

# RESEARCH AND DEVELOPMENT OF ACID MINE DRAINAGE TREATMENT TECHNOLOGY IN JAPAN

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## ABSTRACT

Most mine water contains numerous sulfate ions and ferrous iron. When this water is neutralized, large volumes of neutralizers are needed to remove ferrous iron because of its high solubility.

The Japan Oil, Gas and Metals National Corporation (JOGMEC), a Japanese national corporation established to ensure a stable supply of natural resources and to maintain a healthy living environment, has succeeded in reducing neutralization costs by cutting the volume of neutralizers down in the 2-step neutralizing process. This process uses iron oxidizing bacteria to oxidize ferrous to ferric which precipitates as hydroxide easier.

There are 80 treatment plants for acid mine drainage (AMD) in Japan, all of which use active treatment technology. JOGMEC started to examine the effectiveness of treating acid mine drainage with sulfate-reducing bacteria (SRB) last year. In the case of adding lactate, SRB reduce sulfate ions at a rate of 4.5mg/L/hour. This result shows that SRB are useful in treating AMD.

## 1. INTRODUCTION

Most water from abandoned mines needs to be treated because of its low pH and high concentration of metals. There are 80 treatment plants in Japan, all of which adopt active neutralizing treatments. Some mines treat sulfuric acid mine water which has a pH value of around 2.0 and is heavily contaminated with ferrous iron and therefore large quantities of neutralizers need to be added.

## 2. SITE DESCRIPTION

Matsuo mine has the largest treatment plant in Japan, treating mine drainage at an average rate of 19m<sup>3</sup>/min. The mine water quality is as follows: pH2.3, Fe 225mg/L (mainly as ferrous), SO<sub>4</sub> 1,200mg/L and is strongly acidic.

Generally, pH values of effluent entering a river must be adjusted to fall in the range 5.8 to 8.6. However, this mine water only needs to be treated to a pH of 4 because it is clear that this area had acidic water before it was polluted by mine water.

Most of the iron included in the drainage from Matsuo mine dissolves as ferrous. Ferrous iron can be removed at a higher pH value than ferric iron because ferrous is highly soluble. Therefore, it is important to oxidize ferrous to ferric for treatment. In the oxidation process, iron oxidizing bacteria (IOB) is used for rapid oxidation. IOB is an aerobic organism that can live in an acidic environment and has already been detected in the mine water at Matsuo. This process which oxidizes iron before adjusting its pH value to neutral is called the '2 step neutralizing process'. Matsuo treatment plant uses this method for treatment.

In the first step of the '2 step neutralizing process', drainage from Matsuo mine flows into the oxidization tank to be aerated. Through IOB activity, ferrous iron is oxidized to ferric levels and partial ferric precipitate remains as hydroxide in this tank. The sludge produced in the process, includes levels of IOB at high concentration. If the number of IOB in the tank is kept at the same levels, a part of the sludge extracted from the tank is re-added to the process.

In the second step, calcium carbonate, as a neutraliser, is added to water flow in the neutralization tank. Few treatment plants use calcium carbonate as a neutralizer because it is relatively hard to obtain reaction with water and is not able to increase the pH value to over 5.6. Calcium hydroxide is more efficient in neutralization than calcium carbonate, however calcium hydroxide is more expensive than the carbonate. Moreover, calcium carbonate can adjust the pH value to 4.0, which is enough for the mine water effluent at Matsuo.

Matsuo mine drainage is treated effectively by microorganisms at a cost of around five million dollars per year because of the large volume of water and high metal concentration. There is a desire to make the cost of treatment less expensive as there is a constant flow of mine effluent from the site.

Passive treatment, which needs no maintenance, has been developing around North America and Europe. It is expected that passive treatment will enable the reduction of the costs of treatment of acidic water. However, there is no mine site

adopting passive treatment technology in Japan.

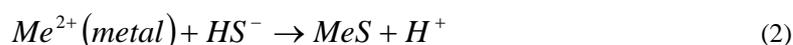
We have initiated research into passive treatment in order to introduce the technology to abandoned mines in Japan.

### 3. EXAMINATION

Acid mine drainage(AMD) often includes highly soluble metals such as zinc, lead and cadmium, which are difficult to aggregate at neutral pH levels. However, such metals can be removed at a relatively low pH, not as hydroxide but as sulfide. It is essential therefore, to introduce passive treatment into water polluted with various materials in order to establish the removal method of metals as sulfides.

