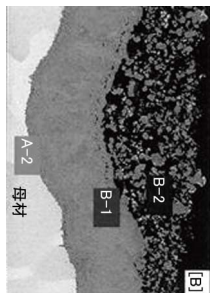


Development of Analysis Method for Iron Tracing in Boiler Feedwater Using Filter Concentration Method



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Boilers that use an oxygen treatment method (OT) for water treatment have the risk where the growth of powder-like scale consisting of eluted iron in feedwater equipment causes heat transfer inhibition and leads to problems such as tube leakage. For this reason, it is necessary to control the iron concentration of boiler feedwater to 2 $\mu\text{g/L}$ or less to maintain stable boiler operation. However, the conventional analysis technique of minute amounts of iron is subject to the environmental effects and has the problem of ensuring analysis accuracy. This time, we developed a double filter concentration method that simultaneously uses a membrane filter and an iminodiacetate type chelate filter as a method to analyze minute amounts of iron easily and inexpensively. This paper presents the developed method. This method is adopted in the JISB8224 Boiler Feed Water and Boiler Water Testing Methods revised and published in March 2016.

1. Introduction

In recent years, an increase of the amount of iron brought into boilers and the adhesion of hematite scale on the inner surface of furnace wall pipes have been occurring and causing an increase in the furnace wall pipe metal temperature in plants that use an oxygen treatment method (OT)⁽¹⁾.

The adhered hematite scale has a low thermal conductivity and a porous shape with a small particle diameter, and is called “powder scale.” In plants that experienced the adhesion of powder scale on the inner surface of furnace wall pipes after the application of OT, the iron concentration in the drain system of the low-pressure feedwater heater increased. It is believed that problems caused by the adhesion of powder scale have a high possibility of occurring if the iron concentration at the boiler inlet exceeds 2 $\mu\text{g/L}$, and therefore the iron concentration at the boiler inlet should be controlled to 2 $\mu\text{g/L}$ or less.

2. Iron analysis method used in thermal power plants

Table 1 shows examples of the methods adopted as analysis methods of the iron concentration in boiler feedwater. In many power plants, a 2,4,6-tris-2-pyridyl-1,3,5-triazine absorptiometric method (TPTZ method) is used because it does not require expensive analysis devices and is easy to operate.

Figure 1 shows a schematic diagram of the reaction between TPTZ and iron. The TPTZ method is a method to quantitatively determine iron by adding hydroxylammonium chloride and 2,4,6-tris-2-pyridyl-1,3,5-triazine into an acid solution, adding ammonium acetate to adjust the pH value to 4 to 5, and then measuring the absorbance of generated blue iron (II) complex. The iron quantitative determination range of the TPTZ method using a 20-mm absorption cell is 1 to 30 μg , and the repeated analysis accuracy ranges from 2% to 10%. For this reason, the quantitative determination of low-concentration iron requires analyzing a concentrated sample using a cell with a long light path length. For the quantitative determination of iron in boiler feedwater containing 2

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$\mu\text{g/L}$ of iron using a 50-mm absorption cell, it is theoretically necessary to concentrate the sample by at least 4 times.

Table 1 Quantitative determination method of iron in boiler feedwater
(extracted from page 506 of Thermal and Nuclear Power Plant Handbook)

Analysis method	Quantitative determination range	Analysis accuracy [%]	Density lower limit of quantitative determination [mg/L]	Sampling amount [mL]
Phenanthroline molecular absorption spectrometry	20 - 500 μg	2 - 10	0.1	200
Frame atomic absorption method	0.3 - 6 mg/L	2 - 10	0.3	—
TPTZ method	0.001 - 0.03 mg	2 - 10	0.005	200
ICP emission spectral analysis method	20 - 5000 $\mu\text{g/L}$	2 - 10	0.02	—

