Arsenic Removal from Geothermal Water Using High Gradient Magnetic Separation

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Abstract

On-site experimentation of high gradient magnetic separation (HGMS) to remove arsenic from geothermal water was conducted at the Kakkonda geothermal power plant in Shizukuishi, Iwate, Japan, from 2000 to 2005. By this HGMS method, the arsenic concentration in the geothermal water was reduced to less than the effluent standard of 0.1 mg/L but slightly higher than the environmental standard of 0.01 mg/L in Japan. To enhance the magnetic properties of arsenic-containing particles in geothermal water, we tried several pretreatment methods and found that the co-precipitation method using Fe(III) hydroxide generates suitable magnetized flocks for magnetic separation. Such treated geothermal water had a pH between 4.0 and 4.5 and a temperature higher than 90ºC. The magnetic susceptibility of the resulting flocks was around $10^{-3}$, which is a typical value for paramagnetic materials. In the experiments we used a superconducting magnet to apply a magnetic field up to 2T to a magnetic filter fabricated by packing 100\textmu m-diameter ferromagnetic thin wires in a 50mm ID paramagnetic stainless tube. With this HGMS system, the arsenic concentration was reduced from 3.25 mg/L to less than 0.07 mg/L at a flow velocity through the HGMS filter, 4.2 and 8.5 cm/s.

Key Words: Geothermal water, Arsenic reduction, HGMS, On-site experiment, Fe(III) co-precipitation

I. INTRODUCTION

If the arsenic (As) level in the geothermal water discharged from the Kakkonda power plant in Japan can be reduced to a safe level, then the several hundred tons per hour of thermal water (60-90 degrees Celsius) can be made available for public facilities such as greenhouses, indoor swimming pools, and heating systems for schools. Currently, the geothermal water contains 3-4 mg/L of As, which is in excess of both environmental (0.01 mg/L) and effluent standards (0.1 mg/L) [1]. The power plant generates 80 MW electricity by using the vapor from the geothermal water, and then returns the water underground at a rate of 3,000 tons/hour [2]. To purify such a large amount of geothermal water both at high rate and high temperature, we developed a superconducting magnetic separation system. We report here the developed pretreatment method of magnetically seeding the As, and the magnetic separator that can reduce the As concentration to less than the effluent standard.

An alternative to purifying the geothermal water is heat exchange with river water. From 1995-2005, a trial heat exchanger was placed at Torigoeno-taki (waterfalls) along the upper reaches of the Kakkonda River near the town of Shizukuishi in Iwate Prefecture, Japan, to heat the river water and then supply it to the designated public facilities at a nominal rate of 50 tons/hour. Due to the low efficiency of the heat exchange, however, the heat exchanger required geothermal water at the rate of 500 tons/hour [2]. Moreover, because the volume of water in the river has decreased year by year, restrictions on water extraction from the river have recently been imposed; namely, only 10 tons/hour is permitted at Torigoeno-taki, thereby allowing sufficient water for rice crops and for hydroelectric power plants to generate electricity at the lower reaches of the river.

II. EXPERIMENTS

A. Experimental Setup

Fig.1 shows the high gradient magnetic separation (HGMS) system built in 2000 in Kakkonda. Arrows in the figure show the geothermal water flow direction through the system, which consists of six components: (1) Reactor tank, (2) two settling tanks, (3) water pump, (4) superconducting (sc) magnet equipped with an HGMS filter in the center of the room temperature bore, (5) helium gas compressor, and (6) power supply to the sc magnet. The temperature and pressure of the geothermal water were respectively 140ºC and 2.5kgf/cm\textsuperscript{2} in the supply pipe into the reactor tank, 100ºC and 1.0kgf/cm\textsuperscript{2} in the reactor tank where magnetic seeding for As removal occurred in the geothermal water.
Two sc magnets were used at different times to apply a high intensity magnetic field to the HGMS filter. In 2000 and 2001, the magnet was a cryocooler-cooled Bi2223 sc magnet that could generate a maximum magnetic flux density of 1.7T. From 2002 to 2005, the magnet was a cryocooler-cooled Nb-Ti and Nb3Sn sc magnet JMTD-10T100M (Japan Superconductor Technology Inc.). Although this latter magnet has a maximum generated magnetic flux density of 10T, we applied a level only up to 2.0T because the magnetization of the HGMS filter saturates at an applied magnetic field of around 1.5T and thus the magnetic attraction force onto As-adsorbed flocks approached saturation in the HGMS filter. In this paper, we therefore introduce experimental results only at 2.0T.