Sulfide reducing bacteria(SRB) are generally used for the removal of metals as sulfides in passive treatment. SRB are anaerobic organisms that live in a neutral environment. Moreover SRB need organic carbon for activity as they are heterotrophic.

SRB uses simple organic carbon as electron donors, and sulfate anions ( $SO_4^{2-}$ ), found in mine water, which are electron accepters in their metabolic pathway. (Formula 1 demonstrates this reaction). The resultant hydrogen sulfide produced reacts with metals in water and sulfide metal precipitates (formula 2).



The primary objective of this examination was to determine the effect of removing metals with sulfate reducing bacteria. Because there is no precedent of passive treatment with SRB in Japan, these experiments are needed to certify whether SRB can remediate mine water or not.

Most mine drainage is acidic with a pH ranging between 2~4, however SRB can survive in pH levels exceeding 4. Therefore in order for SRB to be active the pH value of mine water must be adjusted to neutral. In most cases of passive treatment, limestone is used as the pH adjuster. However there is a problem in that limestone is covered with ferric hydroxide and gypsum which reduces its effectiveness. Accordingly, in place of limestone, we used iron granule which can increase the pH value by reducing hydrogen ions (formula 3).



We examined the effect of remediation by SRB to focus on the reduction of  $SO_4^{2-}$  concentrations. However, we found that  $SO_4^{2-}$  is decreased because of co-precipitation with iron contained in the inflow water or is adsorbed in organic materials in the columns. Therefore, two columns were observed to ascertain the effect of SRB activity. Table 1 shows the inclusion materials of each column. Column 1 had an SRB source to which lactate (3.5g/L) was added continuously as electron donor for maintaining SRB activity. By contrast, column 2 had been sterilized by sodium azide. Moreover, each column was settled in the anaerobic chamber during this examination for keeping the anoxic condition (figure 1).

Table 1. Volume percentages of materials in each columns

	Compost	Woodchip	Iron granule	Glass beads	Gravel	Sewage mud
Column1	20(vol%)	20	10	27	20	3
Column2	20	20	10	30	20	0

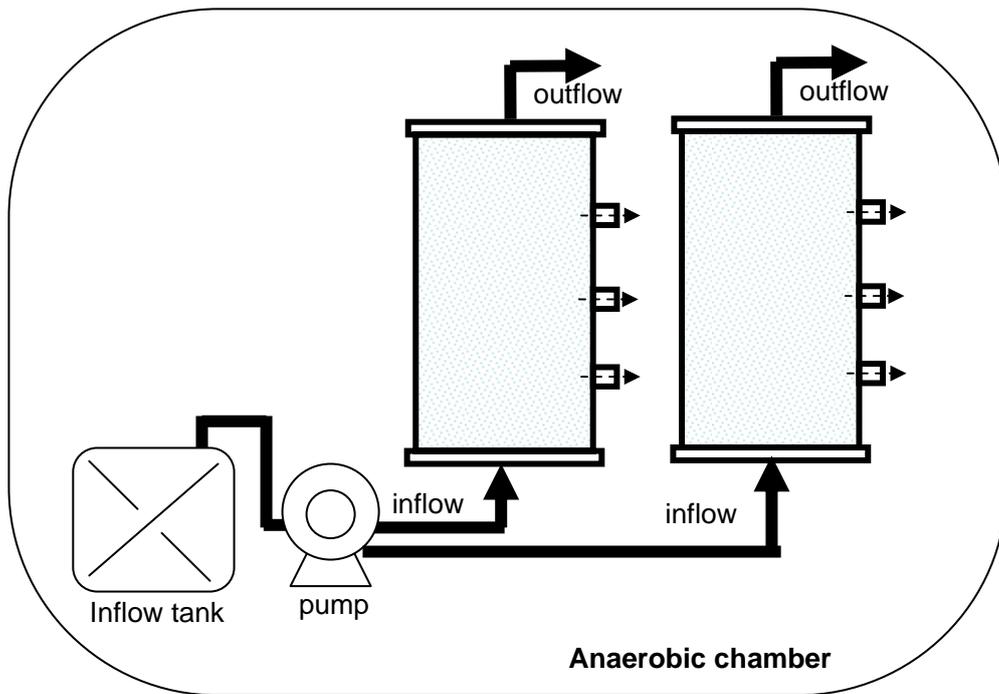


Figure 1. image of column examination

Table 2 shows the quality of water into the columns.

