Removal of Scale from Feed-water in Thermal Power Plant by Magnetic Separation
-Analysis of Oxygenated Treatment Scale-

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Abstract. One of the reasons of the deterioration of the generation efficiency of the thermal power generation is the adhesion of the iron scale generated by the corrosion of the pipe to the inner wall of the feed-water system. Focusing on the magnetic property of scale, we studied on the removal of scales in the feed-water system by high gradient magnetic separation (HGMS) using the superconducting magnet. In this study, we targeted the thermal power plants adopting oxygenated treatment (OT). In order to determine the installation site and the magnetic separation condition of the HGMS system, we analyzed the OT scale and then clarified the aggregation/composite states by magnetic separation experiment. It is concluded that low-pressure feed-water heater drain is suitable for installation site of HGMS system. In addition, it was clarified that homogeneous aggregation particles existed in the OT scale.

1. Introduction

The technology to prevent thermal power plant from deterioration of generation efficiency is needed in order to reduce CO₂ emissions. One of the reasons for the decline is adhesion of the iron scale generated by corrosion on the piping inner wall in the feed-water system. The thermal conductivity of the scale is less than 10% of the piping material, so the scale adhered to the inner wall of the piping causes a drop in heat exchange efficiency. Chemical feed-water treatment such as total volatile treatment (AVT) and oxygenated treatment (OT) is performed in order to suppress the scale generation. However, these methods cannot prevent the scale generation completely. Focusing on the magnetic property of scale, we studied on the removal of scales in the feed-water system by high gradient magnetic separation (HGMS) using the superconducting magnet. In this study, we targeted the thermal power plants adopting OT which is increasing in the power plants with large capacity in recent years.
To determine the magnetic separation condition, analysis of the magnetic properties and particle size of the scale is necessary. The main component of the AVT scale is ferromagnetic magnetite, whereas the main component of OT scale is paramagnetic hematite [1], and also include ferromagnetic magnetite. The aggregation state of the mixture of the paramagnetic and the ferromagnetic particles are divided into homogeneous and heterogeneous aggregation. Homogeneous aggregation is the state in which paramagnetic and ferromagnetic particles are separately aggregated, whereas heterogeneous aggregation is the state in which the paramagnetic particles and the ferromagnetic particles are aggregated each other. Since the magnetic separation efficiency depends on the aggregation state of the scale, it greatly influences the determination of the magnetic separation condition. In order to introduce HGMS device to the thermal power plant, it is necessary to minimize the processing cost and the influence of the magnetic field on the surrounding apparatuses. Therefore, it is important to select an appropriate magnetic separation condition. To clarify the aggregation state of the scale, we analyzed the scale sampled from the feed-water in the actual thermal power plant. Then we conducted the small-scale magnetic separation experiment with the superconducting bulk magnet using the actual sampled scale and the mixed sample simulating the actual scale contents. The aggregation state of the actual scale was considered by comparing these results.

2. High gradient magnetic separation (HGMS)

The high gradient magnetic separation (HGMS) is the method of separating an object applying the magnetic force by high magnetic field gradient generated around magnetic filters. The magnetic filter is installed in the magnet bore and magnetized. The magnetic force $F_M$ (equation 1) and the drag force $F_D$ (equation 2) act on the separation target particles. The magnetic force $F_M$ is the force that attracts the separation target particles to the magnetic filter. Drag force $F_D$ is the force of the resistance to the movement of the particles in the fluid.

$$F_M = \frac{4}{3} \pi r^3 \frac{\mu_0}{\mu} (B \cdot \nabla)B$$

(1)

$$F_D = 6 \pi \eta r \left( \nu_f - \nu_p \right)$$

(2)

Here, $r$ is the particle radius, $\chi$ is the magnetic susceptibility of the particle, $B$ is the magnetic field strength, $\eta$ is the viscosity of the solvent, $\nu_f$ is the velocity of the fluid and $\nu_p$ is the particle velocity. It is possible to estimate whether particles can be trapped by the resultant force of magnetic force and drag force. From the above two equations, it can be seen that the magnetic separation condition greatly differs depending on the particle size $r$ and magnetic susceptibility $\chi$ of the scale.

