Review Article

Research of Superconducting Magnetic Separation in Korea

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Synopsis: In Korea superconducting HGMS has been applied for the treatment of various kinds of wastewater. The wastewater from paper factory was successfully purified by HTS superconducting magnet system after pre-treated with magnetite and coagulant. For the treatment of coolant of hot rolling process in iron manufactory, coagulation conditions were investigated. Three different types of magnetic separation systems were applied and the suspended solids in the coolant were effectively removed. The treatment of condenser water in thermal power plant which mainly consisted of iron oxides was studied by investigating the effect of magnetic field strength, magnetic filter wire size, and filter composition on the turbidity decrease. Recycling of abrasives from waste slurry by magnetic separation was also investigated. The studies demonstrated that superconducting HGMS is feasible to apply to various kinds of wastewater and suggested improvements for better performance of HGMS system.

Keywords: condenser water, coolant, high gradient magnetic separation (HGMS), silicon slurry, wastewater treatment

1. Introduction

High gradient magnetic separation (HGMS) can separate ferromagnetic and paramagnetic particles from other solids, liquids or gases by using large magnetic field gradients. It has great merits to rapid purification of wastewater, the occurrence of small space, and no additional waste.

The superconducting magnetic separation aimed to use in wastewater treatment has recently received great attention. The superconducting HGMS offers many advantages over conventional models because it consumes only a fraction of the power required by conventional HGMS and is capable of generating induced magnetic field higher than 2 T.¹⁾

In Korea, superconducting HGMS has been studied for the application to various kinds of wastewater such as wastewater from paper factory, coolant for hot rolling process in iron manufactory, and condenser water in thermal power plant. Besides, recycling of abrasives from waste slurry was investigated. The studies have demonstrated that the HGMS is very successful in purifying wastewater and suggested improvements for better performance of HGMS system.

2. Purification of Wastewater from Paper Factory²⁾

The Korean paper industry is the 11th largest in the world. Since paper factories use massive amount of water and equivalent amount of wastewater is generated, it is environmentally important to purify the wastewater. Conventional water treatment facilities like precipitation process need large-scale equipment and wide space to purify the wastewater of paper factory. In case of massive waste water, HGMS parts are more effective to purify it rapidly and to occupy relatively small space, since large voids at filter with HGMS are adopted.

In this respect, two types of superconducting magnets were used for paper factory wastewater purification process. Type I: Cryo-cooled Bi-2223 (HTS) superconducting magnet system with a room temperature bore of 70 mm in diameter and 200 mm in height was prepared (**Fig. 1**). Type II: Cryo-cooled Nb-Ti (low temperature) superconducting magnet with a room temperature bore of 100 mm in diameter and 600 mm in height was used for magnetic separator.

Magnetic filters were designed by the analysis of magnetic field distribution at superconducting magnets. In this experiment, 430 mesh type of stainless steel was used as a magnetic filter for magnetic separation. **Figure 2** shows magnetic field distribution at stainless steel mesh filters when the magnet generates 6 T of magnetic field at the center ($R=0$, $Z=0$). According to the distribution of magnetic flux density magnitude around the filter wires those are located along the lines 1–4, great changes of

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Fig. 1 Cryo-cooled HTS magnet parts using Bi-2223 tapes assembled with a cold head for magnetic separator.²⁾

Fig. 2 Magnetic field distribution within the superconducting solenoid magnet when it generates 6 T of magnetic field at the center ($R=0$, $Z=0$).²⁾

Fig. 3 The variation of turbidity of treated water with magnetic particle size for magnetic separation process. Applied magnetic field: 3 T.²⁾

magnetic field around of filter wires that are located along lines 1 and 3 are shown along the cross section of cryo-cooled Nb-Ti superconducting magnet (type II). This means that large magnetic field gradient is generated by the stainless mesh filters, which increases tremendously

magnetic force acting on a particle which passes through the filters. These data can be used to choose proper mesh size of filter and gap distance of filter housing.

A cryo-cooled HTS magnet (Type I) was used superconducting HGMS for purifying wastewater in paper factory. Magnetite (Fe_3O_4) was used as ferromagnetic material and aluminum-sulfate ($\text{Al}_2(\text{SO}_4)_3$) was used as coagulant for magnetic seeding, respectively. As shown in **Fig. 3**, the turbidity of treated water increased as the flow rate of wastewater increased and the larger magnetite particles ($10\text{ }\mu\text{m}$) showed a better performance than smaller ones ($5\text{ }\mu\text{m}$). For the purification of wastewater from paper factory by magnetic separation, it is required to use a proper quantity of magnetite and coagulants.