Table 2. Quality of inflow

pH	ORP(mV)	T-Fe(mg/L)	Fe <sup>2+</sup>	Al	SO <sub>4</sub> <sup>2-</sup>
2.72	380	300	230	120	2,000

The retention time in each column was adjusted to 100 hours by pump. Inflow and outflow were sampled once every week. PH levels, electric conductivity and redox potential was measured at the time and total iron, aluminum, sulfate were analyzed with ICP-AES. Ferrous iron was analyzed with spectrophotometer.

#### 4. RESULTS

This examination took place over a period of 3 months. Figure 2 shows the changing water quality of each of the columns. The graph shows that pH values become approximately 7 in both columns. In addition, redox potential fell to below -200mV (figure 3). The condition of both columns had been kept neutral and anaerobic.

In the early stage of the examination iron concentration had jumped to levels exceeding 2,000mg/L, however, the concentration fell gradually after 30 days (figure 4).The SO<sub>4</sub><sup>2-</sup> concentration of both columns gradually fell and remained stable after 80 days.

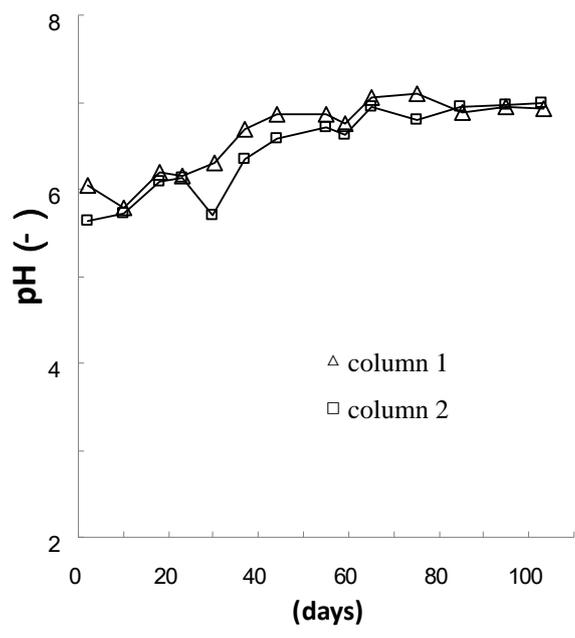


Figure 2.pH

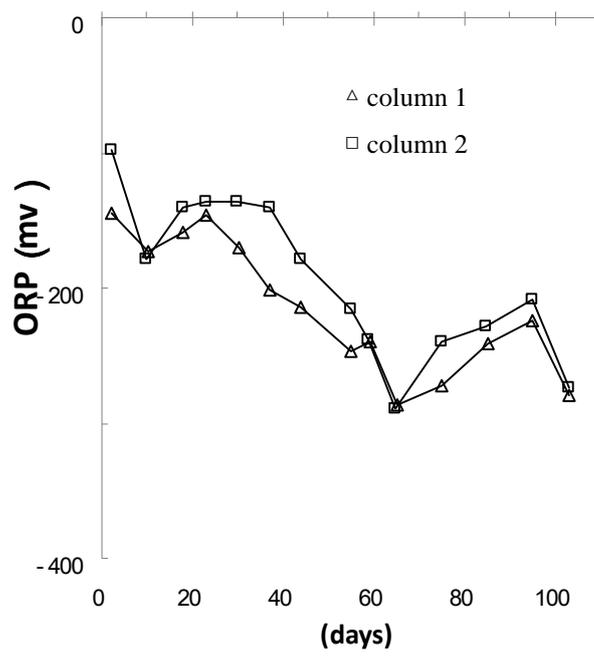


Figure 3. ORP

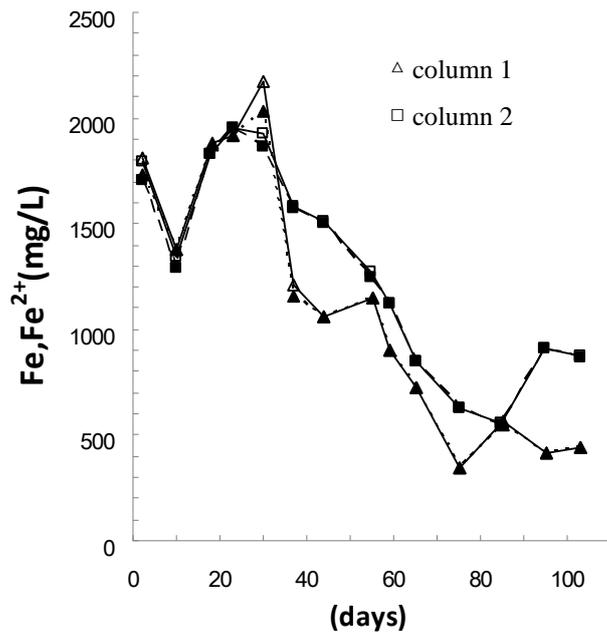


Figure 4. Ferric and ferrous iron

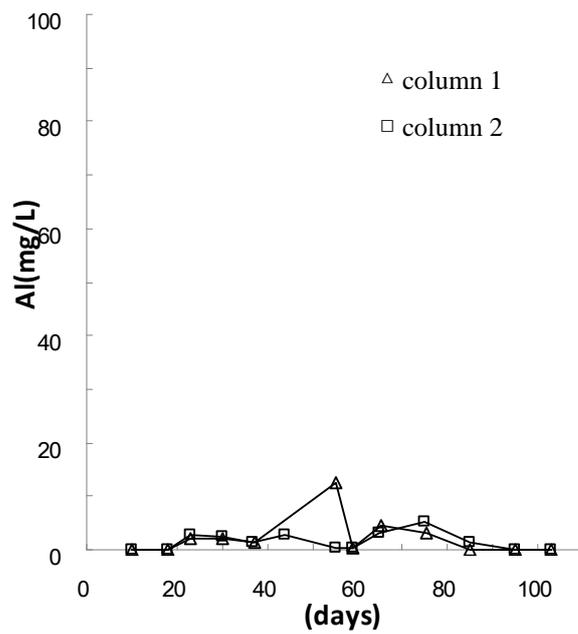


Figure 5. Aluminum

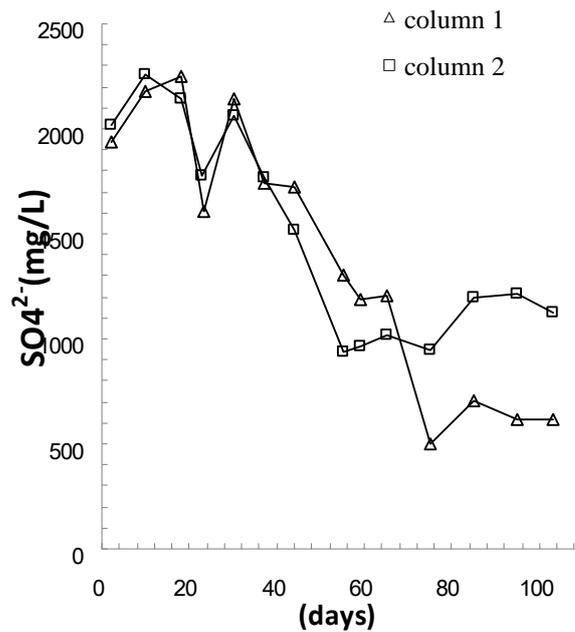


Figure 6. Sulfate ion

