The Sequential Experiments of Passive Treatment System Using Bioreactor for Acid Mine Drainage in Japan

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ABSTRACT

Japan Oil, Gas and Metals National Corporation (JOGMEC) has been researching a low-cost microorganism-based passive treatment system for acid mine drainage (AMD). This system consists of the aerobic reactor and the following anaerobic one that utilizes iron-oxidizing bacteria and sulfate-reducing bacteria, respectively.

The aerobic reactor is filled with iron scales including iron-oxidizing bacteria from the aqueduct of drainage treatment facilities, and iron ions have been oxidized by iron-oxidizing bacteria and removed as iron oxides. In the anaerobic reactor, which is filled with rice husk, limestone, soil, and rice bran, various metal ions (copper, zinc, lead, cadmium, etc.) have been removed as sulfides by the action of sulfate-reducing bacteria. The materials used to be filled in the reactors are either free or very inexpensive to be got in Japan.

Since 2013, the field tests have been carrying out at abandoned mine site. The concentrations of solved metals in the targeted AMD are 35–40 mg/L iron, 18 mg/L zinc, and 8 mg/L copper, and the value of pH is 3.5. The results of field tests showed that 80% of the iron ion has been removed with the retention time of approximately 2 hours in the aerobic reactor, while almost of the other metal ions have been removed with the retention time of 50 hours in the anaerobic reactor. The tests have been running for approximately a year until at present, June 2014. The metals have been continuously removed without another maintenance and addition of materials and reagents during the test period. Moreover, in the reactors, which were not temperature-controlled, the metals continued to be removed even in winter, although the internal temperature dropped to approximately 5°C during the winter.

It is expected that this passive treatment system for AMD can be scale-upped and realized to be a cost-saving and energy-saving treatment system.

Keywords: Passive treatment, Sulfide reducing bacteria, Acid mine drainage, Iron-oxidizing bacteria

INTRODUCTION

Japan Oil, Gas and Metals National Corporation(JOGMEC) has conducted research on the passive treatment of mine drainage since 2007, and has focused on drainage treatment methods that remove metal ions 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). For acid mine drainage, with pH 3.0, containing several types of metal ions, the field tests are being performed using an anaerobic bioreactor filled with “rice bran” and “rice husk” as the organic carbon sources.

In many cases, acid mine drainages contains iron ions, which are difficult to be removed as sulfides because of their relatively high solubility. Therefore, in these field tests, iron oxide bacteria were employed separately to remove the iron ions from the mine drainage, prior to removing the non-ferrous ions as sulfides.

In this paper, the results of these tests are presented.

METHOD

Equipment

A prefabricated testing hut was built on the premise of the mine-drainage treatment plant of the mine site. Test equipment was installed in the prefabricated room. The aqueduct for mine drainage was introduced into the prefabricated hut to guide the drainage to the test apparatus.

Apparatus

A schematic diagram of the bioreactors used for the tests is shown in Fig. 1. For the test apparatus, an aerobic (iron oxidation-removal) bioreactor (left, Fig. 1) and an anaerobic bioreactor (center and right, Fig. 1) were prepared. A multistage process was configured to remove iron in the mine drainage by an aerobic bioreactor, and other metal ions by an anaerobic bioreactor. Both bioreactors are made of vinyl chloride. The iron oxidation-removal bioreactor is a rectangular parallelepiped with a bottom area of 900 cm^2 and a height of 45 cm. The anaerobic bioreactor is a cylinder with a diameter of 25 cm and a height of 110 cm. For the anaerobic bioreactor, four sampling ports (called the 1st, 2nd, 3rd, and 4th ports) were provided, in addition to an output port.

The iron oxidation-removal bioreactor was filled with approximately 15 kg in wet weight of iron scales that had been precipitating in, and sticking to the drainage aqueduct from the mine drainage treatment plant on the mine site (provided free of charge). Once filled with iron scales, the bioreactor was further filled with 20 L of mine water.