As noted above, homogeneous aggregation and heterogeneous aggregation are considered in the mixture of the paramagnetic and the ferromagnetic particles [2]. In the case of OT scale targeted in this research, homogeneous aggregation means that paramagnetic and ferromagnetic particles are aggregated independently, whereas heterogeneous aggregation means that paramagnetic and ferromagnetic particles are aggregated with each other. In the former case, it is easy to capture the ferromagnetic particles, but to capture the paramagnetic particles, high magnetic field and high magnetic field gradient, corresponding to $(B \cdot \nabla)B$ in equation 1, is required. It is possible to capture paramagnetic particles using a high magnetic field and high gradient. However, as the applied magnetic field becomes higher, the amount of electric power required to start-up the superconducting magnet increases. In addition, since the range of the influence of the magnetic field on the surrounding devices also increases, the large space is required for the introduction site. Whereas in the latter case, the apparent magnetic susceptibility of the particles is larger than that of the paramagnetic particles and the magnetization $\chi$ of equation 1 increases. Therefore paramagnetic and ferromagnetic particles can be separated with the relatively low applied magnetic field.

Moreover, in the feed-water system of the thermal power plant, the scale is generated at high temperature and pressure (50 to 290 °C, from 2 to 30 MPa). Hence the particles might be compounded by chemical bonding such as dehydration condensation by heating. In the case that the particles are
compounded among the different kinds of particles, dispersion of aggregates due to the flow of the feed-water does not occur, which is the more favorable condition for magnetic separation.

3. Experiment

3.1. Analysis of actual scale
The scale was sampled at 6 sampling points in the feed-water system of the power plant adopting OT. To clarify the magnetic property of the actual scale, the composition was analyzed with Mössbauer spectrometry and magnetization were analyzed by physical property measurement system (quantum design Inc.). Figure 1 shows the sampling points in the feed-water system of the thermal power plant. The sampling points were as follows; (1) outlet of condensate pump, (2) outlet of condensate demineralize, (3) drain of low-pressure feed-water heater, (4) inlet of deaerator, (5) storage tank of deaerator, (6) inlet of the economizer.

Figure 2 and 3 show composition and the magnetization of the actual scales at 6 sampling points respectively. The composition of the scale was different depending on the sampling points. The scale sampled from the low-pressure feed-water heater drain most contained the ferromagnetic magnetite and maghemite compared with the scales of other sampling points. In addition, the sample showed the highest magnetic susceptibility. Therefore, we assumed the introduction of HGMS system into low-pressure feed-water heater drain. In order to clarify the aggregation and composite states of the ferromagnetic and the paramagnetic particles mentioned in the previous chapter, lab-scale magnetic separation experiments by superconducting magnet were conducted. The experiments were conducted both for the actual scale sampled at low-pressure feed-water heater drain and the sample simulating it by mixing iron oxide and hydroxide.

![Figure 1. The sampling points in the feed-water system of the thermal power generation.](image-url)
3.2. Magnetic separation of actual scale and simulated scale

Figure 4 and 5 show the whole view of magnetic separation experiment and magnetic filter respectively. When we introduce HGMS system in the thermal power plant, we are planning to use the superconducting solenoidal magnet which can apply the strong magnetic field to the large area. However, the purpose of this experiment is the investigation of scale aggregation and small-scale of several hundred mg. Therefore superconducting bulk magnet with GdBaCuO bulk superconductor (Nippon Steel Corp., φ60 mm, Thickness 20 mm) was used to apply the magnetic field. The superconducting bulk magnet was cooled using the GM refrigerator (Aisin Seiki Co., Ltd.) until the temperature of the cryostat reached 30 K. The sample suspension was sent by the constant feed pump (Tokyo Rikakikai Co., Ltd., RP-1000) in the tube flow path. It passed through the magnetic filter on the superconducting bulk magnet in the tube. The particles not captured by the magnetic filter and fluid were recovered in the outlet container.