The reduction by iron granule provided neutral and anaerobic conditions suitable for SRB activity.

The difference of  $\text{SO}_4^{2-}$  concentration between both columns indicates that SRB was more active in column 1. Moreover,  $\text{SO}_4^{2-}$  concentration is observed to have decreased in column 2. This seems to occur by the use of iron granule which reduces partial  $\text{SO}_4^{2-}$ . The amount of  $\text{SO}_4^{2-}$  reduced by SRB is 450mg/L.

## 5. CONCLUSION

This examination shows that metals can be removed by SRB activity. Moreover, SRB could reduce sulfate to sulfide at 4.5mg/L/hour. However, although sulfate reduction was observed, iron was not removed perfectly. For this reason iron concentration jumped up to levels exceeding 2,000mg/L because of the introduction of significant ferrous iron material from iron granule in the acidic inflow water. Though iron granule is effective in adjusting water conditions that are suitable for SRB activity, considering the elution of iron, it is unsuitable for strong acidic water. However, because not all iron is dissolved, as there is little iron eluted in weak acidic drainage in relatively neutral water, it can be expected to remove iron below the water emission standard(10mg/L) with SRB activity.

## 6. REFERENCING

David L. Naftz, Stan J. Morrison, Christopher C. Fuller, James A. Davis (2002) *Handbook of Groundwater Remediation Using Permeable Reactive Barriers*, ACADEMIC PRESS