The anaerobic bioreactor, on the other hand, was filled with the following materials. Soil collected from the surface layer around the mine site was used as a source of bacteria, including SRB. Rice husk was used as a base material of the column and as a carbon source for bacteria. In addition, rice bran was added because it is more easily decomposed by bacteria than rice husk, due to its high levels of protein and lipids. Limestone (5 to 10 mm) was used as a structural material for securing cavities and for buffering the pH value. These materials are either free or very inexpensive to obtain in Japan and were easily collected. The column was filled with these materials to a height of 100 cm.

The weight of each material is as follows: approximately 4.5 kg of rice husk, approximately 1.5 kg of rice bran, 1 g of soil, and 18 kg of limestone. In this case, rice husk, limestone, and soil were combined and evenly distributed throughout the entire column. Rice bran, on the other hand, was filled intensively in the upper portion of the column (described later). The capacity of the column, to a height of 100 cm, is 50 L, and the volumetric composition of the content was approximately 95% rice husk, 3% limestone, and approximately 2% rice bran. In conjunction with the volume of solids, 35 L of mine water was used to fill the water level to 100 cm.

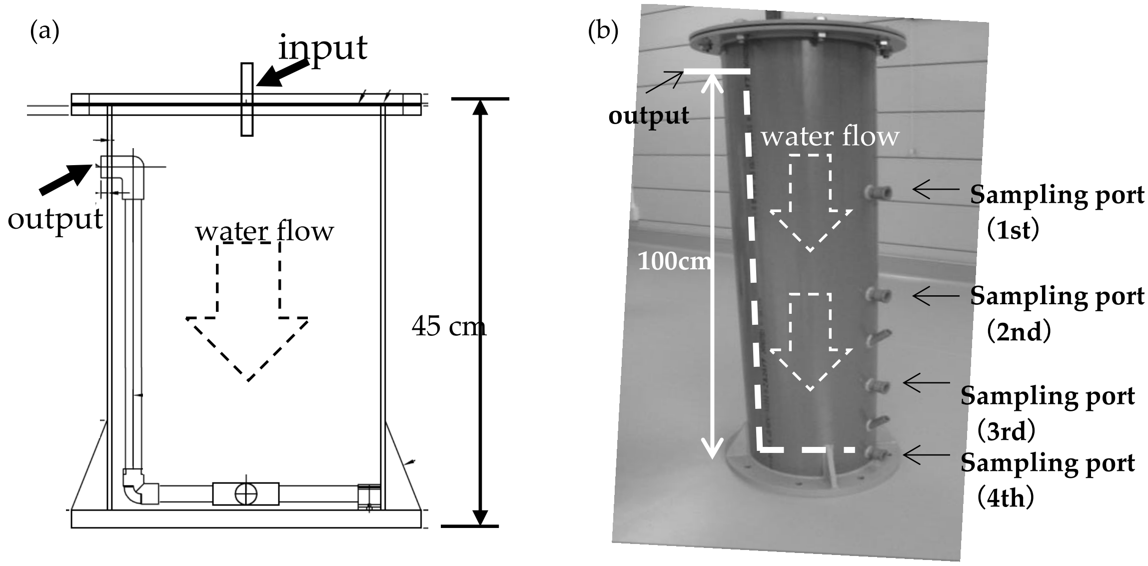

Figure 1 Bioreactor equipment.
Iron oxidation-removal reactor, (b) anaerobic bioreactor

Process

Acclimation of SRB in the anaerobic bioreactor

The anaerobic bioreactor was filled with the above-mentioned mixture of rice husk, limestone, and soil to the height of 100 cm. The contents were water sealed with 35 L of mine water as the sulfate ion source, and the SRB were acclimated under room temperature for approximately 10 days. In this case, rice bran was added to the top of the anaerobic bioreactor after acclimation of the SRB, and immediately before continuous feeding of the mine water. This was done because in laboratory tests it was observed that if bacteria are acclimated with added rice bran, microorganisms other than SRB ferment excessively, and eventually the sulfate reduction activity of SRB becomes non-detectable. Approximately 10 days after starting acclimation, the SRB became active, and the oxidation-reduction potential (ORP) of the water in the bioreactor became approximately -200 to -300 mV.

