacteria(SRB) with rice husk and limestone as the substrate and rice bran as the organic resource of SRB. In addition to this sulfate reducing process, an aerobic process of iron oxidation and removal that utilizes iron-oxidizing bacteria is applied to treat high iron content AMD. Iron scale from the aqueduct of drainage treatment facilities has been used as source of the iron-oxidizing bacteria. This passive treatment process is called “JOGMEC Process”.

In Japan, flat areas that can be used for mine drainage treatment are limited due to geographic conditions. Therefore, it is necessary to introduce a compact passive treatment system with a higher flow rate (shorter hydraulic retention time (HRT)) compared to the other conventional anaerobic processes that utilize SRB. Then, the laboratory tests have been carried out under short HRT conditions about 25 ~ 50 hours.

Since 2014, bench-scale tests have been carried out at an abandoned mine site in Japan. Concentrations of dissolved metals in AMD of the mine are 35-40 mg/L iron (mainly ferrous ion), 18 mg/L zinc, and 8 mg/L copper, respectively, and the value of pH is 3.5. As the AMD contains high concentration of iron, it is firstly removed with the aerobic process of iron oxidation and removal, and then the other metals have been removed with the anaerobic process in the subsequent stage. The results of bench-scale tests show that the metals have been continuously removed for about 300 days under a flow rate of 80 mL/min (the nominal HRT in anaerobic process: 50 hours). During the test term, atmospheric temperature dropped to around -15°C in the winter, and the temperature inside of the reactor of the anaerobic process dropped to around 5°C. The performance of metals removal has been stable even in the lowest temperature during the test term. At present, the metals removal has stably continued for about half a year under challenging conditions that a flow rate has been set to 160 mL/min (the nominal HRT in anaerobic process: 25 hours).

Since rice bran, which contains high amount of carbon as sugar, protein and lipid, would be easily decomposed by bacteria, it seems that much organic acids have supplied to SRB and the metals removal has stably continued under short HRT and low temperature conditions. The results suggest that “JOGMEC Process” is able to treat AMD under shorter HRT compared to the conventional biological processes.

Key words: AMD, Passive Treatment, Sulfate Reducing Bacteria

Introduction

Japan Oil, Gas and Metals National Corporation(JOGMEC) has conducted researches on the passive treatment for mine drainage since 2007, and has focused on treatment methods in which metal ions would be removed as sulfides using sulfate reducing bacteria (SRB). For neutral pH mine drainage, field tests have been carried out using an anaerobic bioreactor filled with “rice husk” as an organic carbon source. The successful removal of metal ions had continued for approximately 1100 days under the appropriate conditions (retention time: 50 h, water temperature: over 15 °C).

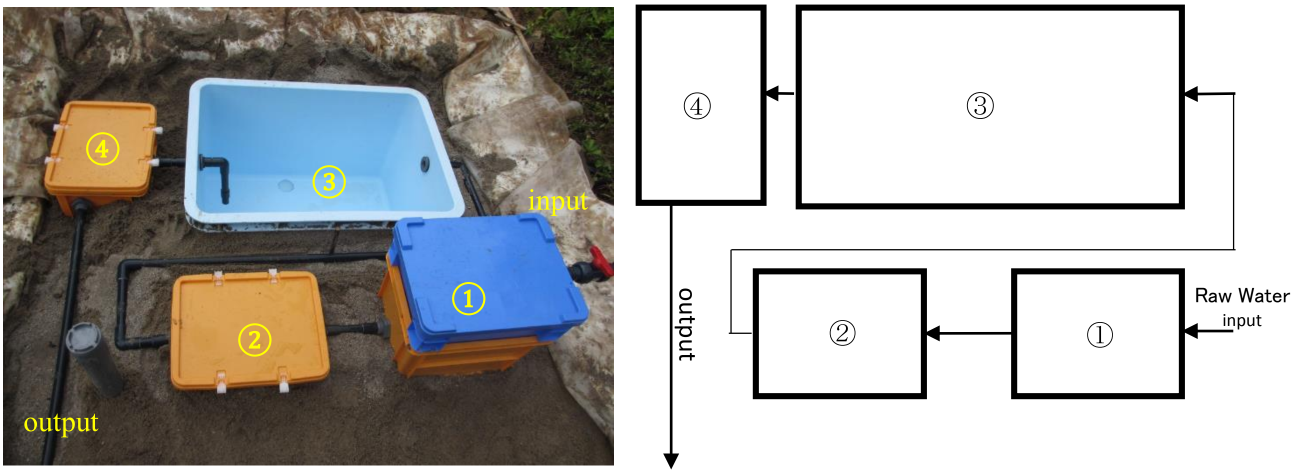
Further, the field test has been carried out using the anaerobic bioreactor filled with “rice bran” in addition to “rice husk” for acid mine drainage since 2014. Continuous removal of metals for more than 300 days has been confirmed with the retention time of 50 hours under natural environment where the atmospheric temperature in the winter reached to around -10 °C.

