Study on Magnetic Separation System Using High Tc Superconducting Bulk Magnets for Water Purification Technique

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Abstract. The application of superconducting bulk magnets to the magnetic separation techniques has been investigated for the Mn-bearing waste water drained from the university laboratories. The research has been conducted in comparison with the electromagnets, and the cryo-cooled superconducting solenoid magnet. The separation ratios of ferrite precipitates including Mn element in the waste slurry were estimated by means of the high gradient magnetic separation method with ferromagnetic iron filters in the water channel and open gradient magnetic separation without them. As the magnetic force acting on the particles is given by the product of a magnetization of particles and a gradient of magnetic field, and a superconducting bulk magnet shows a sharp gradient of the magnetic field on the surface, the performances of the bulk magnet system were almost equivalent to those of the superconducting solenoid magnet with wide bore with respect to the magnetic separation ratios. The separation ratios for Mn have reached over 80 % for HGMS and 10 % for OGMS under the flow rates less than 3 liter/min.

1. Introduction
A water purification process has been operated on the waste water bearing toxic heavy metallic ions such as Mn, Zn, Cu, and Hg, which is drained from the university laboratories (3 tons/year). Figure 1 shows a conventional water purification process using the magnetic separation technique. The ferrite precipitates are formed by adding iron compounds to the waste water and subsequently removed by the magnetic field generated by permanent magnets. A rotating plate with hundreds of permanent magnets attracts the magnetic precipitates from the slurry water containing Fe ions, and the sludge is scraped away the vessel. Since a large amount of additives containing iron compounds have been used to throw them away, the reduction of additives, like iron sulphate and so on, in the process is necessary to reduce the cost to treat the waste water.
It has become well known that the melt-processed REBa$_2$Cu$_3$O$_y$ (RE123; Rare Earth = Y, Sm, Gd) high temperature superconductors (HTS) bearing RE$_2$BaCuO$_5$ (RE211) particles act as permanent magnets when they capture the magnetic fields [1, 2]. The field trapping ability of the superconducting bulk magnets has been substantially improved by synthesizing large grain textured bulk sample and reinforcing the sample to prevent against the fracture that happens due to the magnetic force when they trap the intense magnetic flux density of over several T. As was reported by M. Tomita et al. [3], the maximum trapped field attained in the Y123 bulk sample has reached 17.24 T at 29 K after an activation procedure in 18 T. On the other hand, various kinds of the superconducting permanent magnets using bulk superconductors have been constructed in order to develop the practical and industrial applications [4].

The magnetic force $F_m$ is given by the product of three elements of volume, susceptibility and magnetic field, as is expressed in equation (1). We note that the presence of steep gradient is necessary to obtain high magnetic force in addition to the field strength [5].

$$F_m = \frac{4}{3} \mu_0 \sigma_p \left( \begin{array}{c} 9(\chi_p - \chi_f) \\ (3 + \chi_p)(3 + \chi_f) \end{array} \right) H \cdot \text{grad}H$$

(1)

A couple of magnetic separation systems, high gradient (HGMS) and open gradient (OGMS) magnetic separation, have been precisely studied by Okada et al. [6] and Fukui et al. [7], as shown in

Figure 1. Conventional purification process for waste water including heavy metal elements

Figure 2. Magnetic separation techniques, (a) high gradient and (b) open gradient magnetic separation.
Fig. 2. When ferromagnetic fine wires are inserted in the magnetic field, the flux lines between the magnetic poles are attracted to them, changing their distribution, resultant yielding steep gradient of magnetic field around them (see Fig. 2 (a)). We call the system as HGMS. On the other hand, we know that the magnetic field generated between the poles originally possesses a steep gradient (Fig. 2 (b)). The later is ordinarily used in magnetic separation techniques called as OGMS.

According to the qualitative analysis by ICP, the waste water includes Fe, Mn, B, Ni, Zn, Cr, Cd, Mo, Co, and Cu ions. In this report, we focus on Fe and co-precipitated Mn contents that have major concentrations among them. And we aim to evaluate the separation performances on them by means of a superconducting bulk magnet, a superconducting solenoid magnet, and a conventional electromagnet.

2. Experimental

It is known that Mn ions co-precipitate with iron atoms when FeSO₄ is added. The precipitates were formed by adding FeSO₄ powder and NaOH (until pH 9.5), and then heating to 333-343 K. The mean precipitate size was 8.535 micrometer which was measured by Laser Diffraction Particle Size Analyzer SALD-3000J (Shimadzu Corp.).

