Compact Passive Treatment Process for Acid Mine Drainage, Utilizing Rice Husks and Rice Bran – Process Optimization

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Abstract A biological passive mine water treatment system, which is environment-friendly and energy saving, has been developed by JOGMEC (Japan Oil, Gas and Metals National Corporation). In this “JOGMEC process”, contaminated mine water is treated in a vertical-flow anaerobic bioreactor that utilizes sulfate reducing bacteria (SRB). It is necessary to introduce compact passive treatment system with a higher flow rate (shorter hydraulic retention time (HRT)). Based on column tests, required HRT could be substantially shortened down to 6 hours with above neutralization process.

Key words AMD, Passive Treatment, Sulfate Reducing Bacteria

Introduction

Japan Oil, Gas and Metals National Corporation (JOGMEC) has been conducting survey research on passive treatment since 2007 and has focused on treatment methods to remove metals contained in acid mine drainage as sulfide by utilizing of sulfate reducing bacteria (SRB).

Field tests have been conducted with anaerobic reactors 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 hydraulic retention time (HRT) of 50 hours under the conditions close to natural environment that the temperature in the winter drops to around -10 degrees. Besides, continuous removal for more than one year has been confirmed with the HRT of 25 hours ¹), ²).

As described above, it is becoming clear that acid mine drainage can be treated for a long period under the condition of the HRT of about 50 hours or 25 hours using the “JOGMEC process”, a process of removing metal in mine drainage as sulfide by utilizing SRB, with an anaerobic bioreactor filled with rice bran and rice husk. 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 SRB³), ⁴). Water flow condition such as the HRT of 25 hours is notably short comparing to other tests in other countries, so that the scale of required
equipment may be smaller for treatment per a unit. Yet, further efficiency and optimization of the process is necessary to come into widespread adoption in Japanese acid mine drainage systems.

Therefore, the test (acceleration test) had be carried out to investigate how much the established process can treat mine drainage in this short HRT to evaluate capability of treatment.

**Methods**

**Purpose of experiments**

This is the test to investigate how the JOGMEC process established to show can treat mine drainage in a short HRT. This is the test to investigate the shortest HRT for the drainage treatment with the current JOGMEC capability. More specifically, the purpose is to investigate the condition of the shortest possible HRT by SRB of sulfate ion reduction with the HRT being decreased gradually from 50 hours (i.e., increase in water flow per unit) that used to be confirmed for drain treatment.

In the previous case, acid mine drainage was directly introduced to the bioreactor. When raw water contained iron, the drainage was introduced into the anaerobic bioreactor after iron removal process. However, new process was introduced to this test: increasing pH of the drainage to the level of 5~6 before the conveyance into the bioreactor. In general, SRB is known as reducing sulfate ion actively under neutral pH. In the previous process, the limestone, filled in the anaerobic bioreactor, principally adjusted pH to SRB activity, but it was predicted that the limestone was dissolving as days passing, eventually leading to lower pH. In fact, the pH was confirmed to be decreased significantly around upper part of reactor conducted after 800 days from the beginning. The limestone also played a key role as a structural material of an anaerobic bioreactor; was filled in the whole bioreactor; hence, frequent refilling might not be practical. Therefore, as a new process a “pH controlling tank” filled with limestone was designed before the anaerobic bioreactor.

In this test, two processes were conducted: like previous tests, process for introducing raw water directly into the anaerobic reactors represents as acid condition (hereafter referred to as A-condition); newly designed process for introducing drainage into the anaerobic reactor after adjusting pH 5~6 represents as neutral condition (hereafter referred to as N-condition). This test is to determine how the shortest possible HRT for two processes differed from each other.

**Structure and Contents of reactor**

Column with a diameter of 25 cm and a height of 110 cm was used for the bioreactor, which had a structure that allowed water to be sampled at four levels. Water sampling ports were set at the heights of 40 cm, 65 cm, 90 cm, and 110 cm from the top of the bioreactor. The port nearest to the input was called “the first port” and the port nearest to the output was called “the fourth port.”
The anaerobic bioreactor was filled with the contents as shown below. As a “source of bacteria” related to sulfate ion reduction including SRB, soil collected from the surrounding mine site was used. Rice husk was used as “substrate” of the bioreactor and “nutrient source” for bacteria. Rice bran was also used as “easily degradable organic matter” which was easily decomposed than rice husk by bacteria. Limestone (3 to 20 mm) was used as “structural material” for securing air gap and pH buffering. Each initial filling weight was 4.7 kg of rice husk, 4.5 kg of rice bran, 17.5 g of soil and about 20 kg of limestone. The rice husk, limestones and soil were evenly stirred to achieve homogeneous dispersion, and were filled in the bioreactor. The rice bran was intensively filled on top of the bioreactor. After filling of these contents, the bioreactor was filled with raw water, mine drainage to be treated; the amount was 35 L. The weight of the contents and filling compositions were the same for A-condition and N-condition.