As mentioned above, the “JOGMEC process” which utilizes the SRB growth inside the anaerobic bioreactor filled with rice husk and rice bran to remove metal ions as sulfides has been proven to have enough capability for long term treatment of acid mine drainage with a retention time of about 50 hours. In addition, the analyses on metal precipitates, bacterial flora, and so on, in the bioreactor have revealed various aspects of the reaction mechanisms related to removal of metal ions with hydrogen sulfide ions originated by the reduction with SRB. As the retention time of 50 hours is one third to one fifth shorter compared to those in general test cases, the treatment equipment could be downsized. However further advance in efficiency of the process would be needed to increase applicability to treatment systems for mine drainage in Japan. Thus, it is under investigation to aim at realizing the process with a retention time of 25 hours since 2015.

Methods

(1)Equipment

A test field of about 3 m square in area and 1 m in height was prepared in abandoned mine site in Akita prefecture, northern part of Japan. Each bioreactor was installed in the field surrounded by soil walls. Mound was layered within the field to simulate land burial. There are sequentially placed an “aerobic iron oxidation-removal bioreactor (iron oxidation bioreactor)” which oxidizes ferrous ions to ferric ions and precipitates as oxy-hydroxide and an “anaerobic bioreactor” which utilizes SRB to precipitate metal ions as sulfides. Fig. 1 shows an arrangement of an iron oxidation bioreactor and an anaerobic bioreactor used in this test.



(a) a picture of test apparatus (b) a plain view of test apparatus

Fig.1 *Test Apparatus*

①：iron oxidation bioreactor, ②④：tank for obtaining samples、③anaerobic bioreactor

(2)Structure and contents of the bioreactors

Dimensions of the iron oxidation bioreactor and the anaerobic bioreactor were 422 mm × 320 mm × 300 mm and 1006 mm × 703 mm × 603 mm respectively. As the ion oxidation bioreactor requires air supply to activate aerobic iron-oxidizing bacteria, a tank with numerous drainage holes on the bottom surface is stacked upon the iron oxidation bioreactor and the raw water has been introducing to the upper tank at first and then dropped down on iron oxidation bioreactor through contact with the air. The iron oxidation bioreactor is filled with approx. 20 kg in wet weight of iron-scales that have been precipitating on the aqueduct for mine drainage.

The anaerobic bioreactor is filled with the following materials. Soil collected from the surface layer around the mine site was used as "a resource of bacteria "including SRB. Rice husk was used as "a base material" of the bioreactor and as "a nutrient" for bacteria. Furthermore, rice bran and green tea leaves were added as "easily decomposable organic matters", which is decomposed by bacteria more easily than rice husk. It was shown by the analysis that rice bran in particular contains much protein, lipid and starch and green tea leaves contain much protein, so they would be easily decomposable by bacteria. It is assumed that low-molecular substances will be provided to SRB. Limestone (3 to 20 mm in size) was used as structural material for "securing cavities" and for buffering the pH value. The initial weight of those filling materials were 25.5 kg of rice husk, 24.5 kg of rice bran, 8.5 kg of green tea leaves, 102 g of soil, and 10.2 kg of limestone. Rice husk, green tea leaves, and soil were steered evenly and filled in the column so that they were distributed evenly in the whole reactor but rice bran was filled intensively in the upper portion. A total of 250 L of mine water could be filled into the bioreactor as raw water after the reactor had been filled with those contents. Further 5 kg of rice bran was added to make a total weight of 29.5 kg in May 2015 when the flow rate of the water was doubled.

