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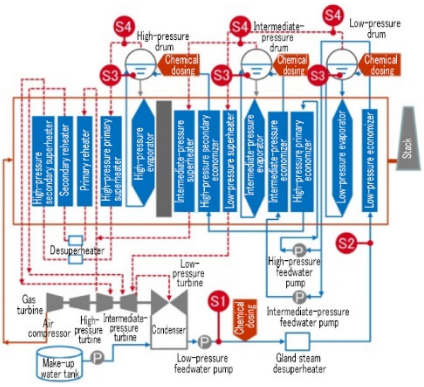
Current Status and New Technologies of Water Treatment in Thermal Power Plants (Non-Toxic Oxygen Scavenger, Japan Industrial Standard Revision, Water Quality Diagnosis)



HIROSHI AKAMINE[*1] SHINGO TAMURA[*2]

MITSURU NAKAMOTO[*3] SENICHI TSUBAKIZAKI[*4]

YUTA NAKATSUCHI[*5] TETSUYA SAWATSUBASHI[*5]

Plant water treatment for thermal power plants is conducted to prevent problems such as corrosion and scale formation/deposition in the boiler and turbine systems, as well as carryover to the turbine. The required water quality for boilers and turbines is stipulated by the Japanese Industrial Standard (JIS) B8223 and this standard is regularly amended based on new knowledge. Mitsubishi Power, Ltd. (Mitsubishi Power) has been participating in this amendment. Mitsubishi Power has also developed the "TOMONI Water Quality Diagnosis" system as an initiative contributing to the early detection of serious problems signs and the improvement of plant efficiency and is expanding its application to actual equipment.

1. Introduction

Plant water treatment for thermal power plants is conducted to prevent problems such as corrosion and scale formation/deposition in the boiler and turbine systems, as well as carryover to the turbine. The Mechanical Engineering Division for “Specialists Group for Boiler Feedwater and Boiler Water” established in the Japanese Industrial Standards Committee deliberated on water quality standards, and in February 1961, JIS B8223 “Conditioning for boiler feedwater and boiler water” was established. The water quality required for boilers and turbines in thermal power plants stipulated by JIS B8223 is amended regularly based on operational results, technological innovation, equipment nonconformities, etc. We have also been participating in the JIS revision(1).

A water quality standard that eliminates the use of hydrazine, which has been restricted in use overseas and carries concerns about carcinogenicity, was established in 2015 in the JIS revision, and has become widely applied in Japan. In addition, High-AVT (LO) water treatment, which we have applied to Japanese and overseas plants as a measure against FAC (flow accelerated corrosion), phosphate corrosion and scale adhesion to control valves, feedwater heaters, etc., has also been adopted by JIS and its application is currently being expanded.

In recent years, it has become apparent that the cause of water quality abnormalities exists not only in the main system, but also in the make-up water (pure water) or raw water supplied to the plant, and a method to detect signs of serious problems at an early stage using a wide range of water quality controls is required. Against such a background, we have developed the "plant water quality monitoring and diagnosis system (TOMONI Water Quality Diagnosis)" that has a wider water quality monitoring range. The TOMONI water quality diagnosis is expected to not only contribute to the maintenance of the long-term integrity and performance of the plant, but also to bring about economic benefits from its adoption, such as a reduction of the environmental burden

*1 Nagasaki Plant Engineering Department, Project Management Division, Mitsubishi Power, Ltd.
*2 Hitachi Power Systems Service Department, Power Systems Service Headquarters, Mitsubishi Power, Ltd.
*3 Chief Staff Manager, Kure Plant Engineering Department, Project Management Division, Mitsubishi Power, Ltd.
*4 Chief Staff Manager, Nagasaki Power Systems Service Department, Power Systems Service Headquarters, Mitsubishi Power, Ltd.
*5 Chemical Research Department, Research & Innovation Center, Mitsubishi Heavy Industries, Ltd.

by reducing the amount of chemical usage and wastewater, shortening of the plant start-up time, lowering of operating costs, etc.