Table 1 shows the filter conditions and table 2 shows the experimental conditions. 1 g of demister (SUS 430) with a wire linear 0.1 mm was used as a filter (filling rate 23.6%). The flow velocity was adjusted with the constant feed pump and set at 87 mm/s. The simulated scale was prepared by mixing commercial samples simulating the composition of the low-pressure feed-water heater drain (table 3). According to calculation using Equation 1 and 2, the paramagnetic particles (α-Fe₂O₃, α-FeOOH and γ-FeOOH, 0.1 µm- 5.5 µm) in the sample cannot be captured at 87 mm/s. The concentration of suspension is 100 ppm, and the amount of feed-water is 1 L. After magnetic separation, the weight of captured particles and particles not captured was measured to investigate separation efficiency. The composition of the captured scale was also analyzed with Mössbauer spectrometry.

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The ferromagnetic particles and it was captured by the filter. In the latter case, it has been reported that non-target particles were captured in the process of attracting the ferromagnetic particles to the magnet [3]. The ferromagnetic particles aggregate each other in a chain-like form under magnetic field [4]. In addition, the ferromagnetic particles are strongly attracted to the filter and are immediately captured by the filter. Therefore, when ferromagnetic particles with chain-like form were immediately attracted to the filter, part of the paramagnetic particles get caught in the chain and captured together. It is also possible that the magnetic field gradient near the filter increases due to capturing of the ferromagnetic particles to the filter and the paramagnetic particles was captured. However, based on preliminary experiments, its influence is considered to be small.

However, it is considered that aggregation of the particles hardly occurs from the result of zeta potential, showing that all the particles are positively charged. In addition, the paramagnetic particles captured in this experiment was about 30-40 wt.% of total contents. Therefore, it is considered that there were also paramagnetic particles in monodispersed or homogeneous aggregation states.

| Table 1. Filter condition. | Filter shape | Wavy mesh (Demister) |
|---------------------------|--------------|---------------------|
| Filter material           | SUS430       |                     |
| Filter wire diameter      | 0.1 mm       |                     |
| Filter weight             | 1 g          |                     |
| Filter filling rate       | 23.6 %       |                     |

| Table 2. Experimental condition. | Flow velocity | 87 mm/s | Flow path diameter | 6 mm | Applied magnetic flux density | About 3 T | Suspension concentration | 100 ppm | Volume of feed-water | 1 L |

| Table 3. The composition of the simulated sample. | Fe$_2$O$_3$ | γ-Fe$_2$O$_3$ | α-Fe$_3$O$_4$ | α-FeOOH | γ-FeOOH |
|------------------------------------------------|----------|-------------|-------------|--------|--------|
| Company, Brand name                             | Mitsui Mining & Smelting Co., Ltd., Sample 2 | CIK Nano Tek corp., | Toda Kogyo corp., 180ED | Toda Kogyo corp., Y-313 | Kanto Chemical Corp., Ltd., 16024-02 |
| Primary particle diameter [μm]                  | 0.1      | 0.03        | 0.5         | -      | -      |
| Composition [%]                                  | 14.3     | 7.00        | 59.0        | 19.3   | 0.400  |

4. Result and discussion

4.1. The result of magnetic separation

Figure 6 shows the separation efficiency and the composition of captured particles. Figure 7 shows the magnetization curves of the captured particles. The composition of simulated scale before separation was a little different by error of weighing at sample preparation. However both the simulated and actual scale showed the same tendency in the composition and the magnetization.