(3)Experiments

・Acclimation of SRB

Before filling the bioreactor, rice husk, green tea leaves, limestone, and soil were mixed in a separate vessel and water sealed with the mine water as sulfate ion source and SRB were acclimated for approx. 2 weeks. Then, the contents were filled into the bioreactor and SRB were further acclimated within the bioreactor up to 5 days. When ORP value of the water filled in the bioreactor became approx. -200 to -300 mV, SRB were thought to be active and mine water has been fed to the bioreactor. Feeding was started in August 2014.

・Quality of treated water

The pH value of drainage is 3.5 and the concentrations of iron, zinc, copper, cadmium, and sulfate ions are around 40 mg/L, 15 to 18 mg/L, 3 to 10 mg/L, 0.06 mg/L, and 300 to 350 mg/L respectively. They have not showed fluctuation so much throughout the year.

・Analysis of items

Samples of the treated water from the bioreactor were collected periodically. Analysis items included temperature, pH, ORP, metal ions concentrations (iron, copper, cadmium, and so on), sulfate ion concentration, sulfide ion concentration, and COD. Concentrations of metal ion were determined using ICP and sulfate ion was determined using ion chromatography. Sulfide ion concentration was colorimetrically measured as hydrogen-sulfide ion and COD value determined titration method.

・Flow rate

Flow rate was maintained at 80 mL/min since August 2014 to May 2015. As the water volume of the anaerobic bioreactor is 250 L, the retention time is 50 hours. The flow rate was increased to 160 mL/min to reduce retention time to 25 hours since May 2015. Time period with retention time of 50 hours was 275 days and that with retention time of 25 hours was 263 days at the end of January 2016.

・Temperature conditions

Neither of the bioreactors was subjected to temperature control except the use of minimal heat insulating material (glass wool) for frost protection of water channel for the raw water. Equipment had not been protected with a roof so that tests were conducted in the condition similar to natural environment, thus they were covered with snow (around 70 to 80 cm in thickness) in the winter.

Results

(1) Inflow rate to the equipment

Fig.2 shows the changes in flow rate of the test equipment (flow rate was measured for the treated water). As the pre-determined flow rate (80 mL/min or 160 mL/min) was kept almost for the test term, it seemed that a natural flow of the water was maintained generally. Decreases in the flow rate were observed on 150th day (at the beginning of January in 2015) and on 400th day (at the beginning of October in 2015) after the start of the experiment. The former was caused by clogging of rice bran within a channel which conducted the raw water to the anaerobic bioreactor and the flow rate was recovered after the removal of it. The latter was caused by iron scales that had been precipitated on the bottom of the tank that was stacked upon the iron oxidation bioreactor. After the removal of scales which had blocked drainage holes of the tank, the flow rate was recovered.

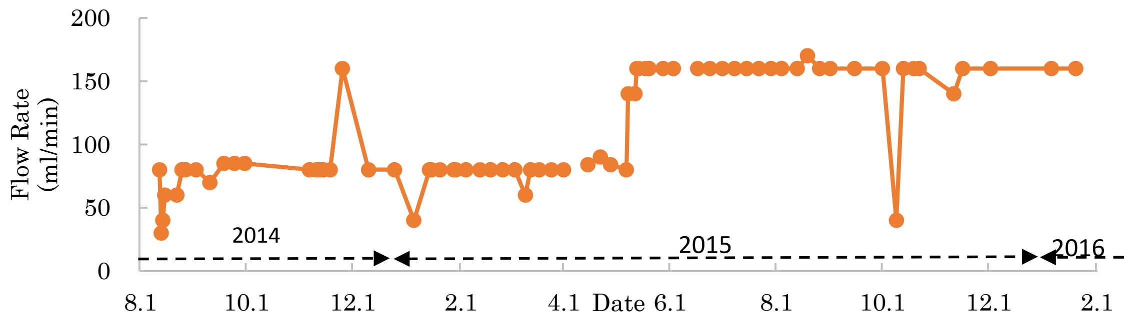


Fig. 2 *Changes in flow rate*

(2) Changes in temperature in the anaerobic bioreactor

Fig.3 shows temperature changes in the inside of anaerobic bioreactor as well as those in the raw water and in the outside air. The temperature inside the bioreactor was measured at the center portion. Fig.3 shows that the mine water used in this test have been flowing in at a constant temperature (12 to 14 °C) throughout the year.