B. Magnetic Seeding of As and a High Gradient Magnetic Separator

Table I summarizes the measured concentrations of the “non-processed” geothermal water, namely, before being processed by the HGMS system. In geothermal water, As exists in form of arsenic trioxide. To enhance the magnetic properties and to increase the particle size, we tried three different methods of magnetic seeding; Ferrite formation, Fe(III) hydroxide co-precipitation, and modified ferric hydroxide co-precipitation methods [3]. We found that the Fe(III) hydroxide co-precipitation method shown in Fig.2 was the most effective to form suitable magnetized flocks with a susceptibility higher than 10⁻³ and a diameter of several tens to hundreds of microns or larger. In this method (Fig.2), the addition of hydrogen peroxide changes As(III) into As(V), and after subsequent addition of Fe(III) sulfate and after the pH is controlled at 4.0<pH<4.5, flocks of Fe(III) hydroxide and As compound appear.

The flocks with a diameter of several millimeters settle to the bottom of the settling tanks as sludge. Because this sludge is still adsorbent to As, it can be reused, as shown by the dotted arrow in Fig.2. After addition of hydrogen peroxide to the geothermal water, the sludge is added to the mixture. After this co-precipitation chemical treatment process, only the top layer of the liquid flows from the settling tank to the magnetic filter. This “reuse” process can reduce the cost of chemicals used in the pretreatment process. Our feasibility study of the “precipitate-reuse cycle” described in the next section shows that the operating expense is 62yen/ton for the 40ton/hour plant [4].

C. Experimental Results

Table I summarizes the measured concentrations of constituents of geothermal water after being “processed” through the HGMS filter (packed in a 50mm-ID tube) at 5L/min. The concentrations were measured after each HGMS filter by extracting sample water through the right-hand side sampling tap shown in Fig.2. The As was reduced by 99.4%. The Fe

<table>
<thead>
<tr>
<th>Table I Concentrations of constituents of non-processed and HGMS-processed geothermal water.</th>
<th>Non-processed</th>
<th>Processed</th>
<th>Non-processed</th>
<th>Processed</th>
<th>Non-processed</th>
<th>Processed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>1,040 mg/L</td>
<td>1,050 mg/L</td>
<td>71.0 mg/L</td>
<td>72.0 mg/L</td>
<td>2.11 mg/L</td>
<td>1.55 mg/L</td>
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<tr>
<td>Na</td>
<td>696</td>
<td>794</td>
<td>28.9</td>
<td>30.7</td>
<td>0.25</td>
<td>0.49</td>
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<tr>
<td>SiO₂</td>
<td>366</td>
<td>332</td>
<td>5.28</td>
<td>4.37</td>
<td>&lt; 0.01</td>
<td>0.24</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>105</td>
<td>105</td>
<td>3.25</td>
<td>0.02</td>
<td>&lt; 0.01</td>
<td>6.4</td>
</tr>
</tbody>
</table>

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concentration, however, increased due to the addition of the Fe(III) hydroxide.

Fig. 3 shows As concentration before and after the HGMS filter at different flow velocities through the HGMS filter where 80mg/L Fe(III) was used and the precipitate-reuse was not used. The red horizontal lines in Fig.3 and 4 indicate the effluent standard of 0.1 mg/L in Japan. The diagonal line in Fig.3 shows the boundary of efficiency of the HGMS filter. The symbols below this diagonal line confirm the effectiveness of the magnetic filtration, and reveal an optimum flow velocity of the water in the HGMS filter between 4.2 and 8.5 cm/s. As the flow velocity decreased, the filtration efficiency increased, although the processing capability decreased. In the following experiment we set the flow velocity of 8.5 cm/s based on this experimental result.

According to calculation [4], 70% of the operating cost of our HGMS system is the cost of the chemicals. To reduce this expense, we performed precipitate-reuse experiments to reduce the required Fe(III) additive required to meet the As effluent standard. Fig.4 shows the relationship between As concentration and the number of precipitate-reuse cycles. The concentration was measured before and after each HGMS filter by extracting sample water through the two sampling taps shown in Fig.2. Fig.4 reveals a strong tendency for As concentration to decrease with increasing number of precipitate-reuse cycles. Only four precipitate-reuse cycles were needed for the As concentration to meet the effluent standards of 0.1 mg/L. Furthermore, the amount of Fe(III) required to achieve this standard can be decreased to less than 40 mg/L by doing five precipitate-reuse cycles.

III. CONCLUSION

Our goal was to develop an effective method for removal of As from geothermal water. We built a test facility at the Kakkonda geothermal power plant in Iwate, Japan. Results showed that the co-precipitation method using Fe(III) hydroxide effectively enhances the magnetic properties of As at about 100°C. Our As filtration experiments with our high gradient magnetic separation (HGMS) system using a superconducting magnet revealed that a filtration efficiency of 99.4% that meets the As effluent standard of Japan can be achieved, and that the consumption of Fe(III) sulfate and the chemicals for pH control required by the system to achieve this standard can be reduced by recycling the precipitates.

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