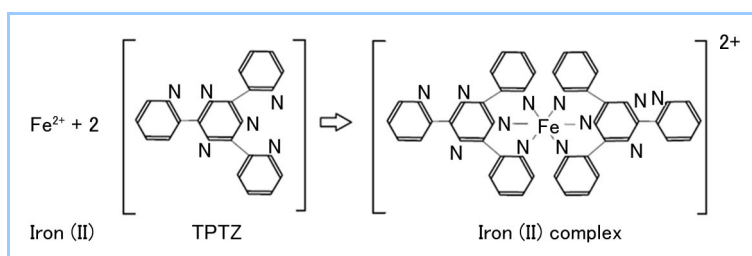


Figure 1 Reaction of TPTZ and iron

3. Problem with application of heating concentration and TPTZ method to boiler feedwater

(1) Problem with operation and analysis time period

As described above, one method to measure the 2 $\mu\text{g/L}$ of iron accurately in a stable manner is to increase the sampling amount and perform concentration. Generally, concentration is performed by heating the sample to evaporate the moisture. However, the heating concentration method is not realistic in terms of operation because the method requires time. It is also considered that heating concentration becomes more subject to contamination when the concentration time period is longer, and thus there is a limit on the usable sample amount.

(2) Problem with characteristics of sample

It is believed that in plants that use OT, the use of high-purity water containing a moderate amount of dissolved oxygen generates less soluble-in-water hematite on steel surfaces and results in various effects⁽¹⁾. Therefore, it is assumed that iron in boiler water exists as hematite particles.

The quantitative determination, using a plasma emission spectrometric analysis device, of iron concentration in a sample collected from a low-pressure heater drain in a plant that uses OT was performed before and after filtration using a 0.45 μm Omnipore membrane filter. **Table 2** shows the quantitative determination results. It was confirmed that about 78% of the iron contained in the sample consists of particles 0.45 μm or larger and the amount of dissolved iron is about 22% or less. The suspended iron to be measured by the TPTZ method needs to be soluble iron, and it may be necessary to take measures such as the extension of the dissolving treatment time in the case of less soluble hematite.

Table 2 Classification of iron in low-pressure heater drain water

Sample	Iron density [$\mu\text{g/L}$]	Proportion [%]
Before filtering	7.6	100
Filtrate (<0.45 μm)	1.7	22
Filtration residue (>0.45 μm) (Calculated value)	5.9	78

4. Filter concentration and TPTZ method

As a method to concentrate a large amount of the sample in a short period of time, we focused on solid phase extraction, and considered a concentration method using a filter (filter concentration method) as the analysis method for minute amounts of iron in the feedwater of a plant that uses OT. Iron in the feedwater of a plant that uses OT exists as iron particles that consist mainly of hematite particles and ionic dissolved iron that is dissolved in water. Thus, we designed a double filter method that collects iron particles on a membrane filter and dissolved iron on a chelate filter. **Figure 2** shows a schematic view of the double filter concentration method.

Iron particles are collected by the membrane filter with a pore diameter of 0.45 μm depending on the particle size. On the other hand, dissolved iron is collected as a complex by resin with an iminodiacetate group and then recovered by eluting with acid. The iminodiacetate group has a high selectivity against transition metal and thus can be used for the collection of minute amounts of iron in boiler feedwater. **Figure 3** shows a schematic diagram of iron collection using a chelate filter.