Regarding the temperature change in the anaerobic bioreactor, it was above 20 °C at the initial stage of the experiment and decreased gradually to 5 °C in December 2014 as the atmospheric temperature decreased. After the flow rate was doubled in May 2015, the temperature variation in the inside of the bioreactor became small and the temperature was stabilized at around 10 °C in December 2015. This is thought to be caused by the increased flow rate in twice, which made the temperature inside the bioreactor less affected by that in the atmosphere. In terms of temperature, the environment inside the bioreactor with the retention time of 25 hours exhibited less variability and was estimated to be more suitable for maintaining microflora and activity of bacterial groups.

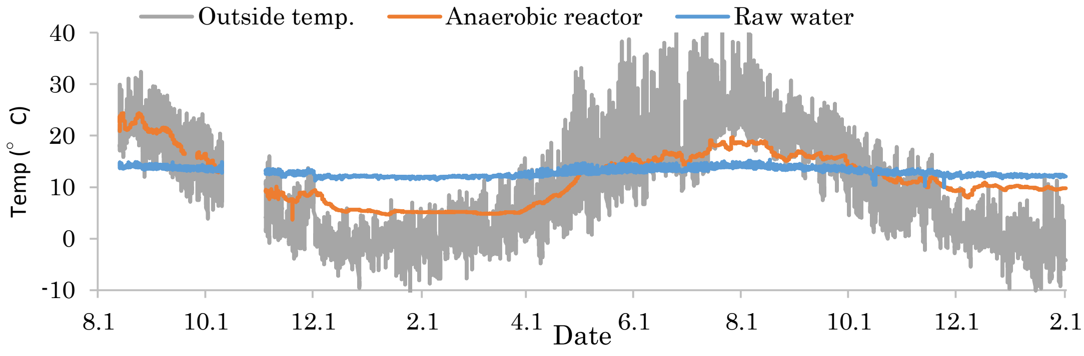


Fig. 3 *Changes in temperature*

(3) Changes in pH and ORP values in the treated water
Figs.4 and 5 show the changes in pH values and ORP values respectively. These show that pH values in the raw water were maintained around 3.5 throughout the year. For the treated water, the pH value increased to over 6 and had become stable below the regulation standard except the initial stage of water feeding. ORP values were also maintained below -200 mV except the initial stage, suggesting a stable reductive atmosphere was formed inside the anaerobic bioreactor. Both the pH and the ORP remained stable without showing instabilities under the retention time of 25 hours. The stable pH was thought to be maintained by continuous neutralization effect due to limestones filling the inside of the bioreactor and the ORP was thought to be stabilized by continuous sulfate ion reduction by the SRB inside the bioreactor. It is suggested that the retention time of 25 hours induced stable expressions for both measures.