3. Treatment of Coolant of Hot Rolling Process³⁻⁵⁾

Steel manufacture factories make an effort to purify and to recycle wastewater because they discharge a lot of wastewater. The iron manufacture in Korea, POSCO also has concerned about the treatment of wastewater for long time. The coolant of hot roller at steel making factory includes suspended solid (SS) like steel fines, iron oxide and emulsified oil. This coolant is generally passed by a re-circulating system that is constituted of screening, grit chamber, sedimentation, and filtration process. A little SS in treated coolant brings about inferior steel plate due to close the nozzle of cooling line. Therefore, it is needed to reduce the content of solid suspension in treated coolant. For the purpose of removing the steel fines, a magnetic separator with permanent magnets and flat-bed filter with filter cloth or paper have customarily been used. However traditional magnetic separator cannot remove completely the SS in coolant of hot-rolling process. The HGMS system by using superconducting magnet was therefore suggested for the effective purification of the coolant.

Prior to HGMS experiment, magnetic flock that was mixed with SS and coagulation substance in coolant was formed by electrochemical coagulation process with several kinds of coagulation substance, and the formation degree of magnetic flock was investigated. When the polymer coagulants (anionic, nonionic, and cationic ones) and inorganic substances ($\text{Al}_2(\text{SO}_4)_3$, FeCl_3 , FeSO_4) were used together, the formation of magnetic flocks was better than when only inorganic coagulants were added without polymer substances.

A laboratory-scale conduction cooled HTS magnet was used for a vertical HGMS system. The experiments were conducted at 4 Tesla of magnetic field with the SUS430 matrix filter and 20 L/min of flow rate. When the effect of flock formation was investigated with various input coagulant, alum ($\text{Al}_2(\text{SO}_4)_3$) and cation polymer mixture coagulant showed better HGMS treatment characteristics

Fig. 4 HGMS treatment of coolant wastewater after coagulation reaction with various coagulants.⁴⁾

Fig. 5 Schematic diagram of a reciprocal HGMS system using a cryo-cooled superconducting magnet.⁵⁾

than other coagulant (Fig. 4). The coolant wastewater was held for 10 min after adding the coagulant and about 30% of turbidity was removed by precipitation. By the HGMS additional 40–50% of turbidity was removed while about 15% of turbidity removal was achieved without the coagulant indicating the coagulation step is needed before the magnetic separation. However, the dose (1–3 mg/L) showed very similar result that meaning 1 mg/L of coagulant dose or less will be enough for the coolant wastewater.

In addition, as the treatment pass number of the HGMS increased, the concentration of turbidity and the SS in water decreased. Removing ratio showed more than 98% in the wastewater containing magnetic particles. The SS in the coolant of hot rolling process in steel manufactory was also treated by using a reciprocal HGMS system with a cryo-cooled Nb-Ti superconducting magnet (Fig. 5). This HGMS was possible to operate continuously because contaminated filters can keep on returning after cleaning. The capacity of the system was about 40 ton/day.

Fig. 6 The various concentrations of SS in purified coolant as the difference of material of filter wire – SUS430 and low carbon steel.⁵⁾

Similarly to the previous study⁴⁾, the proper content of coagulation substance and the effectiveness of coagulation reaction were investigated by the reciprocal HGMS system. The remove rates of SS were 99.9% at coagulated coolant and 96% at non-treated coolant. This implied coagulation process was very effective to purify hot-rolling coolant that contained magnetite particles.

The effect of filter wire material on the SS removal was investigated by using SUS430 and low carbon steel wires. Low carbon steel filter was a little better than SUS430 filter for HGMS because of a little higher saturation value of magnetization than that of SUS 430 for it (Fig. 6).

4. Purification of Condenser Water in Thermal Power Station^{6, 7)}

In thermal power plant, condenser water contains very small amount of impurities and it is important to control condenser water quality because scale on pipes reduces the efficiency of the condenser. The condenser water impurities mainly consisted of hematite ($\alpha\text{-Fe}_2\text{O}_3$) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$) and it was highly magnetized than hematite but less than magnetite. However, it is not easy to remove suspension material by a conventional method using electromagnet. Therefore, to eliminate fine-size suspension of iron oxides from the condenser water, the superconducting HGMS system was applied.

