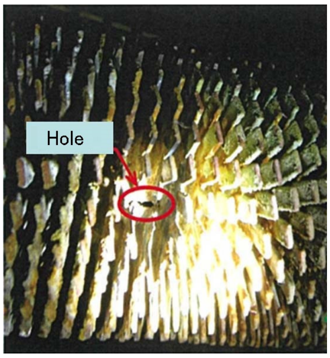
Advanced Water Treatment Technologies (High-AVT) for HRSG Corrosion Control corresponding to New JIS B8223 (Japanese Industrial Standards)



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In October 2015, JIS B8223 (Boiler feedwater and boiler water quality standards) was revised and issued, and for the Heat Recovery Steam Generator (HRSG) of combined cycle plant, the operational standards for High-AVT (high pH) water treatment that Mitsubishi Hitachi Power Systems, Ltd. (MHPS) has applied at actual plants since 2001 were adopted. High-AVT water treatment has been increasingly applied as a measure against Flow Accelerated Corrosion and phosphate corrosion problems both inside and outside Japan and is useful as an alternative technology to hydrazine, the carcinogenicity of which has been pointed out. In addition, from an economic point of view, the advantages of the adoption of High-AVT water treatment, such as the shortening of plant start-up time and the reduction of operating costs, have been verified.

1. Introduction

HRSG installed at combined cycle plants uses the flue gas from the gas turbine as a heat source. Therefore, the heat load is small and the water quality control was considered to be easy. At some plants, however, Flow Accelerated Corrosion (FAC) and phosphate corrosion events have occurred. As countermeasures, MHPS set the pH of feedwater at a high pH exceeding the conventional JIS standards (upper limit of 9.7) and has applied phosphate-free High-AVT water treatment to actual plants since 2001. The adoption of High-AVT water treatment has been promoted at domestic commercial thermal power plants and its operational performance has been recognized. As a result, it was adopted as a standard in JIS B8223, which was revised and issued in October 2015.

2. Revision of JIS B8223-2015 (Boiler feedwater and boiler water quality standards)

The corrosion-related problems at domestic thermal power plants and the history of water treatment are shown in **Table 1**. In the 1950s, subcritical pressure drum type boilers (17 MPa class) were constructed, and operations started with the use of alkali treatment. About half a year after the start of operations, alkali corrosion problems of water-wall tubes frequently occurred, and improvement of the feedwater/boiler water treatment technology was urgently required. The water treatment technology and the boiler chemical cleaning technology were introduced from overseas, and the "Technical Committee for Boiler Feedwater and Boiler Water Quality," which was set up in the Japanese Industrial Standards Committee, deliberated about the water quality standards. As a result, JIS B8223 "Boiler feedwater and boiler water quality standards" was established in February 1961. The water quality required for boilers/turbines at thermal power plants (JIS B8223) has been periodically revised with operational performances, new technologies, equipment nonconformities, etc., being reflected, and MHPS has also taken part in the revision committee.

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Table 1 Identified problems at thermal power plants and the history of water treatment

Year	Major corrosion-related problems	Events for water treatment
1940	- Pitting and brittleness of steam generating tubes - Cracks in turbine components	
1950	- Alkali corrosion in steam generating tubes - Ammonia corrosion in aluminum or brass condenser tubes	- Technological introduction from USA - PT/AVT application - Boiler chemical cleaning application
1960	- Increase of pressure loss and overheating due to steam-generating tube scale deposition - Feedwater heater inlet attack	- JIS criteria (Feb. 1, 1961) - Oxygenated treatment application (Germany and Russia)
1970	- Detachment of deposited scale from the superheater or reheater - Corrosion fatigue	- Adoption of condensate demineralizer
1980	- Feedwater heater drain attack - Increase of boiler pressure loss due to rippled scale generation	- Start of commercial operation of the combined cycle plant - The oxygenation treatment criteria set in JIS (1989)
1990		- Realization of commercial application of oxygenated treatment
2000	- FAC (Flow Accelerated Corrosion)	- Viability assessment of High-AVT for nuclear power plants (as a measure against FAC)

In JIS B8223: 2015, the following revisions were mainly made:

(1) The upper limit value of the pH of feedwater based on the performance at actual plants was reviewed. (**Table 2**) (pH9.7⇒10.3)

(2) The hydrazine-free water treatment method was set. (**Table 3**) (Treatment of volatile substances in oxidized form, low-oxidized form)

(3) The lower limit value for phosphate ion concentration was eliminated. (As a countermeasure against excessive injection, the performance at actual plants was reflected.)