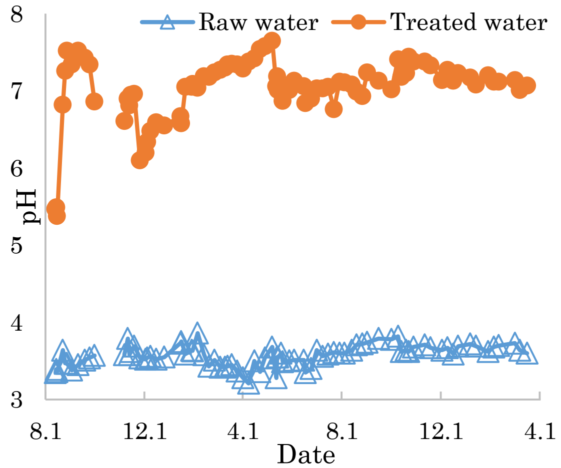


Fig. 4 *Changes in pH values*

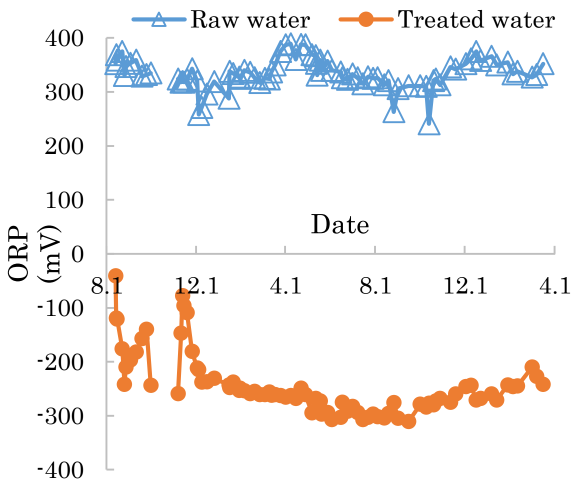


Fig. 5 *Changes in ORP values*

(4) Changes in sulfate ions in the treated water
Changes in the sulfate ion concentration in the raw water are compared to those in the treated water in Fig.6. The concentration of sulfate ion in the bioreactor decreased immediately after the start of water feed and was kept at stable decreased level in the winter season. A decrease in ion concentration was approx. 150 mg/L. Soon after the increase in flow rate in May 2015, the concentration of sulfate ion was shown a temporary increase, and then began to decrease again. A decrease in ion concentration was over 200 mg/L in the summer season. Since October 2015, the concentration of sulfate ion in the treated water tended to increase. After that, however, the deference between the sulfate ion concentration

in the raw water and that in the treated water was stably kept during the winter. This showed that the reduction by SRB adequately lasted even in the winter. Compared to the trend in the winter season with the retention time of 50 hours, decrease in sulfate ion in the bioreactor with retention time of 25 hours was small but the amount of reduction was approx. 100 mg/L and maintained stably in the winter season. Along with the results shown in Fig.5, continuous and stable reduction of sulfate ions by SRB is suggested

(5) Changes in the concentration of metal ions in the treated water
Fig.7 shows the changes in the concentration of iron, zinc, and cadmium in the treated water. Slightly higher concentrations, especially higher iron concentration, were observed immediately after both the start and the interruption of the test, but all of metal ion concentrations were at an appropriate lower level thereafter. Mean metal ions concentrations throughout the test period were 1.26 mg/L for iron, 0.16 mg/L for zinc, and 0.002 mg/L for cadmium.