Condition of Experiments

Quality of Raw Water
Figure 1 shows the quality of the raw water to be treated in this test. As described above, the raw water contained iron. Thus, the raw water of the A-condition was the water that passed through the iron oxidation and removal process, and the raw water of the N-condition was the water that passed through the pH controlling tank. Although the pH of the raw water rose to around six in the N-condition, the concentration of the metal such as copper and zinc was almost the same as the raw water of the A-condition.

<table>
<thead>
<tr>
<th>Average Quality of Treated Water (Unit : mg/L)</th>
</tr>
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<tbody>
<tr>
<td>pH</td>
</tr>
<tr>
<td>-----</td>
</tr>
<tr>
<td>Drainage</td>
</tr>
<tr>
<td>A-condition</td>
</tr>
<tr>
<td>N-condition</td>
</tr>
</tbody>
</table>

Analysis of items
The raw water to be treated and the water after treatment were periodically sampled and analyzed. Items for testing were temperature, pH, Oxidation-Reduction Potential (ORP), metal concentrations (such as iron, copper, zinc, and cadmium), sulfate ion concentration, sulfide ion concentration (hydrogen sulfide, hydrogen sulfide ion, and other sulfide ion were fixed as sulfide ion in strong alkaline condition, and analyzed with a spectrophotometric method using methylene blue), and chemical oxygen demand (COD).

Water Flow rate
A-Condition
Raw water was pumped by a liquid feed pump into the bioreactor from the upper side to increase the water flow rate gradually. The HRT of the bioreactor was adjusted to 50 hours (about 12 mL/min), 25 hours (about 24 mL/min), 20 hours (about 30 mL/min), 12 hours...
(about 50 mL/min), 8 hours (about 72 mL/min), 7 hours (83 mL/min). It allowed at least 10 days for each water flow period. The water flow rate was increased at the stage where the system was thought to stabilized to some extent in terms of, for example, the level of pH, ORP, and sulfate ion concentration. This test was conducted in winter beginning from December 4, 2015 and ending on April 26, 2016 to examine the processing capacity at low temperature. On February 26, 2016 which was 84th day from the beginning of the test, because clogging inside the bioreactor prevented water from passing temporarily, a part of the rice bran which caused the clogging was removed. Then water flowing was resumed.

**N-condition**

Water passing through the pH adjustment tank was used as raw water for passing through the bioreactor from the top using pump in the same way as A-condition. The HRT of the bioreactor was set to 25 hours, 20 hours, 12 hours, 8 hours, 6 hours (about 100 mL/min) to 5 hours (about 120 mL/min.) This test began on January 28, 2016 and ended on June 2 of the same year. Table 2 shows conducted days for each HRT for both A- and N-conditions.

<table>
<thead>
<tr>
<th>HRT</th>
<th>50 hours</th>
<th>25 hours</th>
<th>20 hours</th>
<th>12 hours</th>
<th>8 hours</th>
<th>7 hours</th>
<th>6 hours</th>
<th>5 hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-condition</td>
<td>12 days</td>
<td>28 days</td>
<td>15 days</td>
<td>50 days</td>
<td>18 days</td>
<td>21 days</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>N-condition</td>
<td>-</td>
<td>13 days</td>
<td>26 days</td>
<td>11 days</td>
<td>25 days</td>
<td>-</td>
<td>14 days</td>
<td>37 days</td>
</tr>
</tbody>
</table>

**Results**

(1) pH, ORP, the Concentration of sulfate concentration under A-Condition

Figure 1, Figure 2 and Figure 3 shows the change in pH, ORP and the concentration of sulfate ion-respectively under A-Condition.