(4) The iron concentration during the operation of oxygenated treatment (OT) (Measure against deposition of powder scale)

(5) The conformity to international standards was considered. (Oxygenated treatment: CWT ⇒OT, the name of acid electrical conductivity adopted, etc.)

Table 2 Control items and control values of water conditioning for feedwater of heat recovery boiler for power plants (excerpt)

Division		All-volatile treatment		
	Treatment method	All-volatile treatment		
	Reducing agent	yes	no *1	
	Redox properties	Reducing [AVT (R)]	Low oxidizing *1 [AVT (LO)]	Oxidizing *1 [AVT (O)]
Feedwater	pH (at 25°C)	8.5 to 10.3 *2	8.5 to 10.3 *2	8.5 to 10.3 *2
	Acid electrical conductivity (at 25°C) mS/m (μ S/cm)	0.05 max. (0.5 max.)	0.05 max. (0.5 max.)	0.02 max. (0.2 max.)
	Dissolved oxygen O : μ g/l	7 or under	Under 5	5 to 20
	Iron Fe : μ g/l	20 max.	20 max.	10 max.
	Copper Cu : μ g/l	5 max.	5 max.	5 max.
	Hydrazine N_2H_4 : μ g/l	10 min.	—	—

*1 Hydrazine (deoxidizer)-free all-volatile treatment method is set.
*2 The upper limit value of the pH of feedwater is changed 9.7⇒10.3. (High-AVT is applicable for water treatment.)

Table 3 Comparison of AVT (R), AVT (LO), AVT (O) and oxygenated treatment (OT)

Water treatment	Water conditions	Reducing agent	Dissolved oxygen μ g/L	Form of iron oxides	Note
AVT (R)	Reducing	Used	7 or under	Fe_3O_4	—
AVT (LO)	Low oxidizing	Not used	Under 5	When pH value and the concentration of dissolved oxygen are low, only Fe_3O_4 film is formed in many cases. When pH value and the concentration of dissolved oxygen are high, very thin Fe_2O_3 film is formed on Fe_3O_4 film.	If hydrazine injection is suspended in power plants in Japan, such water conditioning state occurs.
AVT (O)	Oxidizing	Not used	5 to under 20	Thin Fe_2O_3 film is formed on Fe_3O_4 film.	If hydrazine injection is suspended in power plants in other countries, such water conditioning state occurs.
Informative OT (oxygenated treatment)	Oxidizing	Not used	20 to 200	In feedwater and boiler whole systems, stable and dense Fe_2O_3 film is formed on Fe_3O_4 film.	Oxygen injection control facility is required.

R: Reducing, LO: Low Oxidizing, O: Oxidizing

In the conventional all-volatile treatment, dissolved oxygen is chemically removed using a deoxidizer such as hydrazine to inhibit corrosion in the reducing atmosphere. As shown in Table 3, by this revision of JIS, instead of the term AVT, AVT (R) (Reducing condition) was adopted in keeping with the overseas standards such as Germany's VGB.

In addition, as a hydrazine-free water treatment by which a low concentration of dissolved oxygen can be maintained, AVT (O) (Oxidizing condition), which is in conformity with overseas standards, was newly added. In many cases at thermal power plants overseas where the injection of hydrazine has stopped, the concentration of dissolved oxygen in feedwater becomes 5 µg/l or more. Therefore, the water condition of AVT (O) is set at the concentration of dissolved oxygen of 5 to under 20 µg/l. It has been reported that in AVT (O), hematite (Fe_2O_3) film is formed, which has an effect in inhibiting FAC.

It has been verified that the water condition in Japan is such that the concentration of dissolved oxygen in feedwater is 5µg/l or lower in many cases depending on the difference in performance of the condenser, deaerator, etc., and hematite (Fe_2O_3) film is not formed, which is different from the water condition of AVT (O) under overseas standards. Therefore, AVT (LO) (Low oxidizing condition) is set as a new water condition.

3. Application of High-AVT (LO) water treatment to HRSG

Table 4 shows a comparison of the conventional phosphate treatment and the High-AVT water treatment. It has been verified that at a high pH, the tube thinning rate by FAC is reduced, and the inhibition effect has been expected. **Figure 1** presents an example of FAC, and **Figure 2** provides the relationship between pH and the thinning rate of FAC.