2. Water quality control of thermal power plants[2]

A thermal power plant consists of a water-steam cycle, as shown in **Figure 1**, and has the important issue of dealing with corrosion problems that are caused between water-steam and plant component materials. Corrosion products generated in the condensate and feedwater systems are brought into the boiler system and are deposited and accumulated as scale, causing various types of corrosion. In the boiler system, impurities in the boiler water are carried over into the steam and brought into the turbine system. Then in the turbine system, they are deposited and concentrated on the rotor blades, etc., causing a decrease in turbine efficiency and corrosion damage such as stress corrosion cracking, corrosion fatigue, etc. In the steam system, when scale generated by steam oxidation grows thick and peels off, it scatters in the turbine system and causes erosion.

In recent years, there has been a trend toward dealing with the overall environmental embrittlement problems of materials such as corrosion, stress corrosion cracking, flow-accelerated corrosion, etc., by having the person in charge of chemical management of the power plant take responsibility for the entire water-steam cycle of the condensate system, feedwater system, boiler system, steam system and turbine system, and properly manage the water quality.

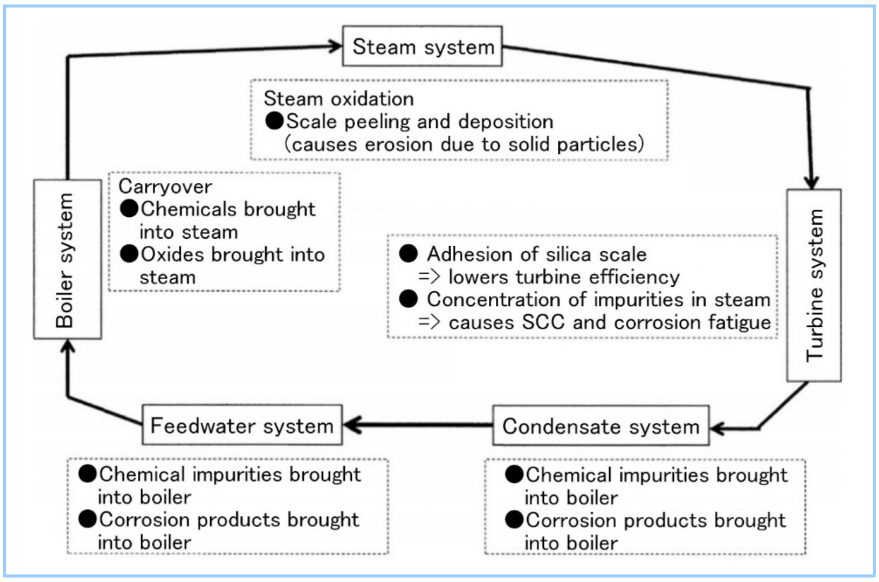


Figure 1 Concept of water-steam cycle

3. New technology for water treatment of thermal power plants

Table 1 lists the main feedwater and boiler water treatment methods in thermal power plants. The water treatment methods used include AVT (all volatile treatment) and OT (oxygen treatment) for feedwater treatment, and AVT, PT (phosphate treatment) and OT for boiler water treatment. We are developing new technologies for water treatment methods and diagnostic systems in order to deal with problems caused by water, higher temperature and pressure of the boiler and environmental measures such as the elimination of hydrazine, as well as an increase in plant load fluctuations and start/stop behaviors due to the introduction of renewable energy (water quality fluctuations).

Table 1 Major treatment methods for boiler feedwater and boiler water in thermal power plants

<table>
<tr><th>Power generation system</th><th>Pressure classification</th><th>Boiler type</th><th>Feedwater treatment method</th><th>Boiler water treatment method</th></tr>
<tr><td rowspan="4">Steam power generation</td><td rowspan="2">Subcritical pressure</td><td rowspan="2">Circulation boiler</td><td rowspan="2">All volatile treatment</td><td>All volatile treatment</td></tr>
<tr><td>Phosphate treatment</td></tr>
<tr><td>Supercritical pressure</td><td rowspan="2">Once-through boiler</td><td colspan="2">All volatile treatment</td></tr>
<tr><td>Ultra-supercritical pressure</td><td colspan="2">Oxygen treatment</td></tr>
<tr><td rowspan="3">Combined cycle power generation</td><td rowspan="2">Subcritical pressure</td><td rowspan="2">Waste heat recovery boiler (circulation type)</td><td rowspan="2">All volatile treatment</td><td>All volatile treatment</td></tr>
<tr><td>Phosphate treatment</td></tr>
<tr><td>Supercritical pressure</td><td>Waste heat recovery boiler (once-through type)</td><td colspan="2">All volatile treatment</td></tr>
</table>

3.1 Elimination of hydrazine (JIS B 8223 revision)[3]

Figure 2 is an example of GHS (Globally Harmonized System of Classification and Labeling of Chemicals) labeling of hydrazine tanks. Hydrazine has been indicated as carcinogenic and it is being discontinued and replaced with alternative technologies progressively mainly in new overseas projects.

