Magnetic Separation Using HTS Bulk Magnet for Cs-Bearing Fe precipitates

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Abstract. A peculiar magnetic separation technique has been examined in order to remove the Cs-bearing Fe precipitates formed of the waste ash from the withdrawn incinerator furnaces in Fukushima. The separation system was constructed in combination with high temperature superconducting bulk magnets which generates the intensive magnetic field over 2 T, which was activated by the pulsed field magnetization process. The separation experiment has been operated with use of the newly-built alternating channel type magnetic separating device, which followed the high-gradient magnetic separation technique. The magnetic stainless steel filters installed in the water channels are magnetized by the applied magnetic fields, and are capable of attracting the precipitates bearing the Fe compound and thin Cs contamination. The experimental results clearly exhibited the positive feasibility of HTS bulk magnets.

1. Introduction
In Fukushima, the combustion ash bearing radioactive Cs from disused incineration furnaces yields from the withdrawal process of incinerator furnaces. Then, it is necessity to recover Cs from the contaminated water extracted from the washed ash. The authors examined the feasible application of magnetic separation with use of HTS bulk magnets¹,²). The major merit of this magnet system is regarded as its intense magnetic field, high field gradient, and its compact system configuration³, ⁴).

2. Experimental
2.1. Precipitate forming
Since Cs element, in general, is not ‘magnetic,’ it should be given the magnetic properties by combining ferromagnetic iron molecular. As shown in Fig. 1, first, the adsorbent was added

Fig. 1. Magnetizing procedure of Cs-bearing precipitates.
to the waste water, and then, the Fe-bearing particles were formed. The ferrocyanic compound was practically employed to form the precipitate after adding NaOH solution to control the pH value. The precipitate thus formed was roughly separated by the conventional magnet roller installing the permanent magnets. Figure 2 shows the photo of the separation process, showing the slurry attracted on the magnet roller.

The water thus purified was then led through the fine filter to collect the very fine precipitates remaining in the treated clear water. As the filter would possibly become radioactive by the substantially thin Cs solution, the purification process which releases no extra radioactive waste is preferable on this stage in order to purify the water to high level. The HTS bulk magnet is one of the candidates for this purpose, which needs no excess filters in the process.

As shown in Fig. 3, the sample water drained from incinerator furnaces is treated by the magnetic roller bearing 0.4 T permanent magnets, and the separation ratio reached over 99.88% at this stage. The flow rates in the magnet roller operations were chosen as 60 and 120 ℓ/h for the samples to which the flocculant was added beforehand to enlarge the particle sizes of the precipitate. In ordinary processes, the separation ratios reach over 99.91% by filtering the water in final, the target value of the separation ratio should be 99.91% when we employ the HTS bulk magnet.

The flocculant addition formed the coarse precipitates with the averaged sizes of 122.7 μm with concentration of 3.40ppm after the magnet roller process with the flow rate of 60 ℓ/h, and 149.6 μm with 5.06ppm and 120 ℓ/h. In the case without any flocculant addition, the averaged size of the precipitates

Fig. 2. Recovery of precipitate with use of conventional magnet roller. Fig. 3. Conventional purification process for Cs-bearing waste.

Fig. 4. Magnetic separation system carrying HTS bulk magnet system of mono-pole (a) and face-to-face poles with shifting channels (b).
3.1. Characterization of magnetic separation

The separation ratio was 4.10 μm with concentration 15.93 ppm after the magnetic separation by the magnet roller in the slow flow rate of 40 ℓ/h.

2.2. Equipment for magnetic separation

Two types of the magnetic separation experiment were employed in the experiment. Figure 4 shows the systems using HTS bulk magnet of mono-pole (a) and face-to-face poles with shifting channels (b). The magnet was activated by the pulsed field magnetization method by feeding the current to the cryo-cooled pulse-coil, resultantly generating 2.03 T at the pole surface, which installs Gd-Ba-Cu-O bulk compound with the size of 60 mm in diameter, which was cooled to 30 K by GM-cooler.

The water channel made of stainless steel (Japan Industrial Standard JIS:SUS304) with the size of 27 mm in thickness was attached on the magnetic pole, in which the stainless steel filter (JIS:SUS430) with the size of 0.1 mm in diameter was filled with the density of 10% in weight.