According to these results, it was found that in the A-condition, the pH of the first port greatly decreased at the HRT of 12 hours, and the ORP increased and showed a positive value. Those values were rather stable at each port at the HRT of 20 hours, but in the latter half of the 12 hour, the pH was low and the ORP showed a high value. The sulfate ion concentration decreased greatly in the bioreactor up to the middle of the 12 hour of HRT but it decreased only by about 30 mg/L in the latter half of the HRT of 12 hours. The sulfate ion concentration did not decrease almost all the time in the HRT of 8 hours and no decrease was confirmed at the HRT of 7 hours.
(2) Changes in pH, ORP and Sulfate Ion Concentration under N-condition

Figure 4 shows the change in pH under N-condition, Figure 5 the change in ORP, and Figure 6 sulfate ion concentration. Figure 4 shows that the pHs in the bioreactor remained stable throughout the test, and there were few changes although the HRT was short. This means that neutral pH in advance contributed to pH stabilization in the bioreactor. Figure
5 indicates that, although the ORP at the first port of the bioreactor was somewhat unstable throughout the test, the one at second and subsequent ports indicated extremely strong reduction states up to the HRT of 6 hours. At the HRT of 5 hours, the ORP sharply rose in each port, suggesting that the reduction was not possible and it was in a state of oxidizing. From Figure 6, as in the same way as the ORP of Figure 5, the sulfate ion was found to be reduced well up to the HRT of 6 hours. The capability of sulfate ion reduction was abruptly lost at the HRT of 5 hours. When the HRT was up to 6 hours, the sulfate ion reduction reaction by SRB was possible but should not be expected much at the HRT of 5 hours.

(3) Metal Treatment Performance under A-Condition

Figure 6 shows the change in zinc concentration under A-condition. According to Figure 6, the zinc ion concentration rose at the first port of the bioreactor during the water flowing with the HRT of 12 hours, at the second port with the HRT of 8 hours, and at the third port with the HRT of 7 hours. As shown in Figure 3 that shows no sharp decrease in the sulfate ion concentration, it was conceivable that the zinc ion was present at the bottom of the bioreactor without being removed as a sulfide.

![Figure 4](image-url) **Figure 4** Change in pH in the Reactor under N-Condition N

![Figure 5](image-url) **Figure 5** Change in ORP in the Reactor under N-Condition
(4) Metal Treatment Performance under N-Condition

Figure 7 shows the change in zinc concentration under N condition. As shown in Figure 7, few zinc ions were detected in the second and subsequent ports of the bioreactor up to the HRT of 6 hours, which means that the zinc ions were removed stably. However, zinc ion concentration increased at each port in the HRT of 5 hours.

Discussion

As shown in Figure 1 to 3, in the process constructed in this test, the bioreactor maintains its reduction condition, which means that metal ion is removed resulting from sulfate reduction caused by SRB in the first half of the treatment period under the HRT of 12 hours. According to the results of this test that shows that some part of metal is being removed at the HRT of 12 hours, it is better to secure the HRT of around 20 hours for continuous sulfate reduction. Contrary to this, under the N-condition, sulfate ion reduction occurs even though the HRT is shorter than the one under the A-condition, as shown in Figure 4 through to 6, so that maintaining the steady rate of sulfate reduction is confirmed. Specifically, it is...
confirmed that sulfate ion reduction occurs and metal ions are removed even if under such a remarkably short HRT of 6 hours. However, in the HRT of 5 hours, the state in the bioreactor changed drastically leading to stronger oxidation function so that it is confirmed that sulfate ion concentration hardly decreases.

Therefore, mine drainage treatment can be achieved in short HRT under A- and N-condition comparing to the previous method. Under N-condition the treatment can be possible even in shorter HRT, 6 hours, leading to greatly downsizing necessary treatment facilities.

Conclusions
In this basic test, the JOGMEC process can provide the stable mine drainage treatment even in a remarkably short HRT of about 6 hours. A factor of this success is the installation of a newly devised “pH adjustment tank” in this test for adjusting the pH slightly acidic or neutral before the stage of that the anaerobic reactor provides high concentration of low molecular organic matter such as organic acid, which can supply many nutrients to SRB. This successful short HRT may enhance applicability of the JOGMEC process for other mine drainage treatment. Particularly, the introduction of this process can be suitable for sites where available surface areas for the treatment system are small. Another improved point is that it is not necessary to wait for a certain period for the start-up process that has so far sealed or left with water to be treated. Even though water supply begins immediately after filling the contents into the bioreactor, SRB can be acclimated in about 20 days, resulting in increasing versatility of this process.

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