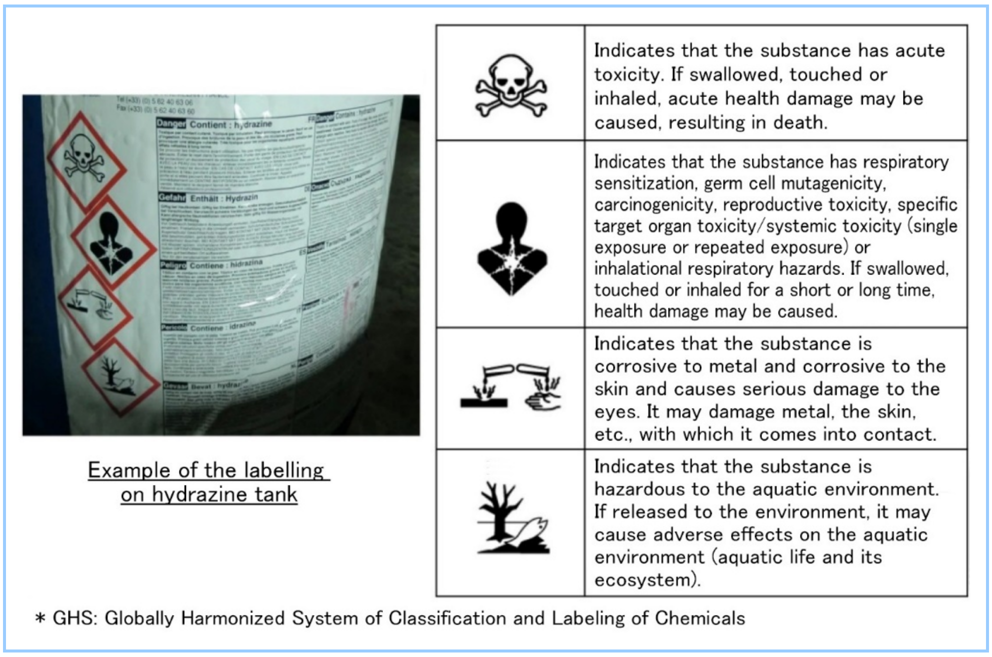


Figure 2 GHS labelling for hydrazine tank

Table 2 compares AVT (R), AVT (LO), AVT (O) and OT (JIS B 8223). The JIS revision in 2015 changed the conventional AVT to AVT (R) (Reducing condition) (R) following overseas standards, and additionally stipulated AVT (LO) and AVT (O), which are water treatment methods using no reducing agent (hydrazine, etc.). Hydrazine-free low-oxidizing-type AVT (LO), oxidizing-type AVT (O) and OT are effective options for the elimination of hydrazine.

Table 2 Comparison of AVT (R), AVT (LO), AVT (O) and OT (JIS B8223)

Water treatment	Water conditions	Reducing agent	Dissolved oxygen concentration μ g/L	Form of iron oxides	Note
AVT (R)	Reducing	Used	7 or under	Fe_3O_4	-
AVT (LO)	Low oxidizing	Not used	7 or under	When the pH value and concentration of dissolved oxygen are low, only Fe_3O_4 film is formed in many cases. When the pH value and 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 Japan, this water quality becomes AVT (LO).
AVT (O)	Oxidizing	Not used	Higher than 7 and 20 or under	Thin Fe_2O_3 film is formed on Fe_3O_4 film.	If hydrazine injection is suspended in power plants in overseas countries, this quality becomes AVT (O).
Informative OT (oxygen treatment)	Oxidizing	Not used	Higher than 20 and 200 or under	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

3.2 OT (oxygen treatment) and high temperature filter for iron removal (once -through boiler plant)[4]

Figure 3 illustrates the difference in scale on the steam generating tube inner surface between AVT and OT for a once-through boiler. The effects of applying OT include (1) a reduction of the chemical cleaning frequency due to the suppression of the scale growth rate, (2) a reduction of the increase in the boiler differential pressure due to the suppression of liquid scale generation, (3) a reduction of scale adhesion to components and (4) the elimination of hydrazine. In Japan, as of October 2020, OT has been applied to 56 plants.