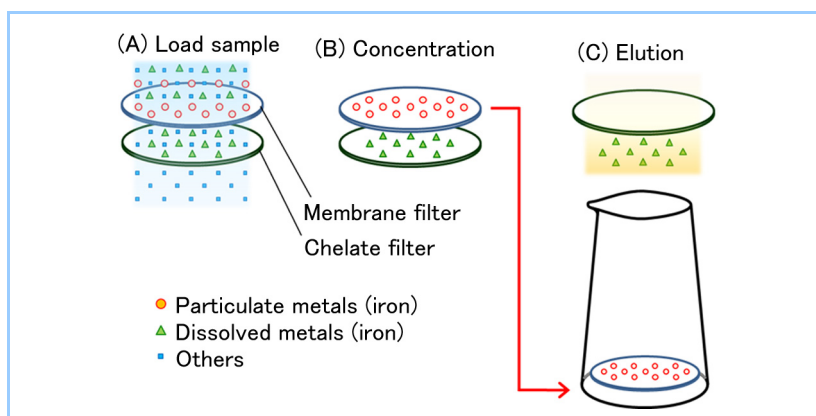


Figure 2 Schematic diagram of double filter concentration method

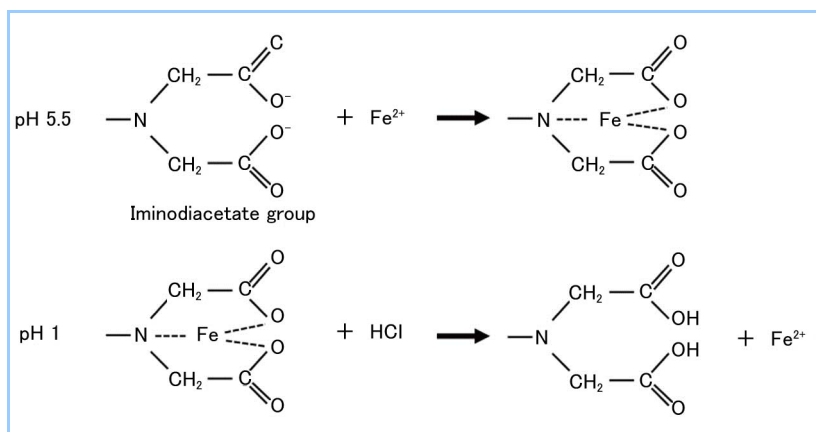


Figure 3 Schematic diagram of iron collection using a chelate filter

5. Comparison with conventional method

(1) Analysis time period

Figure 4 compares the analysis flow between the heating concentration method and the filter concentration method. The heating concentration method takes approximately 180 minutes to concentrate 300 mL of sample (six-times concentrated) using a hot plate. On the other hand, the filter concentration method takes 70 minutes in total (20 minutes for filter concentration and 50 minutes for heating concentration) to concentrate 2000 mL of sample (forty-times concentrated). In this way, the filter concentration method can complete concentration in about 1/3 of the time in the case of heating concentration. In addition, the filter concentration method has the advantage where the sampling amount can be increased arbitrarily within the iron collection capacity of the filter regardless of the sampling amount.

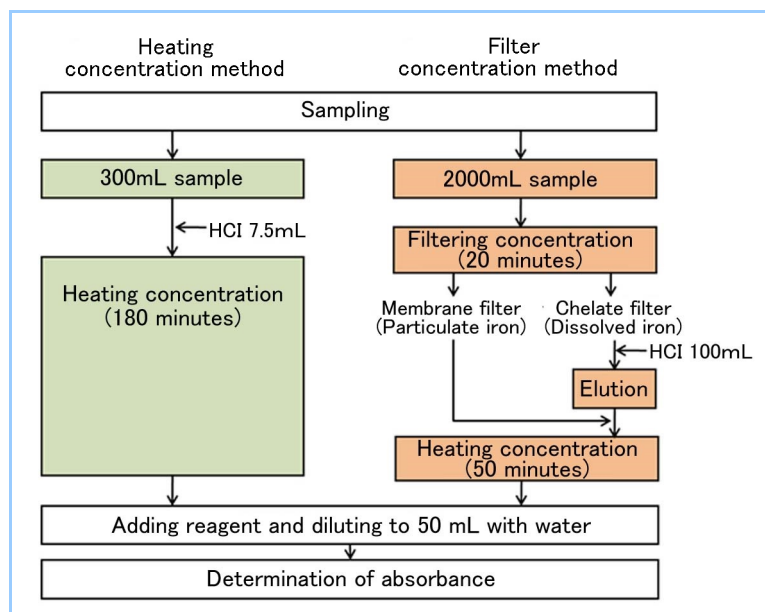


Figure 4 Comparison of analysis flow between heating concentration method and filter concentration method