Water feeding method

After acclimation of the SRB, mine water was gravity-fed to the iron oxidation-removal bioreactor, with the flow rate adjusted to approximately 125 ml/min. Air was fed into the iron oxidation-removal bioreactor with an air pump so that the concentration of dissolved oxygen was approximately 3 to 4 mg/L. The mine water passing though the iron oxidation-removal bioreactor was guided to the upper part of the anaerobic bioreactor with a pump. The flow rate was adjusted to 11.7 ml/min so that it passed through the anaerobic bioreactor as gravitational flow.

Quality of treated water

The mine drainage for the continuous test was sampled at the abandoned mine in Akita Prefecture, located in the northern part of Japan. The concentrations of zinc, copper, and iron in the drainage are shown in Table 1. These values exceed the national effluent standard; therefore, the drainage was selected as the sample in this investigation. Most of the iron was removed from the drainage after passing through the iron oxidation-removal bioreactor, and contained only 6 to 8 mg/L of iron (almost all the volume is ferric), while the pH value decreased to about 3.0. The concentrations of other metal ions in the mine water did not change after passing through the iron oxidation-removal bioreactor.

The temperature of treated water did not fluctuate very much throughout the year; it exited at a temperature of 12 to 14 °C.

Table 1 Water quality of the drainage and the national effluent standard values.

	pH	**Zn (mg/L)**	**Cu (mg/L)**	**Fe (mg/L)**	**SO_4^{2-} (mg/L)**
Mine drainage (min–max)	3.3–3.8	15–18	3–10	33–38	350–400
National effluent standard	5.8–8.6	2.0	3.0	10	

Analysis of items

Samples were collected periodically from the raw mine water, the treated water of the iron oxidation-removal bioreactor, as well as from the outlet and water sampling holes at each height of the anaerobic bioreactor. The samples were subjected to analysis, which included temperature, pH, ORP, metal ion concentrations (iron, copper, zinc, and cadmium), 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.

Retention time

The retention time for the raw mine water to pass through the iron oxidation-removal bioreactor was adjusted to approximately 1.5 to 2 h. The time to pass through the anaerobic bioreactor was set to 50 h.

Temperature conditions

Neither of the bioreactors was subjected to temperature control with a heater or air conditioner. Although no heating or cooling was applied, minimal heat insulating material (glass wool) was used to protect the test equipment from the elements, thus ensuring that the tests were conducted under natural temperature conditions. In addition, in the prefabricated hut, air conditioning was not employed, but minimal ventilation and lining of walls with heat insulating material was applied.

RESULTS AND DISCUSSION

Iron oxidation-removal bioreactor

Figure 2 shows the changes in the concentration of iron (total iron concentration, T-Fe) from the raw mine water (input) to the water that was treated with the iron oxidation-removal bioreactor (output) during the field test. The iron ion concentration in the bioreactor decreased gradually over the first 20 days, but it became steady at a low concentration after 50 days. The performance of the treatment did not change, even in the winter. Throughout the year, the iron concentration in the treated water was approximately 20% of that in the raw mine water. Moreover, there was no need for maintenance, such as replacement or replenishment of iron scales or other agents.

Anaerobic bioreactor

Changes in temperature in the anaerobic bioreactor

Figure 3 shows the changes of the temperature inside the anaerobic bioreactor in the field test and that of the mine water used for the test. The temperature inside the bioreactor was measured at the lateral center, at a depth of 40 cm from the top of the bioreactor. Figure 3 shows that the mine water used in this test entered at a constant temperature (12 to 14 °C) throughout the year. In contrast, the temperature inside the column exceeded 20 °C in the summer (September) and decreased to approximately 5 °C in the winter.

