

## Research on the applicability of anaerobic passive bioreactor for mine water treatment in Japan

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### Abstract

Anaerobic bioremediation with sulfate-reducing bacteria is well-known as an effective passive mine drainage treatment technology. In this study, the treatment test for acid mine drainage (pH: 3.3 ~ 4.1, Zn: 4.89 ~ 12.32 mg/L, Pb: 0.48 ~ 1.07 mg/L, Cu: 2.48 ~ 5.60 mg/L) was conducted with the anaerobic bioreactor containing rice husk and composted bark with cow manure in order to research the applicability of this technology to abandoned mine sites in Japan. The results show that high metal removal efficiency and continuous sulfate reduction were maintained in the bioreactor for more than 300 days.

**Key words:** passive mine drainage treatment, sulfate-reducing bacteria, anaerobic bioreactor, rice husk

### Introduction

Passive treatment system which uses natural purification processes has attracted a lot of attention as a low cost and maintenance mine drainage treatment technology, and many research results of verification tests on this passive system have been reported mainly in the United States and Europe (e.g. Gusek et al. 1998, Younger et al. 2003). In Japan, however, no passive treatment system is actually introduced. All mine drainage treatment plants use active systems where neutralizer, electricity and daily maintenance are required. However, recently, from the viewpoint of cost reduction for the mine drainage treatment, the research on the applicability of passive treatment system in the domestic abandoned metal mine sites has been started by Japan Oil, Gas and Metals National Corporation.

In this research, some fundamental tests were carried out in order to design the treatment system with anaerobic bioreactors. In the bioreactor containing sulfate reducing bacteria (SRB), dissolved heavy metals are capably removed as metal sulfides because sulfide is more insoluble compared with hydroxide.

From our previous works, it was found that the neutral pH drainage could be treated in the anaerobic bioreactor consisting of rice husk and composted bark with cow manure with the hydraulic residence time of 50 hours. Based on this

result, the pilot scale test is being conducted at an abandoned mine site located in western Japan since 2009 (Furuya et al. 2011).

Furthermore, the same kinds of tests have been conducted for the treatment of the lower-pH and more metal-loaded mine drainage. This paper shows the monitoring results at the laboratory-scale (hereafter: lab-scale), continuous treatment tests and the metal removal effectiveness and sulfate reducing performance of the bioreactors.

## Methods

### *Mine drainage*

The mine drainage for the lab-scale test was sampled from the abandoned mine in the Akita prefecture located in the northern part of Japan. As shown in Table 1, zinc, copper and lead concentrations in the drainage constantly exceed the national effluent standard. At present, the drainage, which is a mixture of three kinds of seepage water from an old tailing dam, is treated with slaked lime at the active treatment plant. Sampling work at the mine site was carried out about once in the three months. Therefore, the water quality of the influent water often changed during the test.

**Table 1** Water quality of the mine drainage for the test and the national effluent standard values. pH Zn (mg/L) Cu (mg/L) Pb (mg/L) SO<sub>4</sub><sup>2-</sup> (mg/L)

	pH	Zn (mg L <sup>-1</sup> )	Cu (mg L <sup>-1</sup> )	Pb (mg L <sup>-1</sup> )	SO <sub>4</sub> <sup>2-</sup> (mg L <sup>-1</sup> )
Mine drainage (min ~ max)	3.3~4.1	4.89~12.32	2.48~5.6	0.48~1.07	120~364
National effluent standard	5.8~8.6	2.0	3.0	0.1	