(2) Analysis accuracy

Table 3 shows the results of quantitative determination using a standard iron solution. The recovery rate was favorably within the range of 100+/-5% excluding samples of 4 $\mu\text{g/L}$ or less recovered by the heating concentration method. **Table 4** shows the average value, the standard deviation (σ) and the coefficient of variation (C.V.) obtained as a result of five repeated analyses of distilled water. The lower limit of the quantitative determination calculated based on 10σ is 4.1 $\mu\text{g/L}$ for the heat concentration method and 0.8 $\mu\text{g/L}$ for the filter concentration method. This indicates that the use of the filter concentration method allows higher-accuracy analysis in comparison with the heating concentration method.

Table 3 Evaluation of recovery rate using standard iron solution

Method	Density	Recovery rate	C.V.
	$\mu\text{g/L}$	%	%
Heating concentration method	2	116.6	19.1
	4	110.4	10.1
	6	104.8	6.6
	8	103.2	6.3
	10	99.7	2.9
Filter concentration method	2	100.7	8.1
	4	101.7	3.5
	6	99.6	2.3
	8	97.4	7.8
	10	97.2	1.9

C.V.: Coefficient of variation

Table 4 Lower limit of quantitative determination obtained by repeated analysis (n=5) of distilled water

Concentration method	Unit	Heating concentration method	Filter concentration method
Iron density average value	$\mu\text{g/L}$	1	0.75
Standard deviation (σ)	—	0.41	0.08
Coefficient of variation (C.V.)	%	39	11
Density lower limit of quantitative determination (10σ)	$\mu\text{g/L}$	4.1	0.8

(3) Application to real sample

The developed filter concentration method was applied to an ultra-supercritical thermal power plant that uses OT. **Figure 5** shows a schematic system diagram of the plant. **Table 5** shows the results of analysis of time variation in the iron concentration in feedwater performed using the heating concentration method and the filter concentration method, respectively. The sampling was performed in a period when the load was in a static state. The sampling was performed from the sampling rack of each point in the system when the load was in a static state after three hours or more from the moment the load became static, and the iron concentration of each point in the system water at the same time was determined. At the economizer inlet, which was the main evaluation target, the sample amount used for the filter concentration method was 2000 mL. At the low-pressure heater drain and the high-pressure heater drain, analysis was performed using the heating concentration method only. Because iron concentration in the feedwater varies depending on the boiler state, samples collected at different times were handled as separate samples.

The quantitative values of certain areas, which could not be obtained by the heating concentration method, could be obtained by the filter concentration method. Thus the mass balance evaluation of the system became possible.

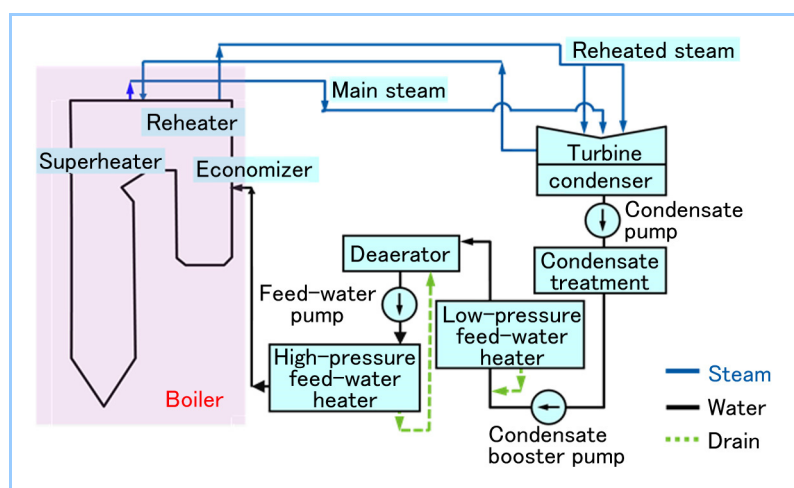


Figure 5 Schematic diagram of water and steam system in ultra-supercritical thermal power plants