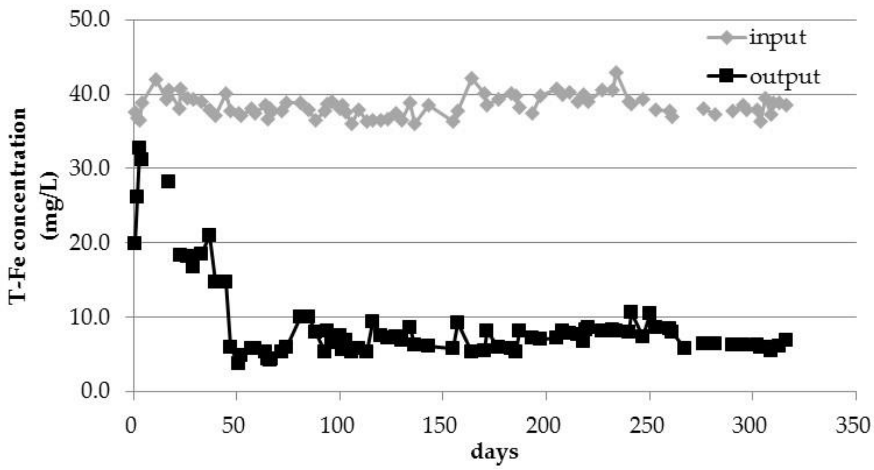

Figure 2 Changes in the concentrations of T-Fe in the mine drainage before and after treatment in the iron-oxidation removal bioreactor.

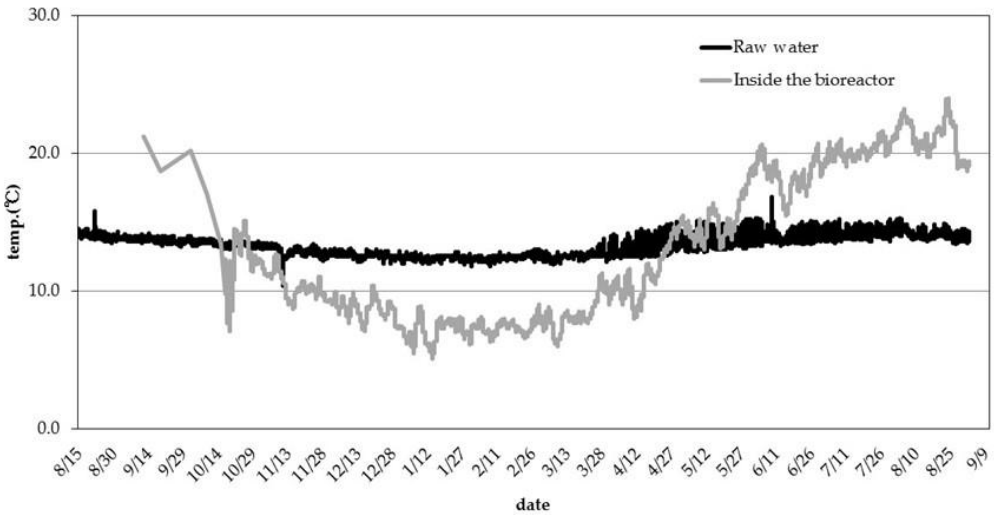

Figure 3 Changes in temperatures of raw mine water and inside the anaerobic bioreactor throughout the year.

Changes in pH and ORP values in the anaerobic bioreactor

Figure 4 shows the changes of the pH values in the anaerobic bioreactor. In the first port (1st) of the bioreactor, although the pH value was slightly lower in the winter, it was raised in the spring due to the rising atmospheric temperature. In the second (2nd) and subsequent (3rd and 4th) ports of the bioreactor, the neutral pH values remained steady, regardless of the fluctuations in the temperature. Figure 5 shows the changes in ORP values in the anaerobic bioreactor. The ORP in the first stage of the bioreactor was slightly unstable in the winter, sometimes exceeding -100 mV. In the second and subsequent stages of the bioreactor, the ORP was stably maintained below -200 mV. It is commonly said that the appropriate ORP for SRB is -200 to -300 mV. Accordingly, the ORP in this process remained within the above-mentioned range for one year after starting the test.