Table 4 Comparison of phosphate treatment (PT) and High-AVT (LO) water treatment

	Chemical used			pH of feedwater
	Feedwater		Boiler water	
	Ammonia	Hydrazine	Disodium phosphate	
Feed water: AVT (R) Boiler water: PT	Used	Used	Used	8.5 to 9.7
Feed water/Boiler water: High-AVT (LO)	Used	Not used	Need not be used	9.8 to 10.3

* In cases where PT is replaced with High-AVT, it is recommended that chemical cleaning should be performed at the time of replacement to remove risks due to phosphorus remaining in scale.

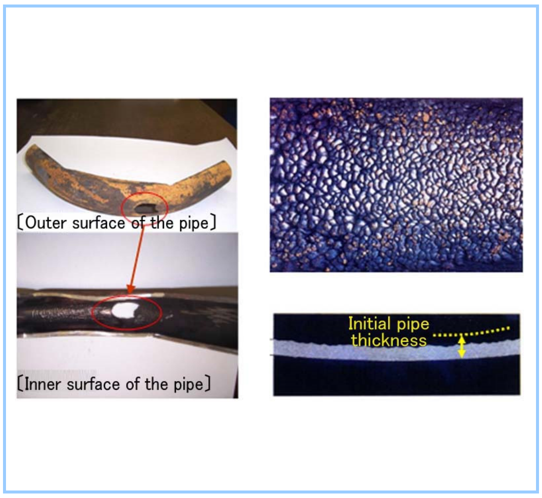

Figure 1 Example of FAC

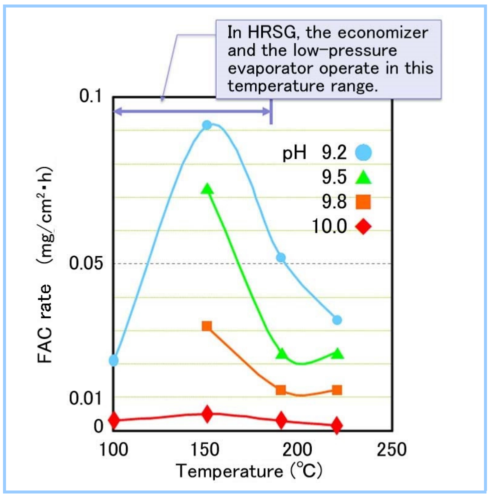

Figure 2 Relationship between pH and FAC rate

If a change in electrical conductivity of a boiler due to a change in the concentration of phosphate (hide-out/hide-out return phenomena) shown in **Figure 3** is observed, phosphate may be excessively injected and corrosion problems such as the thinning of pipe walls or leakage are highly likely to occur.

Figure 4 shows one example of the labelling on a hydrazine tank under GHS (Globally Harmonized System of Classification and Labelling of Chemicals). It has been pointed out that hydrazine is carcinogenetic, and the Global Plan of Action in the Strategic Approach to

International Chemical Management indicates "Toward 2016-2020, alternative substances to carcinogenic or mutagenic substances (hydrazine, etc.) shall be identified and used." Hydrazine-free low oxidizing water treatment High-AVT (LO) is an effective option for eliminating the use of hydrazine.

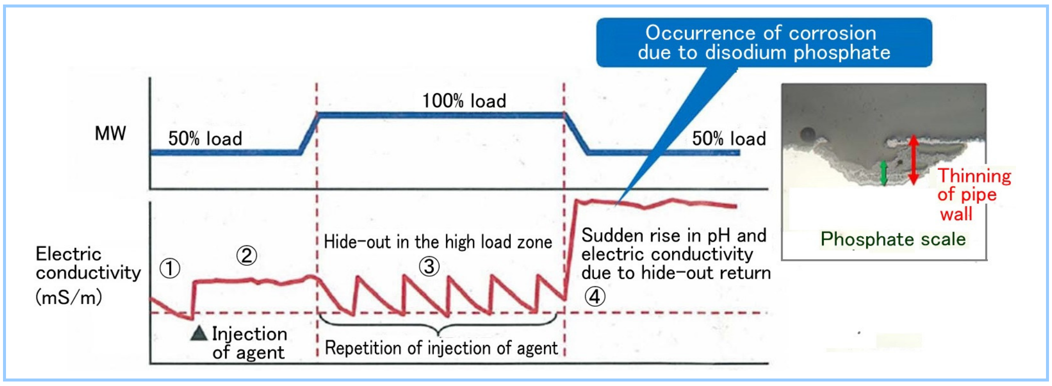

Figure 3 Example of corrosion caused by phosphate hide-out/hide-out return phenomena