### *Organic carbon resources*

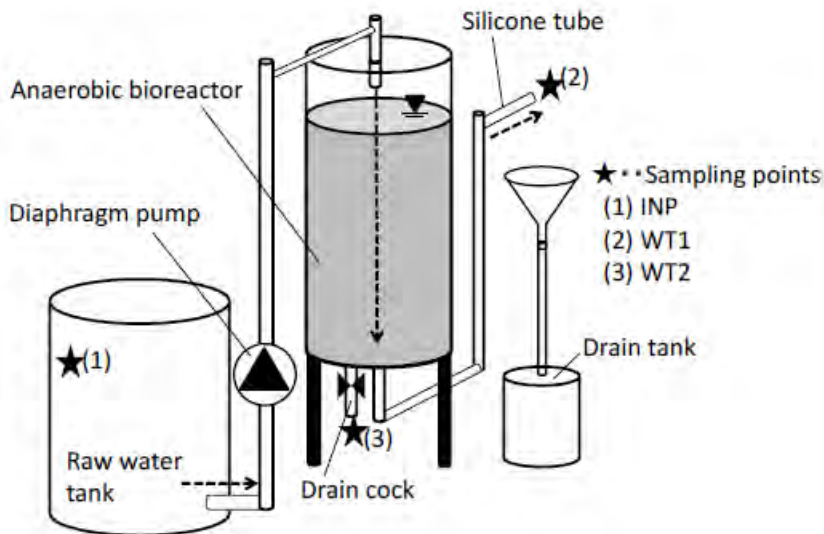
Generally, carbon resources for anaerobic biological passive treatment systems are prepared by mixing relatively biodegradable materials and more recalcitrant materials (Johnson and Hallberg 2005). In this study, a mixture of composted bark with cow manure and rice husk was put into the bioreactor. Especially rice husk is a common agricultural waste in Japan and it is easily available without cost. Moreover, this material was found to be effective as a carbon resource for microbes in the past research (Furuya et al. 2011). Crushed silica stones with a grain diameter of around 5 mm, were mixed in the organic materials in order to prevent the contents in the reactor from being compressed or floating out. Volume and weight fractions of each component in the bioreactor are shown in Table 2.

**Table 2** Composition of mixture in the bioreactor.

Components	Rice husk	Composted bark with cow manure	Crushed silica stone
Vol.%	25	25	50
Wt.%	3	14	83

### Apparatus

A schematic diagram of the setup for the treatment test with anaerobic bioreactor is shown in Figure 1. The bioreactor was made of vinyl chloride pipe with an inner diameter of 100 mm. Organic carbon resources and the mine drainage were filled into the bioreactor to the height of 450 mm. After three weeks of static incubation at 15~20 °C, the continuous treatment tests started. The mine drainage, the influent water, was pumped up to the top of the bioreactor with constant flow rate and treated by passing through to the bottom with gravity flow. The treated water was discharged from the silicone tube which extended from the bottom to a static water surface level. The drain cock was also attached to the bottom in order to directly sample from the inside of the bioreactor. The flow rate of the influent water was set at 33 mL/h for the first 310 days and after that, its rate was increased to 52 mL/h. Each hydraulic residence time, which was decided by flow rate and pore volume inside the bioreactor, was about 50 and 33 hours respectively. Water temperature in the reactor was kept at 15~20 °C by attaching a heating belt around the bioreactor. After 440 days since the start of the test, the temperature was controlled at 25~30 °C.



**Figure 1** A schematic diagram of the setup for continuous treatment test with anaerobic bioreactor.

### Monitoring parameters

The treated water was sampled from silicone tube (WT1) and drain cock (WT2) once a week. The water quality of WT1 and WT2 were monitored from 14 days after and 266 days after the test started, respectively. In addition, the influent water quality was also monitored once a month. The monitoring parameters of

each sample are shown in Table 3. The pH and oxidation-reduction potential (ORP) were measured with portable water quality meters (pH: TOA-DKK, HM-21P, ORP : HORIBA, D-54 with Ag-AgCl electrode). Concentrations of heavy metal ions, such as zinc, copper and lead, and sulfate were analyzed by ICP-AES (Seiko Instrument Inc, SPS3100) and Ion Chromatography (TOA-DKK, ICA-2000), respectively.

