Removal of Iron Oxide Scale from Feed-water in Thermal Power Plant by Using Magnetic Separation

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Abstract. One of the factors of deterioration in thermal power generation efficiency is adhesion of the scale to inner wall in feed-water system. Though thermal power plants have employed All Volatile Treatment (AVT) or Oxygen Treatment (OT) to prevent scale formation, these treatments cannot prevent it completely. In order to remove iron oxide scale, we proposed magnetic separation system using solenoidal superconducting magnet. Magnetic separation efficiency is influenced by component and morphology of scale which changes their property depending on the type of water treatment and temperature. In this study, we estimated component and morphology of iron oxide scale at each equipment in the feed-water system by analyzing simulated scale generated in the pressure vessel at 320 K to 550 K. Based on the results, we considered installation sites of the magnetic separation system.

1. Introduction

Recently, reduction of carbon dioxide (CO₂) has been required to prevent the global warming. It is necessary to keep the efficiency of thermal power plants high, because they account for the most of CO₂ emission accompanied with the electric power generation. One of the factors of deterioration in the efficiency is the adhesion of the iron oxide scale to the inner wall of pipe in feed-water system. [1] Iron oxide scale is main corrosion product with thermal conductivity as low as 10 % of pipework material. Therefore, the scale adhesion to inner wall of pipework decreases heat exchange efficiency. It is reported that the decline of thermal power generation efficiency caused by scale adhesion is 25 kW/µm in the 200 MW grade coal thermal power generation. [2] Thermal power plants have employed All Volatile Treatment (AVT) or Oxygen Treatment (OT) to prevent scale formation, though these treatments cannot prevent it perfectly. The effective method for removal of the scale has been required.

We proposed a high gradient magnetic separation (HGMS) system [3, 4] that can remove iron oxide scale without stopping thermal power plant. HGMS is a method to separate substances from fluid utilizing magnetic force. Ferromagnetic filters are installed into the flow channel and magnetized by external magnetic field. It is necessary for this system to treat 400~500 m³/h feed-water, and hence we employed HGMS using superconducting magnet that can generate high magnetic field in wide area. Magnetic separation efficiency is largely influenced by component and morphology of scale. Scale
changes their property depending on the type of water treatment and temperature of feed-water. In this study, we estimated component and morphology of iron oxide scale at each equipment in the feed-water system by analyzing simulated scale generated at 320 K to 550 K in the pressure vessel. Based on the results, we considered installation sites of magnetic separation system.

1.1. Water treatment
Two kinds of treatments, All Volatile Treatment (AVT) and Oxygen Treatment (OT), are performed in thermal power plants to prevent scale formation. In AVT, ammonia as pH adjuster and hydrazine as deoxidizing agent are added to feed-water. Corrosion of piping metal is reduced by keeping pH of feed-water high, and dissolved oxygen that induces corrosion is removed by hydrazine. On the other hand, ammonia and oxygen are added to feed-water in OT. Ammonia reduces corrosion of piping and oxygen changes the iron component into hematite (α-Fe₂O₃) that has lower solubility compared with piping materials. Passive film of hematite formed on inner wall protects piping material from corrosion. In this study, we subjected thermal power plant using AVT and OT since component and morphology of scale are different depending on the type of water treatment.

1.2. Mechanism of iron oxide scale formation
Figure 1 shows schematic diagram of thermal power plant. Feed-water treated by AVT or OT is kept pH high around 9, but the corrosion of pipe metal is promoted due to decrease in pH around 7 by degassing in the condenser. Then, pH of feed-water is raised by addition of ammonia, and eluted iron ions deposit as fine particles such as iron oxyhydroxide. Most of iron components change into iron oxide particles at high temperature area. [4] These particles deposit on the inner wall, and declines heat exchange efficiency.

![Figure 1. Schematic diagram of thermal power plant.](image)

2. Experimental procedure
Figure 2 shows experimental procedure of simulated scale generation. We employed ferrous chloride solution and ferric chloride solution to simulate feed-water containing iron ion eluted from pipework. These solutions were prepared by dissolving iron (II) chloride tetrahydrate (KISHIDA CHEMICAL Co., Ltd.) and iron (III) chloride hexahydrate (KISHIDA CHEMICAL Co., Ltd.) to distilled water respectively, whose densities of iron ion were adjusted to 100 mg/L. When we simulated feed-water using AVT, ferrous chloride solution was used. The reason is that concentration of dissolved oxygen in feed-water using AVT is smaller than 10 µg/L and iron ion is hardly oxidized. 1 mol/L ammonia solution (NACALAI TESQUE, INC.) and hydrazine monohydrate (KISHIDA CHEMICAL Co., Ltd.)
were added to the solution. The pH of this solution and the concentration of hydrazine were adjusted to 9 and 10 mg/L respectively. On the other hand, ferric chloride solution was employed in simulation for OT. This is because feed-water using OT contains oxygen about 20–200 µg/L, so iron ion is well oxidized. Ammonia was added to ferric chloride solution to adjust pH to 9. These samples were enclosed into pressure vessel (Taiatsu Techno Corporation, TVS-N2) and heated for 24 hours. Heating condition is shown in table 1. Heating temperature was determined from temperature of feed-water at respective equipment of thermal power plant. Suspensions after heating were filtered and solid products were analyzed by XRD (Rigaku Corporation, Ultima IV) to identify the component of simulated scale. Particle size distributions of suspensions were measured before and after ultrasonic treatment to investigate morphology of simulated scale.