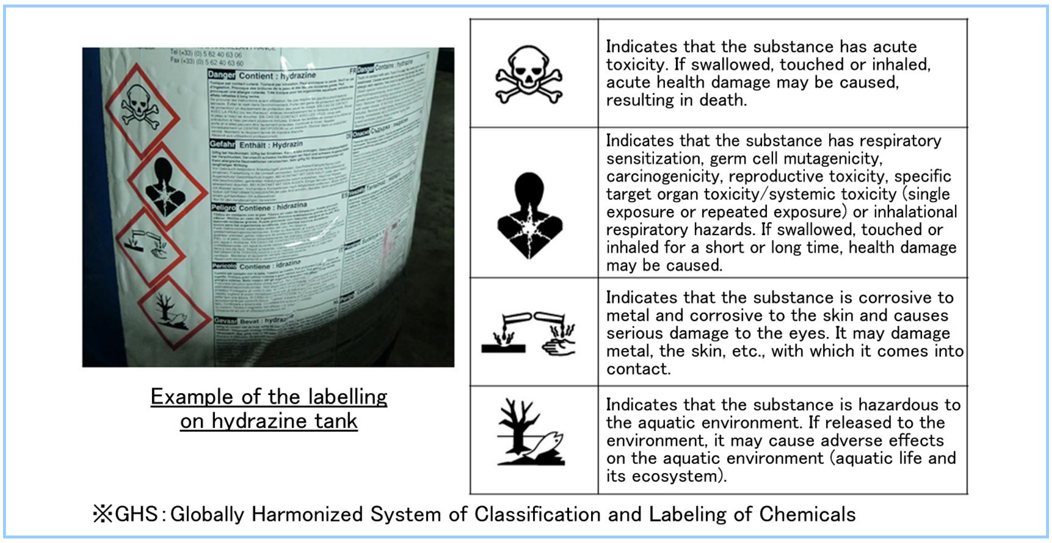

Figure 4 GHS labelling for hydrazine tank

Currently, for long-term storage, high-concentration hydrazine water is added after the boiler water is blown off, and the hydrazine water is blown off before start-up. In High-AVT water treatment, occurrence of corrosion during storage at a high pH can be inhibited. Therefore, as shown in **Table 5**, the boiler water can be stored under the same water condition as in operation, and the start-up time can be shortened and the usage of pure water used and the drain treatment cost can be reduced.

Table 5 Shortening of stop/start-up process by introduction of High-AVT (LO)

Water treatment	Processes					Comparative operation time and volume of pure water used
	Blow down	Filling water for layup	Preservation	Blow down of layup water	Water filling for start-up	
AVT	Boiler	Hydrazine				▪Operation time: About 420 min ▪Volume of pure water used: About 500 ton
High-AVT	Boiler	To be maintained as under the conditions of water quality during operation (i.e., no replacement of water)				▪Operation time: 0 min ▪Volume of pure water used: 0 ton

* For one unit of 501F-class HRSG

* In High-AVT operation, the boiler water can be stored under the same water condition as in operation, and the simplification of stop/start-up process and the reduction of the amount of pure water used can be expected.

4. Steps for introducing High-AVT (LO) water treatment to HRSG

Figure 5 presents the steps for introducing High-AVT (LO) water treatment. The water condition of feedwater is pH9.8 or higher, and therefore, after the steps of (1) prior study about the water control procedure, (2) hydrazine stop test, (3) pH change test, and (4) modification of agent injection equipment/control logic based on (3) pH change test, the operation of High-AVT (LO) water treatment can be started. For the investigation of the thinning of pipe wall due to corrosion caused by phosphate treatment in the past, the tube-inserted ECT (Eddy Current Testing) shown in **Figure 6** is recommended.

Even if thinning is minor, it is considered to be necessary to remove scale including phosphate on the tube inner surface at the time of conversion to High-AVT (LO) water treatment, to avoid the development of corrosion in the future. **Figure 7** indicates one example of the results of the scale dissolving test by neutral/unheated (low-temperature) chemical cleaning which was developed as a scale removal method for HRSG fin tubes, which dissipate a large amount of heat (and therefore, make it difficult to maintain the cleaning temperature).