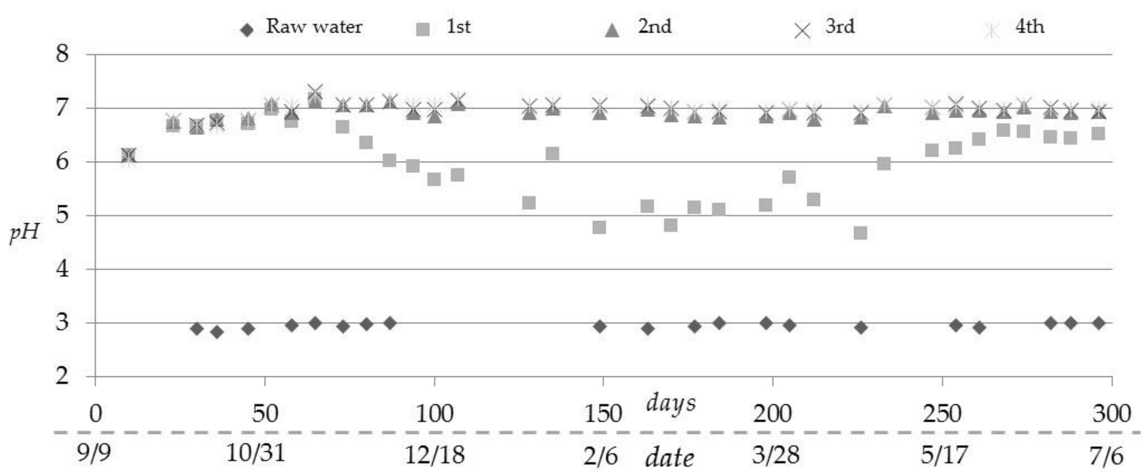

Figure 4 Changes in the pH values over time in the anaerobic bioreactor."1st, 2nd, 3rd, and 4th denote the location at which the sample was drawn"

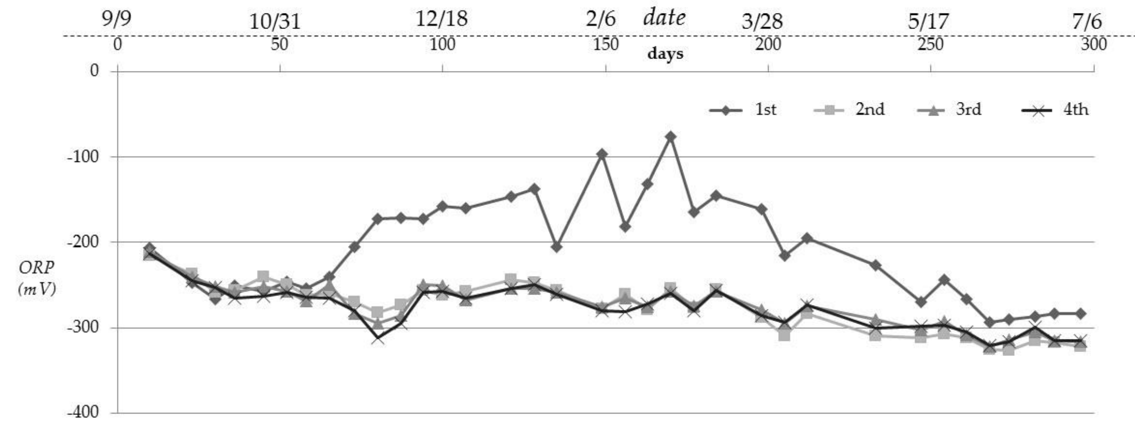

Figure 5 Changes in the ORP values over time in the anaerobic bioreactor.

Removal of metal ions in the bioreactor

Figure 6 shows the changes in the concentration of sulfate ions before and after treatment with the anaerobic bioreactor. In accordance with the fluctuations of the ORP values in Figure 5, the concentration of sulfate ion in the treated water did not be stabilized until 60 days from the start of the water feed. In the spring and summer seasons, after passing winter, the concentration of sulfate ion greatly decreased due to the high performance of sulfate reduction by the SRB in the bioreactor.