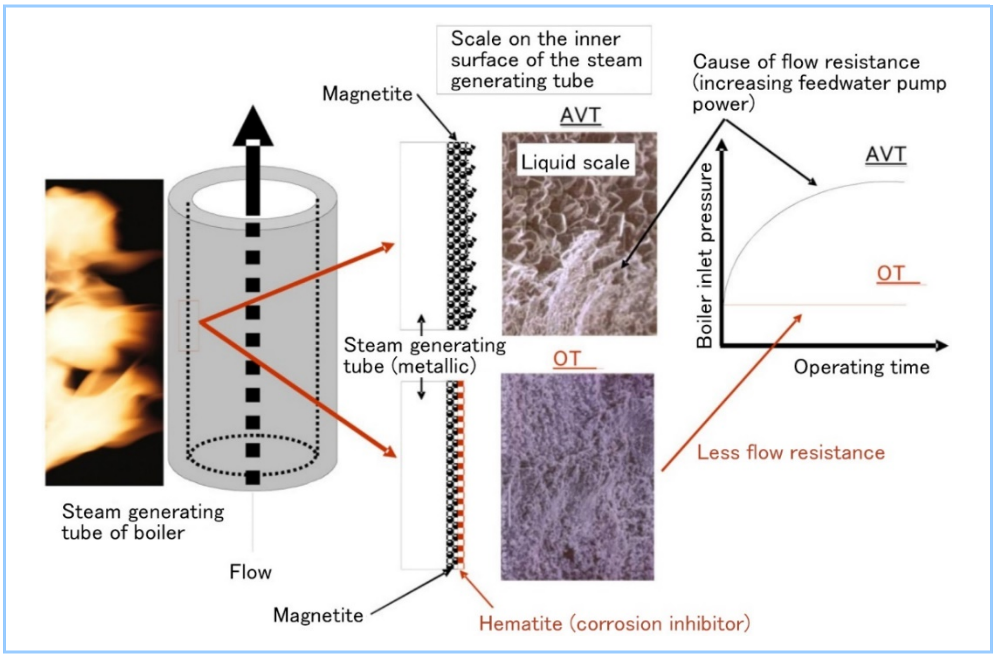


Figure 3 Difference of scale on the inner surface of boiler steam generating tube between AVT (all volatile treatment) and OT (oxygen treatment)

In recent years, in some plants to which OT has been applied, an increase in the amount of iron brought into the boiler and the adhesion of small-particle porous hematite scale (powder scale) to the inner surface of the boiler furnace wall tube have been observed, which are factors in the temperature increase of the furnace wall tube metal. In order to reduce powder scale, it is considered essential to reduce the iron concentration in the drain system of the low-pressure feedwater heater, which is presumed to be its main generation source. We optimized the water quality and developed an iron removal device (**Figure 4**) using a high-temperature filter. As a result of applying these technologies to actual plants, good results have been obtained.