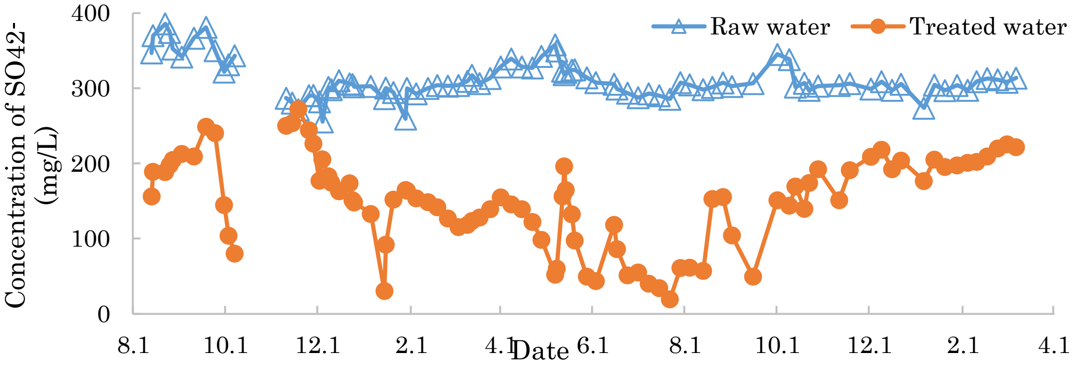


***Fig. 6** Changes in concentrations of sulfate ion*

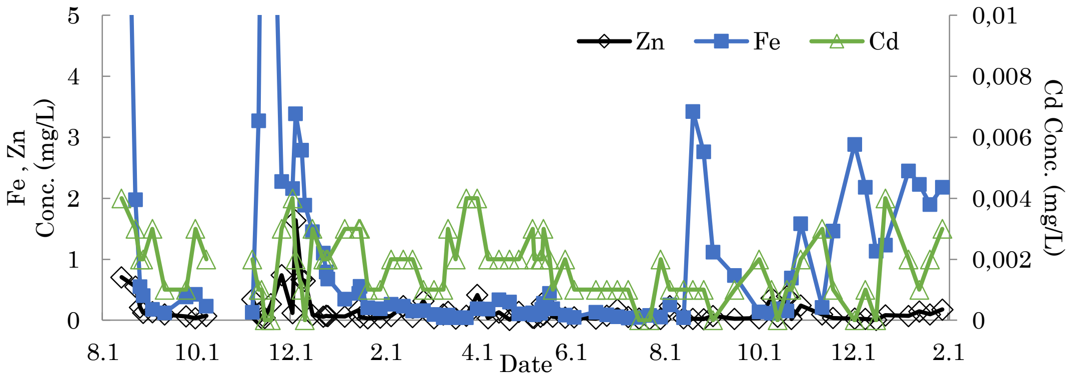


***Fig. 7** Changes in concentrations of Zn, Fe and Cd*

Discussion

・Treatment performance for metal ions with the retention time of 25 hours

Based on the results shown in Figs. 5 to 7, it can be estimated that the sulfate ion in the raw water has been reduced by SRB, and hydrogen sulfide ion has been produced, and metal ions have been precipitated as sulfides, and then metal sulfides have been collected by the rice husk. Although decrease in concentration of sulfate ion with the retention time of 25 hours have been smaller than that with the retention time of 50 hours, the concentration of metal ions has been reduced to the similar level in the treated water in the both cases. Thus, these treatment performances for metal ions have been thought to be about same.

Fig.3 shows that the temperature fluctuation in the bioreactor with the retention time of 25 hours was as small as around 10 °C even in the winter season, in which condition activities of bacteria groups including SRB to reduce sulfate ion could be more effectively maintained. In spite of increased load with doubled flow rate, a suitable environment for bacteria groups might be provided in terms of temperature. Increased flow rate imposes load to the bioreactor from the viewpoint of the increase of volume to be treated, while it reduces load related with the temperature fluctuation. This may be suggestive to design more efficient and compact processes.

When the flow rate was doubled, rice bran was refilled to the bioreactor. Therefore the low molecular organic carbons provided to SRB also increased. This might contribute to enhance the capability of metal treatment. So, rice bran added could supply sufficient amount of low molecular organic carbons to the SRB to reduce sulfate ion efficiently and stably even with the retention time of 25 hours. Here, only rice bran was added and tested. The production/supplying area of green tea leaves are limited compared to that of rice bran in Japan, and so only rice bran was refilled in terms of availability. In consequence, in case of rice bran significant effect could be obtained as described above, and then, rice bran seems to have good aptitude as the easily decomposable organic matter in this process.

The results suggest that the structure of the bioreactor, filling content, and filling volume used in this experiment with the retention time of 25 hours could successfully treat AMD. As for the continuity of the treatment, it has run stably over 250 days so far and further stable processing would be anticipated for a long-term stability.

Conclusions

During the field test on the JOGMEC process utilizing the activity of the SRB to treat AMD, the stable metal removal with the retention time of 25 hours continues currently. Therefore, it could be said that more effective metal removal would be realized compared to the conventional process. Firstly, the seasonal fluctuation of temperature in the bioreactor has resultantly become smaller due to the increase of flow rate of water through the reactor. Secondly, appropriate refilling of rice bran which supplies low molecular organic carbons has adequately improved the activity of bacteria including SRB. Thus, the compactification of the JOGMEC process could be expected and the applicability to AMD treatment would be extended in Japan.

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