**Table 3** Monitoring parameters.

<b>Monitoring Sample</b>	<b>pH</b>	<b>ORP</b>	<b>Zn</b>	<b>Cu</b>	<b>Pb</b>	<b>SO<sub>4</sub><sup>2-</sup></b>
Influent water, WT1	0	-	0	0	0	0
WT2	0	0	-	-	-	0

## Results and discussion

### *The first monitoring period (14 ~ 310 days)*

The pH values of WT1 and WT2 were between 6.5 and 8.0 (Figure 2(a)). These results show that the influent water was neutralized in the bioreactor. This rise of pH supposedly occurred by composted bark with cow manure which was found to be able to increase the alkalinity by our previous test results. As shown in Figure 2(b), the ORP values of WT2 were kept around -300 mV during this monitoring period. The result shows that the influent water was treated under anaerobic condition.

As shown in Figure 2(c), sulfate concentrations at WT1 were lower than that of the influent water. From 266 days after the test started, the sulfate concentration in WT2 was also monitored. The concentrations at WT2 were obviously lower than that in WT1. From these results, it is supposed that sulfate reduction reaction occurred nonuniformly in the bioreactor.

The concentrations of zinc, copper and lead in the influent water and at WT1 varied as shown in Figure 2(e) ~ (g), respectively. In this period, where the flow rate of the influent water was set at 33 mL/h, these dissolved metals in the influent water were sufficiently and stably removed in the bioreactor. As the pH values at WT1 and WT2 were remained between 6.5 ~ 8.0, zinc and lead hydroxide precipitates could not be formed sufficiently. Therefore, these metals were probably removed by sulfide precipitation or adsorption to the surface of organic materials.

### *The second monitoring period (310 ~ 440 days)*

In this period, where the influent flow rate was increased from 33 mL/h to 52 mL/h, pH of the treated water samples decreased and ORP at WT2 increased with time. Although pH values at WT2 were between 6.36 and 6.75, that at WT1 dropped steeply to 4.17 ~ 4.31. These results show that acidic and oxidized condition began to be predominant in a part of the bioreactor with the increase of flow rate.

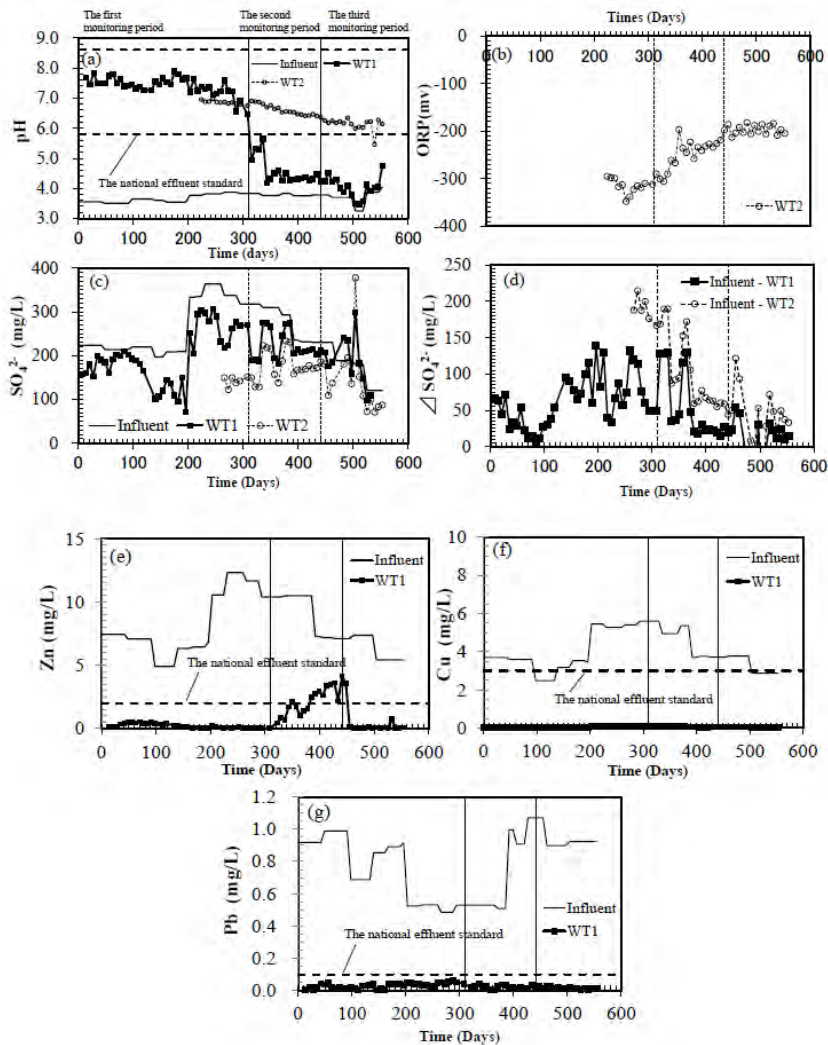
The concentrations of sulfate at WT1 and WT2 continued to be lower than that in the influent water. The result shows that sulfate reduction could take place even though the influent flow rate was increased. However, the reduction extent of the concentration of sulfate ion in both samples decreased to around 20 mg/L and 50 mg/L, respectively at the end of this period (Figure 2(d)).