Table 5 Time variation in iron concentration in ultra-supercritical thermal power plant

Sampling location	Concentration method	Sample amount (mL)	Iron density ($\mu\text{g/L}$)				
			9:00	11:00	13:00	15:00	17:00
Condensate pump outlet	Heating	300	5.0	N/A	N/A	N/A	N/A
	Filter	1000	4.9	3.6	3.7	3.7	4.9
Condensate booster pump outlet	Heating	300	N/A	N/A	N/A	N/A	N/A
	Filter	1000	2.5	1.4	1.3	1.4	2.7
Deaerator inlet	Heating	300	N/A	5.1	4.5	4.2	N/A
	Filter	1000	6.2	4.7	4.4	4.8	4.6
Deaerator outlet	Heating	300	N/A	4.1	N/A	N/A	N/A
	Filter	1000	5.2	4.1	3.2	4.0	4.5
Economizer inlet	Heating	300	N/A	N/A	N/A	N/A	N/A
	Filter	2000	2.7	2.4	1.8	1.8	2.0
Main steam	Heating	300	N/A	N/A	N/A	N/A	N/A
	Filter	1000	1.3	N/A	1.1	1.2	1.3
Low-pressure feedwater heater drain	Heating	300	29	24	21	21	18
High-pressure feedwater heater drain	Heating	300	15	15	15	14	15

6. Countermeasure for powder scale

For reduction in the risk of damage to heat transfer tubes caused by the adhesion of powder scale, it is necessary to reduce the iron amount brought to the boiler. Methods for this include the adjustment of the feedwater quality (change in pH), the installation of an iron removal high-temperature filter (**Figure 6**) in the low-pressure feedwater heater drain system that is assumed as the main iron generation source, etc. For the evaluation of the risk of powder scale deposition, on the other hand, it is necessary to perform daily management of the mass balance of iron in the plant system in order to understand the elution and deposition behaviors of iron, and therefore evaluation using the filter concentration method described above is important.

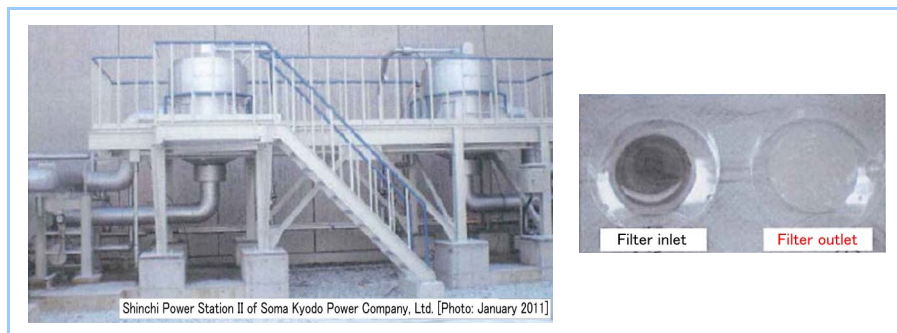


Figure 6 External view of iron removal device for low-pressure feedwater heater drain system

7. Conclusion

As a result of the application of the filter concentration method that simultaneously uses a membrane filter and a chelate filter, as an analysis method for minute amounts of iron, instead of the conventional heating concentration and TPTZ method and the ICP-MS method for the iron concentration analysis of boiler feedwater, it was confirmed that the filter concentration method can more accurately analyze minute amounts of 2 $\mu\text{g/L}$ of iron or less by the application of the filter concentration method, and also that the filter concentration method allows a reduction in analysis time and is suitable for operational sites.

It is believed that the optimization of analysis conditions and improvement in operability will allow even workers that are unfamiliar with the analysis method to minimize the error and perform the analysis of minute amounts of iron accurately, because the analysis of minute amounts of a substance is greatly influenced by contamination. In the future, we will apply this method to the analysis of minute amounts of iron in various power plants in order to continue to accumulate and evaluate data.

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