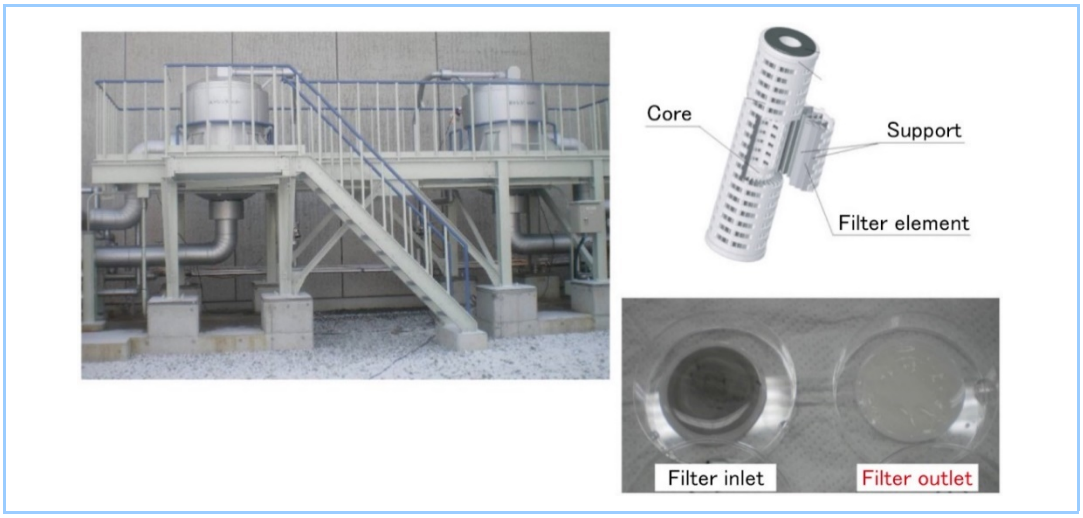


Figure 4 External view of iron removal device in low-pressure feedwater heater drain system

3.3 High-AVT (LO) (GTCC)[5]

Table 3 compares the conventional GTCC plant water treatment method (AVT for feedwater and PT for boiler water) with High-AVT (LO). By setting the pH of the feedwater higher than before (max. 9.7), the pH of the boiler water can be maintained without feeding phosphate. Due to the use of a water treatment method that does not use hydrazine (AVT (LO)), ammonia can be treated independently and hydrazine feeding equipment can be omitted. In addition, by making the water quality conditions during operation and storage the same, it is possible to omit the blow and water filling steps for storage and shorten the plant start-up time.

Table 3 Comparison of PT (phosphate treatment) and High-AVT (LO)

	Chemical used			pH of Feedwater
	Feedwater		Boiler water	
	Ammonia	Hydrazine	Sodium phosphate	
AVT (R) + PT	Used	Used	Used	8.5 to 9.7
High-AVT (LO)	Used	Not used	Not used	9.8 to 10.3

Benefits of introducing High-AVT (LO)
- No sodium phosphate used: Phosphate corrosion does not occur.
- Storable under water quality conditions for operation: Easy storage and simple start-up processes
- No hydrazine used: Little impact on humans and the environment
- AVT operation at high pH (9.8 to 10.3): Suppression of FAC generation

GTCC plants have experienced tube wall thinning due to FAC (flow accelerated corrosion) in the HRSG economizer. In a system where the tendency of wall thinning was observed, the material was changed to low alloy steel, which has better FAC resistance than carbon steel, as a countermeasure against tube wall thinning. The effect of suppressing tube wall thinning was obtained also by changing the water treatment conditions (applying High-AVT). **Figure 5** presents an external view and the installation of the heat-resistant thin film UT sensor used for our developed tube wall thinning monitoring. **Figure 6** gives an example of the tube wall thinning preventive effect after applying High-AVT (R) observed using the thin film UT sensor. It was found that the tube wall thinning rate after applying High-AVT (R) was reduced to about 50% or less compared with that before application. By using the thin film UT, monitoring tube wall thinning during operation of the unit was made possible, and the preventive effect of tube wall thinning after applying High-AVT (R) could be directly confirmed. (In this case, the FAC inhibitory effect of pH adjustment was confirmed and hydrazine was used without change.)