While the dissolved copper and lead in the influent water continued to be removed, only the concentration of zinc at WT1 gradually increased from 0.02 mg/L to 4.13 mg/L which exceeded the national effluent standard of 2.0 mg/L. However, filtering WT1 sampled at this period with 0.45 micron filter, zinc concentrations decreased to less than the effluent standard (not shown in Figure 2(e)). From the result, it is supposed that the effluence of the precipitate caused the rise of the concentration and that dissolved metals in the influent water were removed by precipitation in the bioreactor.

*The third monitoring period (440 days ~553 days)*

From 440 days after the test started, the water temperature was controlled at around 25 °C by heating belt in order to stimulate the activity of anaerobic bacteria. However, remarkable decrease in ORP at WT2 was not observed and the values were maintained around -200 mV during this monitoring period. Sulfate concentrations at WT1 and WT2 decreased around the beginning of this period, and since then, the concentrations increased rapidly to the level near that of the influent. Some monitoring data significantly exceeded the concentration of the influent. It was probably caused because some amount of sulfur precipitate, which was once generated by bacterial sulfate reduction and accumulated in the bioreactor or the silicone tube, was dissolved again in the form of sulfate ion.

Nevertheless, zinc concentrations at WT1 decreased again at 455 days after the test started, and the values were kept at 0.02 ~ 0.74 mg/L. This reduction occurred with the same tendency as the sulfate reduction. Therefore, the dissolved metals in the influent water were probably precipitated as sulfides in the bioreactor. Additionally, from the results shown in Figure 2(e) and (f), copper and lead in the influent water were completely removed during all the monitoring periods.



**Figure 2** Water quality changes of the treated water samples (WT1 and WT2)

#### Probability of metal sulfide formation

According to the past research, the metal removal mechanism in a passive bioreactor was described as follows (Neculita et al. 2007): "The metal removal mechanisms change during the life of a passive bioreactor. Upon startup of a passive bioreactor, the adsorption of dissolved metals onto organic sites in the substrate material will be an important process", "Once sulfate-reducing conditions are established, sulfide precipitation becomes the predominant mechanism of metal removal from acid mine drainage".

Considering the corresponding solubility products for metal sulfide such as ZnS, CuS and PbS under the experimental conditions in this research, the sufficient amount of sulfide ions were probably generated for the stable sulfide precipitation. Therefore, the similar removal process as mentioned above was assumed to proceed in the bioreactor.

## Conclusions

The lab-scale anaerobic passive bioreactor consisting of a mixture of rice husk and composted bark with cow manure could efficiently treat the acid mine drainage, which contained zinc, copper and lead, especially with the flow rate of 33 mL/h (estimated residence time : 50 hours). Sulfate reduction was observed during almost all the test period. This result shows that sufficient sulfide ion was generated by bacterial sulfate reduction in the bioreactor and that the dissolved metals in the influent water were probably precipitated and accumulated in the form of metal sulfide in the bioreactor. These results on this lab-scale test indicate the applicability of the anaerobic passive bioreactor to on-site pilot scale test .

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