Another magnet system is a face-to-face type magnet system composed of face-to-face settled HTS bulk magnets. The components are the same as the former case. A couple of water pipes are positioned in the space between the 2-T magnetic face-to-face poles, which can move aside along the moving part in the figure. As schematically shown in Fig. 5, the pipes alternately move in and out of the intense magnetic field space to attract the slurry. So-called HGMS (high gradient magnetic separation) is operated in the pipe positioned between the magnetic poles, while the compressed air gushes in the water pipe positioned out of the field to clear the slurry away in every alternating 1 min interval. The flow rate of the water was 3.0 ℓ/min. The small amount of water samples were picked after each motion for ten times.

In the experiment, we employed the non-radioactive Cs fine powder. In exchange for thin Cs content, the concentration data for Fe ions were precisely estimated by ICP analysis by following equations, \( S = (C - C')/C \times 100 \), where \( S \) means the separation ratio in %, \( C \): concentration of original liquid, and \( C' \): concentration of picked-up liquid. The flow rates were varied from 1 to 3 ℓ/min, as well as the separation time of 1 to 5 min.

3. Results and discussion

Figure 6 shows the separation ratios for the flocculant-added precipitate and without flocculant as a function of flow rates of 1-3 ℓ/min. When we add the flocculate, the performances reached over 90% for both cases of 60 and 120 ℓ/h samples, reaching the best separation ratios up to 96.80% and 99.89%,
respectively. As for the sample without floculant addition, the performance stays in the region less than 86%. One sees that the floculant addition, which means the enhancement in volume, is quite effective to obtain high separation performances, which follows the theoretical estimation \(^7\). Since we observed only weak descending against time in the figures, we see that the filter in the water channel has not reach its saturation, yet.

When we adopt the face-to-face type magnetic poles, the separation performance has a bit improved by its intense and wide magnetic field space between the poles. As shown in Fig. 7, the separation ratio data reached over 97% and 98% for 60 and 120 ℓ/ h, respectively. The ratios for the sample without floculant addition, however, stayed less than 67%, as well in the case of mono-pole operation. When we compare these data to the initial Fe concentration of 647.71 ppm measured before the operation in the magnet roller process, the whole separation performance including the magnet roller process were estimated as 99.98% and 99.99% for 60 and 120 ℓ/ h samples, respectively, as shown in Table 1. This performance exceeds the target value of 99.91%, exhibiting that the operation with use of HTS bulk magnet system is well profitable, as it was expected.

![Fig. 7. Iterative cycle dependence of separation ratios as a function of flow rates by face-to-face magnets for various flow rates at the magnet roller process.](image_url)

| Number of cycle | Separation ratio(%) |
|-----------------|---------------------|
| 0               | 100                 |
| 1               | 90                  |
| 2               | 80                  |
| 3               | 70                  |
| 4               | 60                  |
| 5               | 50                  |
| 6               | 40                  |
| 7               | 30                  |
| 8               | 20                  |
| 9               | 10                  |
| 10              | 0                   |

Table 1. Maximum separation ratios in the face-to-face HTS bulk magnet process.

| Concentration(%) | 60 ℓ/ h (with floculant) | 120 ℓ/ h (with floculant) | 30 ℓ/ h (without floculant) |
|------------------|--------------------------|--------------------------|-----------------------------|
| Before bulk magnet | 4.82 ppm | 2.20 ppm | 9.24 ppm |
| Final concentration (%) | 0.11 ppm(97.71%) | 0.04 ppm(98.11%) | 2.96 ppm(67.92%) |
| Separation ratio/initial | 99.98% | 99.99% | 99.54% |

Initial Fe-concentration: 647.71 ppm, Flow rate: 3.0 ℓ/ min

4. Conclusion
After the conventional processes by the magnet roller containing the permanent magnets which attract the major portion of precipitates, the separation performance of the bulk magnets reached up to 98%, which exceeded the research target of 99.91%. Thus, the data suggest the feasible prospects for the high performance of magnetic separation for the purification of Cs-contaminated waste water. On the other, since the separation for the sample water without floculant showed the low ratios, it is necessary to fabricate the coarse precipitate without adding any floculant in order to reduce the whole mass of radioactive waste.

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