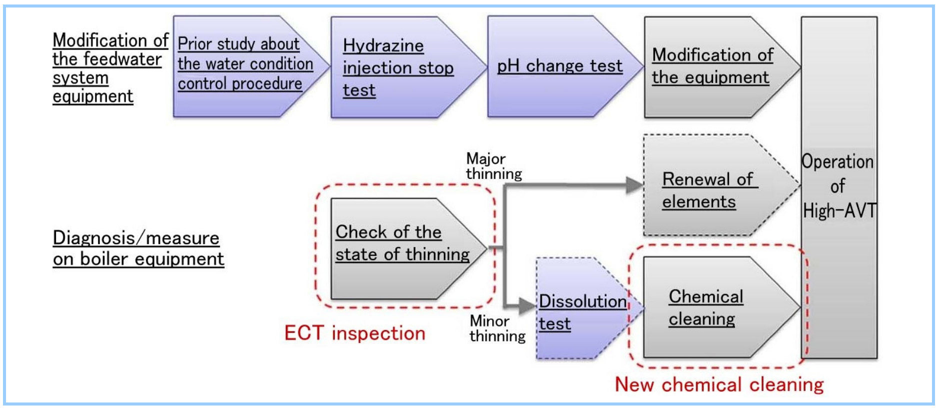

Figure 5 Steps for introducing High-AVT (LO) water treatment

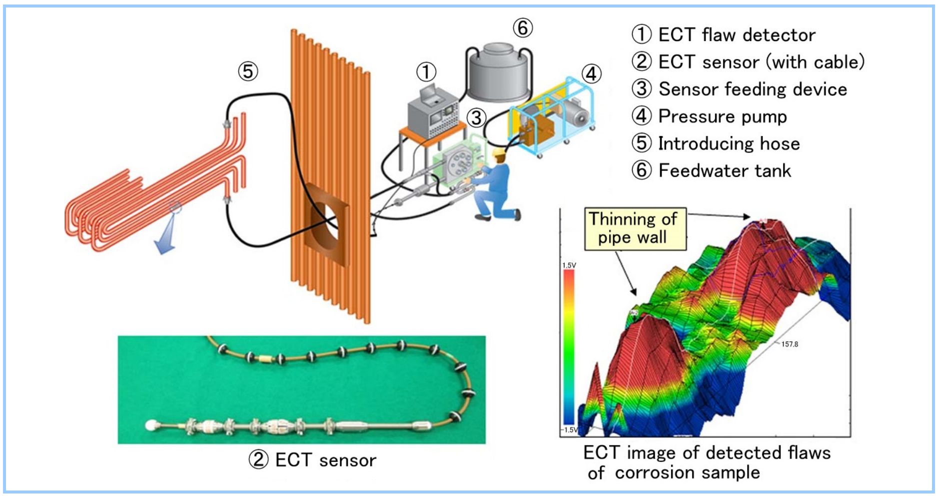

Figure 6 Tube-inserted ECT (Eddy Current Testing) system

(1) Test condition (new low-temperature chemical cleaning)

Item	Condition
Sample	HRSG steam generating tube (high-pressure evaporator)
Test liquid	Neutral rust removal (MK-04), reducing agent, corrosion inhibitor
Test temperature	Room temperature (25°C)
Cleaning method	Still standing + swing (every 12 hrs.)
Testing hours	96 hrs. (four days)

(2) Test results (outer appearance and cross section of sample tube)

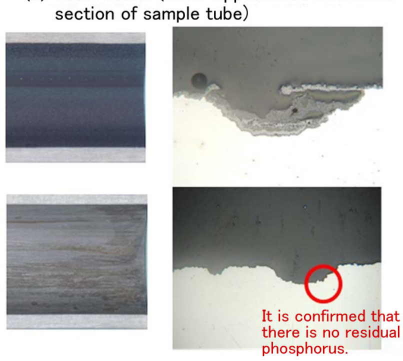

Figure 7 Results of the scale dissolving test of HRSG phosphate corrosion part

5. Conclusion

The actual performance of High-AVT water treatment, which is a water treatment method for HRSG at combined cycle plants, has been well-received, and High-AVT water treatment was adopted as the standard in JIS B8223 which was revised and issued in October 2015. It has been verified that its high-pH operation has the effect of reducing FAC and phosphate corrosion and also allows hydrazine-free operation/storage. In addition, from economic points of view such as the shortening of start-up time and the reduction of pure water/amount of waste water, advantages in adopting High-AVT water treatment can also be expected, and the rate of adoption is increasing at domestic thermal power plants.

In introducing High-AVT water treatment, it is recommended that the states of the occurrence of corrosion thinning caused by phosphate treatment in the past should be investigated, and scale on the inner surface of tubes, which will cause the development of corrosion in the future, should be removed (by chemical cleaning).

References

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