A schematic of the experimental setup of magnetic separation is shown in Fig. 3, where SC and EM mean “superconducting” and “electromagnet”, respectively. 5 liters of waste water including 91.6 ppm Fe and 5.85 ppm Mn was circulated and a part of it was led to the glass channel (20 mm in diameter) settled in the magnetic field, where the electromagnet and superconducting bulk magnet

![Figure 3](image_url)

**Figure 3.** Experimental set up

![Figure 4](image_url)

**Figure 4.** Magnetic field distribution in the open gap between magnetic poles constructed by face-to-face HTS bulk magnets.
generate up to 1.2 and 2.3 T at the surface of each pole surface. When we use a superconducting solenoid magnet, the channel was settled through the bore (100 mm in diameter), and 5 T magnetic field of was applied to it. The stainless steel mesh (SUS430 standardized in Japanese Industrial Standards) with a diameter of 0.1 mm was inserted into the channel with a volume density of 8.1 % for the HGMS, whereas the channel was settled without any filters in it for the OGMS. The separation ratio $S \%$ is defined as $S=100(c_0-c_1)/c_0$, where $c_0$ presents the initial ion concentration of whole waste water, $c_1$ shows that of clear water after the magnetic separation process.

The magnetic field distribution of a face-to-face type superconducting bulk magnet system is shown in Fig. 4, as a function of the gap between the magnetic poles, which consists of a pair of Sm-Ba-Cu-O bulk samples with a size of 60 mm in diameter, and they are mounted on the respective cold stages of the GM refrigerators in each vacuum vessel [8, 9]. The bulk samples were cooled to 35 K and magnetized by feeding pulsed currents by a condenser bank through the magnetizing pulse coils. The capacity of the power supply was 60 mF and the rise time of the magnetic pulses was 10 ms. The trapped field distribution was measured by scanning a Hall sensor (F. W. Bell BHA921) on the surface of each magnetic pole. As shown in Fig. 4, the performance of magnetic property has exhibited over 2 T at the surfaces of magnetic poles and has already exceeded the maximum values of the conventional permanent magnets such as Nd-Fe-B and even that of the large scale electromagnets. The magnetic field gradients are 173 T/m, 43.5 T/m, and 14.7 T/m for the bulk magnet, the superconducting solenoid, and the electromagnet, respectively.

![Figure 5](image1.png)  
**Figure 5.** Separation ratios of Fe precipitates after (a) HGMS and (b) OGMS.

![Figure 6](image2.png)  
**Figure 6.** Separation ratios of Mn-bearing precipitates after (a) HGMS and (b) OGMS.
3. Results and discussions

Figures 5 shows the separation ratios of Fe, large amount of which is added to co-precipitate heavy ions such as Mn, Zn, Cu and Hg in the disposal process. The analyzed data are plotted against the flow rates of slurry water with respect to the HGMS (a) and OGMS (b), respectively. It may be easy to understand that the separation ratios of HGMS exhibit the data more than 85% whereas that of OGMS showing less than 30% and they decrease with increasing flowing rate up to 3 liter/min. The data of bulk magnet and SC magnet occupy the superior region to that of electromagnet. It must be noted that the lines come close to each other without showing any substantial differences between the bulk magnet and SC magnet. This implies that the steeper magnetic field gradient residing around the bulk magnet attributes to this phenomena in spite of the narrower space than that of SC magnet.

Figure 6 shows the separation ratios of Mn, which co-precipitates with Fe, against the flow rates with respect to three magnetic field generators in the case of HGMS (a) and OGMS (b), respectively. The disposal processes should be originally conducted with a purpose to remove this heavy element from the waste water. As the data generally follow the tendency of Fe shown in Fig. 5, the separation ratios drastically decreases with increasing flow rates of the water. The fact that the performances of separation are slightly inferior to those of Fe can be easily explained by the reason that the Mn ions are not perfectly involved to the Fe-based precipitates. Since the stronger magnetic field would have an advantage in attracting the ferromagnetic precipitates, performances of bulk magnet and SC magnet should be superior to that of electromagnet. On the other, it may be expected that the data among three magnetic field generators would have no substantial differences in the regions where the flow rate is relatively low. The superconducting bulk magnets are characterized as compact and strong magnets with steep gradient, whereas the superconducting solenoid magnets are featured as field generators with vast spaces and uniform fields. We must choose the most appropriate device to adapt to the process depending on the practical conditions such as size, cost and so on.

4. Conclusions

The ferromagnetic precipitates containing Mn in the waste water drained from the laboratories were effectively removed by magnetic separation techniques with a trapping efficiency over 80% for HGMS and 10% for OGMS experiment using superconducting bulk magnets, which was conducted under the region of flow rates up to 3 liter/min. As the performances of superconducting bulk magnet and superconducting solenoid magnet are estimated as approximately equal in spite of the size of exposure space and time, the superconducting bulk magnets can be adapted to the disposal processes for Mn ions as well as large scale superconducting solenoid magnet. This attributes to the steep magnetic gradient of a bulk magnet system, which apparently is an advantage to other strong magnetic field generators.

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