For the study, the superconducting HGMS system with a vertical type superconducting magnet and wire mesh disk filters was used (Fig. 7). The system was equipped with a 6-Tesla cryo-cooled Nb-Ti superconducting magnet and the magnetic filters were made of stainless steel 430.

The effect of magnetic field strength on the turbidity decrease was investigated with various magnetic field strength. While the permanent magnet of 0.5 T obtained only 62% decrease of the condenser water turbidity, the superconducting HGMS tests achieved the effective

Fig. 7 Schematic diagram of superconducting HGMS system (a) and Nb-Ti superconducting magnet (b).⁶⁾

Fig. 8 Effect of magnetic field strength on the turbidity change of purified condenser water by superconducting and permanent magnetic separators.⁶⁾

Fig. 9 Effect of the wire diameter and mesh size of magnetic filter on turbidity changes of the magnetic separation.⁶⁾

reduction of the turbidity up to 99.6%. As the strength of magnetic field increased in the range of 1–6 T, the more turbidity was removed (**Fig. 8**).

This result indicates that the superconducting HGMS system is much more effective to treat the condenser water of thermal power plant than a magnetic separation using permanent magnet.

Figure 9 shows the effect of the wire diameter and mesh size of magnetic filter on turbidity changes of the

magnetic separation. As the wire diameter decreased from 0.8 mm to 0.35 mm in diameter and as the mesh size increased from 5 to 15, the turbidity removal of the sample was enhanced. Besides, the addition of double filter in the middle part of the magnet and the repeated treatment enhanced the turbidity decrease.

These studies demonstrated that superconducting HGMS system is suitable to remove iron oxide impurities from condenser water in thermal power plant and suggested a high magnetic field, a proper double filter configuration and re-treatment of the treated solution for the improvement of the removal efficiency.

5. Recycling of Silicon Powder from Waste Silicon Slurry⁸⁾

As the development of solar and semiconductor industry is accelerating, the production of silicon wafer and silicon ingot has been increasing. The slurry produced in the wire sawing process contained silicon and silicon carbide as main components. The waste slurry also contained a lot of mineral oil and a few iron particles. Iron segments of the wire saw were found to attach to the SiC abrasives. The iron segments magnetize the abrasives in the mechanochemical process and thus reduce the cutting performance of the abrasives.⁹⁾ In this study, the separation and recovery of silicon particles from the waste silicon slurry was performed.

A HGMS and open gradient magnetic separation systems were used for the separation of iron particles. The system equipped with cryo-cooled Nb-Ti superconducting magnet that can generate up to 6 T and magnetic filters made of SUS430 steel wire mesh were used.

The SEM images in **Fig. 10** shows that iron segments were still attached to the SiC surfaces when the wasted slurry was treated by permanent magnet. In the tests of the superconducting magnetic separation, however, most iron segments were removed. Besides, the removal was enhanced with magnetic field strength and magnetic filter.

Figure 11 shows the magnetization behavior of particles in silicon slurry treated by magnetic separation at various magnetic field strength (3–6 T). The VSM measurement shows the magnetization value of the treated slurry was significantly reduced when the magnetic separation was applied at the strength of over 4 T. This implies that a high strength (> 4 T) of magnetic field is required to remove iron segments from the silicon slurry. Therefore, it can be concluded that superconducting magnetic separation technology is able to recover the SiC abrasives and oil from the wasted slurry successfully.

Fig. 10 SEM images of silicon slurry treated by magnetic separation with different conditions: (a) permanent magnet, (b) superconducting magnet at 6 T tilted by 15°, (c) superconducting magnet at 6 T tilted by 5°, and (d) superconducting magnet at 6 T tilted by 5° with magnetic filter.⁸⁾

Fig. 11 Magnetization behavior of particles in silicon slurry purified by magnetic separation at various magnetic field strength (3–6 T).⁸⁾

6. Conclusions

In Korea there were many studies dealt with the application of the superconducting magnetic separation. The studies applied the magnetic separation for the reduction of the turbidity of wastewater from paper factory, the removal of suspended solids from coolant in iron manufactory, the removal of iron oxides from condenser water in thermal power plant, and the removal of iron segments from silicon slurry waste.

Several Korea research institutes have experience to develop cryo-cooled superconducting magnets. KERI has developed many of cryo-cooled high- T_c superconducting magnets. And KBSI has developed 5 T cryo-cooled NbTi superconducting magnet.

The results demonstrated that superconducting HGMS is feasible to apply to various kinds of wastewater and slurry, and in some cases pre-treatment is required for magnetic seeding. For a practical application of the HGMS system, further study is needed.

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