![Diagram](image)

**Figure 2. Experimental procedure of simulated scale generation experiment.**

| Equipment                  | Temperature[K] | Pressure[MPa] |
|----------------------------|----------------|---------------|
| Inlet of low pressure heater| 320            | 0.10          |
| Outlet of low pressure heater| 400            | 0.27          |
| Outlet of deaerator        | 450            | 1.0           |
| Drain of high pressure heater| 450            | 1.0           |
| Outlet of high pressure heater| 550            | 6.4           |

### Table 1. Heating condition.

3. **Results and Discussions**

#### 3.1. Simulation for AVT

Figure 3 shows XRD spectrums of generated scales simulating AVT thermal power plant. From this figure, the characteristic peak positions of simulated scales at every heating temperature were corresponded to that of magnetite. It indicates that main component of the scale is magnetite in AVT thermal power plant. Magnetite is ferromagnetic that can be removed by magnetic separation easily. Figure 4 shows spectrum half-width of simulated scales and commercially available magnetite (MITSUI MINING & SMELTING CO., LTD.) at the peak of $\theta = 35.4^\circ$ in XRD spectrum. Figure 4 shows low crystallinity of simulated scales compared with commercial magnetite because low half-width represents high crystallinity. Low crystallinity means low magnetic property and hence we should consider difference of magnetic property between literature data and real scale’s characteristic in developing magnetic separation system.
Figure 3. XRD spectrum of scale in the case of simulation for AVT.

Figure 4. Spectrum half-width of simulated scale and commercial magnetite.

Figure 5 shows particle size distribution of generated scales simulating for AVT. These measurements were conducted before and after ultrasonic treatment. From this figure, particle size of simulated scale at all heating temperature became smaller by ultrasonic treatment. This result indicates aggregation of simulated scale. In practical condition, it is supposed that the scale is aggregated, and hence the dispersion due to flow of feed-water is also considered. Particle size of simulated scale heated at 320 K was smaller than that at other heating temperatures. It can be estimated that particle
size of practical scale at low-temperature area such as inlet of low-pressure heater is smaller than that in high temperature area.

![Figure 5. Particle size distribution of simulated scale.](image)

From the above, main component and median size of scale in AVT thermal power plant estimated are shown in figure 6. In magnetic separation, larger particle size of target particle increases higher magnetic separation efficiency. Therefore, it is thought that magnetic separation system should be installed into high temperature area after low-pressure higher in AVT thermal power plant.

![Figure 6. Component and median size of scale estimated from analysis (AVT).](image)

3.2. Simulation for OT
Figure 7 shows XRD spectrums of generated scale simulating OT thermal power plant. XRD spectrum of simulated scale heated at 320 K had no peak, whereas peak positions of scales heated at 400, 450 and 550 K were corresponded to those of hematite. From this result, the scales in OT thermal power
plant are noncrystalline at inlet of low-pressure heater and hematite at high temperature area. This noncrystalline substance is inferred iron oxyhydroxide which was generated when ammonia was added to solution containing iron ion [5]. Iron hydroxide and hematite are both paramagnetic and hence they can be removed by HGMS using superconducting magnet. The spectrum half-width of simulated scales and commercially available hematite (TODA KOGYO CORP.) at the peak of $2\theta = 33.1^\circ$ in XRD spectrum are shown in figure 8. Low crystallinity of simulated scales compared with commercial hematite was suggested by the figure. We should consider that crystallinity effects on the magnetic property in examining magnetic separation system as with the case of AVT.

![Simulation for OT](image)

**Figure 7.** XRD spectrum of scale in the case of simulation for OT.

![Spectrum half-width of simulated scale and commercial hematite](image)

**Figure 8.** Spectrum half-width of simulated scale and commercial hematite.
Figure 9 shows particle size distribution of generated scales simulating for OT. These measurements were conducted before and after ultrasonic treatment. Figure 9 shows aggregation of simulated scale because particle size became smaller by ultrasonic treatment for all heating temperature. In practical condition, it is supposed that the scale is also aggregated, though dispersion due to flow of feed-water is considered. Particle size distributions of these simulated scale heated at 400, 450 and 550 K after ultrasonic treatment had broader peak in respect of those of generated scale simulating for AVT. Therefore, it is thought that the scale in OT thermal power plant has wider particle size distribution compared with that in AVT. It is reported that particle size of amorphous ferric oxyhydroxide is observed to be less than 8 nm by transmission electron microscope [5], and consequently the simulated scale heated at 320 K would not be dispersed by ultrasonic treatment completely.

Figure 9. Particle size distribution of simulated scale.

Main component and median size of scale in OT thermal power plant estimated from the analysis are shown in figure 10. In magnetic separation, larger particle size of target particle results in higher magnetic separation efficiency. Therefore, it is considered that we should install magnetic separation system into outlet of deaerator (DEA) or drain of high-pressure heater (HPD) in OT thermal power plant.
4. Conclusion
We proposed a HGMS system using superconducting magnet in order to remove iron oxide scale. In this study, simulated scales generated by using pressure vessel heated at 320–550 K were analyzed. Based on the results, we estimated component and morphology of practical scale generated in the AVT or OT feed-water of thermal power plant. Iron oxide scale can be removed efficiently by magnetic separation when we install this system at high temperature area in feed-water system of AVT thermal power plant, and outlet of deaerator or drain of high-pressure heater of OT thermal power plant. In practical condition, flow flux or density of iron oxide scale should be also taken into account for decision of installation site. Moreover, difference of magnetic property between commercial iron oxide and real scale products should be examined. In future, we are going to investigate magnetic separation efficiency with magnetic separation experiment for these simulated scales.

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