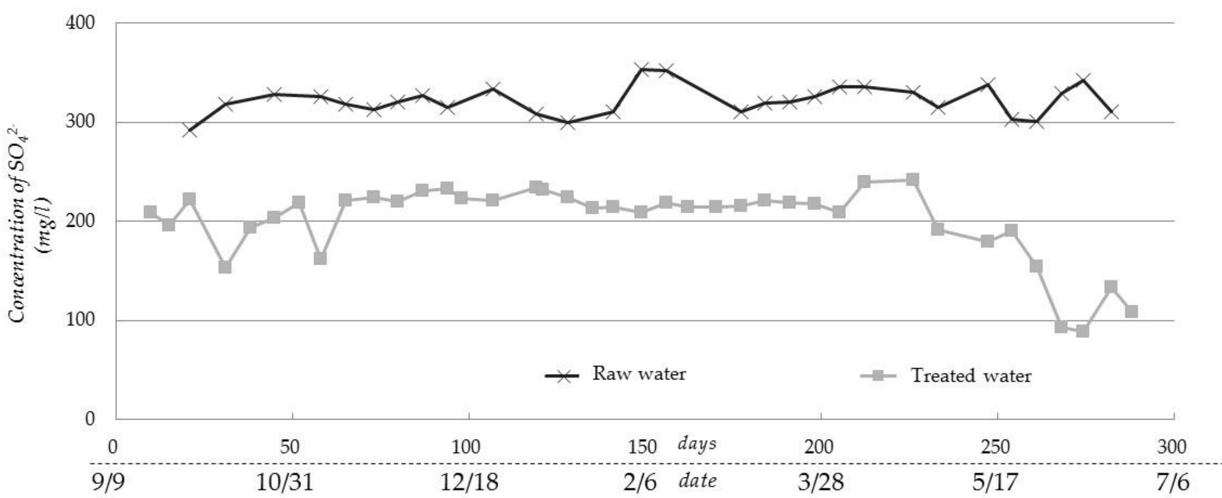

Figure 6 Concentration of sulfate ions in the mine drainage before and after treatment with the anaerobic bioreactor.

Figure 7 shows the changes in the concentration of zinc ions before and after the treatment with the anaerobic bioreactor. The concentration of zinc ions in the raw mine water was approximately 17 mg/L, with no large fluctuations throughout the test period. The water quality therefore always exceeded the national effluent standard in Japan. After the treatment with this process, the concentration of zinc in the treated water was very low, indicating that the treatment had stably cleared the national effluent standard of 2 mg/L for one year. Other metal ions (copper, and cadmium) were also almost completely removed in the bioreactor. Although the temperature inside the bioreactor was as low as about 5 °C in the winter (as shown in Figure 5), no deterioration of the treatment performance was observed.