In this experiment, the flow velocity was set to a condition that paramagnetic particles could not be captured. Nevertheless, paramagnetic particles were captured and total capture rate was about 50%. Two reasons are considered heterogeneous aggregation of particles, or paramagnetic particles involved by the ferromagnetic particles. In order to discuss the former heterogeneous aggregation, zeta potential of each component was measured. Table 4 shows the zeta potential (in the distilled water, pH 5.7) of each component in the sample. The zeta potential at pH 5.7 at which magnetic separation experiment was conducted in all components showed a positive value. Therefore, it is considered that the particles were difficult to aggregate due to electrical repulsion between the particles. However, the zeta potential of hematite shows a slightly smaller value than the other components. It indicates that heterogeneous aggregation may occur partly between hematite and other components. It is considered that the apparent magnetic susceptibility of the particles increased due to heterogeneous aggregation of hematite and ferromagnetic particles and it was captured by the filter. In the latter case, it has been reported that non-target particles were captured in the process of attracting the ferromagnetic particles to the magnet [3]. The ferromagnetic particles aggregate each other in a chain-like form under magnetic field [4]. In addition, the ferromagnetic particles are strongly attracted to the filter and are immediately captured by the filter. Therefore, when ferromagnetic particles with chain-like form were immediately attracted to the filter, part of the paramagnetic particles get caught in the chain and captured together. It is also possible that the magnetic field gradient near the filter increases due to capturing of the ferromagnetic particles to the filter and the paramagnetic particles was captured. However, based on preliminary experiments, its influence is considered to be small.
Also from figure 6, it can be seen that the capture rates showed similar results in actual and simulated scale, indicating the aggregation state of the particles of the simulated and the actual scale were similar, and it is considered that there was almost no composite state in the particles. Figure 7 shows the distribution of magnetic susceptibility and particle size of the actual scale. In this method, the volume magnetic susceptibility of each particle was measured by monitoring the magnetophoresis velocity of the particles, and each particle size was measured by image analysis. In this experiment, the actual scale was sufficiently dispersed in the glycerin solution. A tendency that the distribution of the magnetic susceptibility was divided into high and low ones, confirming the result of magnetic separation experiment.

![Figure 6](image1.png)

**Figure 6.** The separation efficiency and the composition of captured particles.

![Figure 7](image2.png)

**Figure 7.** Magnetization curve of captured particles.

![Figure 8](image3.png)

**Figure 8.** Distribution of magnetic susceptibility and particle size.

### 4.2. Proposal of HGMS system

The result in section 4.1 showed that there were almost no particles in the composite state in OT scale. Moreover, there were both non-heterogeneous and heterogeneous aggregation particles. In thermal power plants which OT is applied, scale adhering to pipework are removed by chemical cleaning approximately every 10 years. However, one chemical cleaning costs ordinary tens of millions of yen
and a three-month shutdown of the power plant. By introducing the HGMS system, it is possible to postpone the interval of chemical cleaning. In order to extend the interval as much as possible, we set it to 80% as the immediate goal. The reason is as follows. In the previous study, we conducted the magnetic separation experiment simulated the thermal power plant adopting AVT. That experiment was one-seventh of actual power plant and its capture rate was 91.5%. OT scale contain over 80% of paramagnetic particles and that particle size is smaller than AVT scale, so capturing OT scale isn’t easy unlike AVT scale. Nevertheless, 80% of removal rate is considered to extend the interval of chemical cleaning. Consequently, we need to design a device that can also capture paramagnetic particles in monodispersed or homogeneous aggregation states.

In order to capture paramagnetic particles, large magnetic field its gradient is required. We propose the HGMS system that the ferromagnetic particles and the paramagnetic particles can be captured separately in multiple-stages with different filters. Firstly, ferromagnetic particles are captured with rough mesh filters arranged at the inlet side, and then paramagnetic particles are captured with fine mesh filters arranged at the outlet side. By applying such filter composition, we can capture OT scale with one superconducting magnet system.

5. Conclusion
We analyzed OT scale and clarified the aggregation/composite states by magnetic separation experiment, in order to determine the installation site of HGMS system and the magnetic separation condition in the thermal power plant adopting OT. Composition analysis and magnetization measurement of the scale sampled at six points in the feed-water system were carried out. As a result, the ratio of ferromagnetic particles and the magnetization was the highest in the scale sampled from low-pressure feed-water heater drain. Hence, it is considered that low-pressure feed-water heater drain is the most suitable installation site of HGMS.

In order to clarify the aggregation/composite states of scale, the magnetic separation experiment was conducted using the scale sampled from low-pressure feed-water heater drain and its simulated sample. Both heterogeneous and not heterogeneous aggregation between ferromagnetic and paramagnetic particles are present both in the actual and simulated OT scale. In addition, there are almost no composite state of particles. Therefore, we concluded that it is necessary to design a device capable of capturing single paramagnetic particles with small magnetic susceptibility for removal of the OT scale from feed-water in the thermal power plant.

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