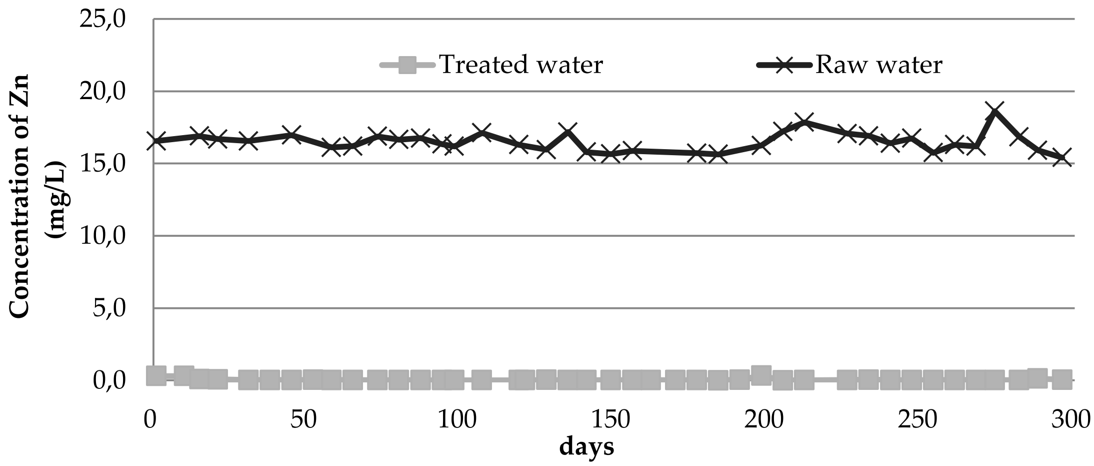

Figure 7 Concentration of zinc ions in the mine drainage before and after treatment with the anaerobic bioreactor.

Degree of pH, ORP, and sulfate ion reduction in the winter

Figure 4 and Figure 5 show that the pH decreased in the 1st stage of the anaerobic bioreactor and the ORP increased in the winter, respectively. The cause of the increase of pH in this process might be considered to be the neutralization effect of limestone and the progress of the sulfate ion reduction reaction of SRB. In the winter, the performance of sulfate ion reduction by SRB in the anaerobic bioreactor was lower than in other seasons, as shown in Figure 6, and so, it could be considered that the pH value in the 1st stage of the bioreactor was lower because the pH increasing effect of the sulfate ion reduction action was weakened. In the 2nd and subsequent stages of the bioreactor, it could be considered that the pH value was maintained stably even in the winter, mainly due to the neutralizing effect of limestone.

In the 1st stage of the anaerobic bioreactor, the observed increase in the ORP during the winter likely resulted from the decrease in activity of SRB due to the drop in the temperature. Moreover, the ORP tended to increase gradually because the raw mine water, which was always in an oxidation environment at the water channel from the mine site, was supplied in the 1st stage of the bioreactor. Therefore, generally the reduction condition was already weakened and the activity of the SRB was decreased, as mentioned above. Then, it could be conjectured that a stable reducing condition was revived in the 1st stage of the bioreactor and the activity of SRB increased again thereafter due to the temperature rise in the spring.

Treatment performance on metal ions (zinc, copper, and cadmium) in the winter

It is generally considered that the capability of sulfate ion reduction by SRB is weakened with a decrease in temperature. However, Figure 7 shows that almost all of the zinc ions contained in the raw mine water was removed after passing through the anaerobic bioreactor. Consequently, it could be considered that a sufficient volume of hydrogen sulfide ions, which were used for precipitating metal ions in the raw mine water as sulfides, were generated in the anaerobic bioreactor. It was so far confirmed that this test apparatus could remove metal ions stably over a long period at a temperature of 15 °C. Furthermore, it was confirmed in the field test at this time that metal ions could be removed over a long period, even in an environment with low and seasonal temperature changes.

CONCLUSION

During the field tests in approximately one year, at the mine drainage treatment plant, iron was removed with the iron oxidation removal bioreactor, and other metal ions were removed with the anaerobic bioreactor stably and successfully without additional maintenance, such as replacement or replenishment of some materials. The materials used to be filled in both reactors are either free or very inexpensive to obtain.

Although the reaction temperature changed in the range of twenty degrees and it lowered to 5 °C in the winter, the sufficient reduction of sulfate ions occurred and the removal of metal ions continued very stably. This field test suggested that this process was applicable in low temperature environments, as low as approximately 5 °C, and therefore, it was probably applicable in environments with a wide range of temperatures.

For practical use of this passive treatment system, it is important that metal ions are removed stably for a long period, without any maintenance and even in the low temperature conditions. In our field tests, it was confirmed that metal ions were removed over a long period, even in the environment with lower temperatures and changing temperatures. Furthermore, in the case that mine drainage contained iron ions, it was confirmed that placing the iron oxidation-removal bioreactor before the anaerobic bioreactor during the treatment process was very useful. To develop a new cost-saving and energy-saving process, JOGMEC is now continuing the researches to make this multistep bioreactor process ("JOGMEC PROCESS") more useful and durable.