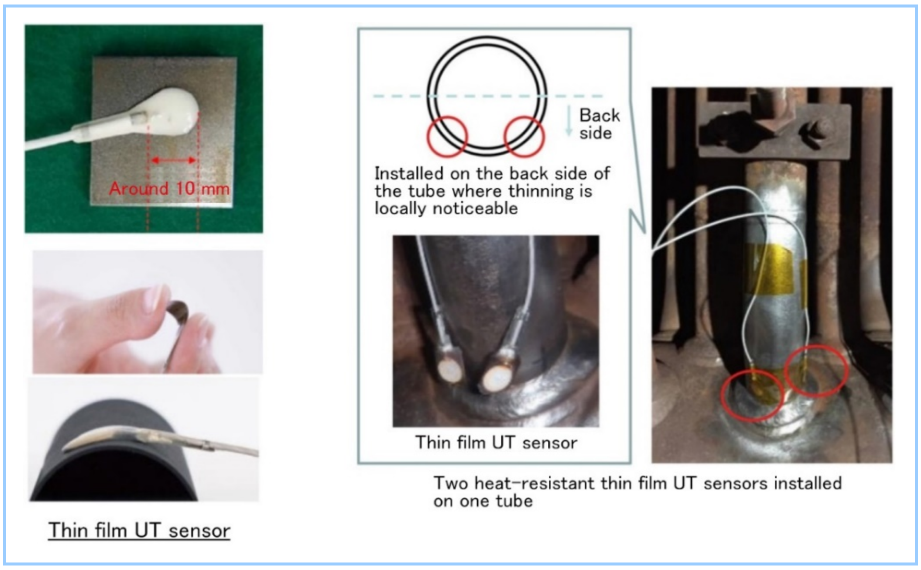


Figure 5　External view and installation of heat-resistant thin film UT sensor

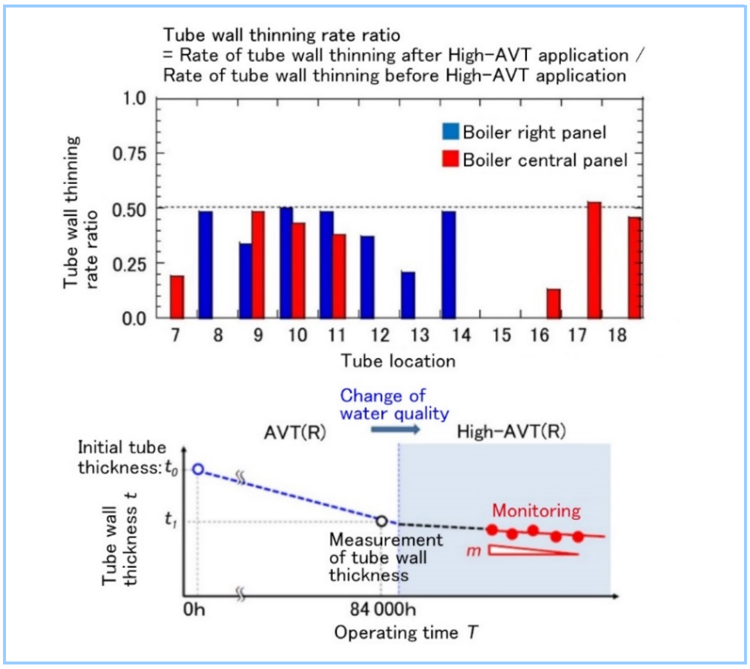


Figure 6　Example of preventive effect of High-AVT (R) application against tube wall thinning

Figure 7 is an example of improvement after applying High-AVT (LO) to a subcritical-pressure drum boiler. After applying High-AVT (LO), the increase in the differential pressure of the high-pressure feedwater heater due to scale adhesion was prevented.

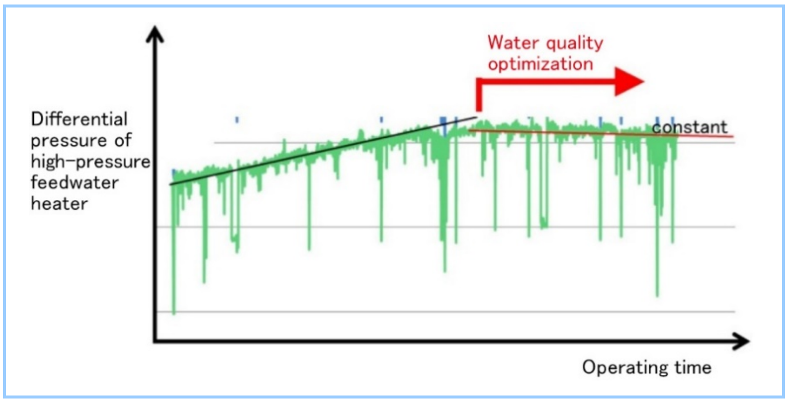


Figure 7　Example of improvement of High-AVT (LO) application (suppression of differential pressure increase of high-pressure feedwater heater)

4. TOMONI Water Quality Diagnosis(6)

Figure 8 depicts an example of the screen image of TOMONI Water Quality Diagnosis and **Figure 9** gives an example of TOMONI Water Quality Diagnosis service content. In order to prevent problems of thermal power plants caused by or related to water, TOMONI Water Quality Diagnosis focuses on the boiler condensate and feedwater systems, steam system, make-up water system (pure water production facility), circulating water system, wastewater treatment system, etc., and collects and analyzes water quality monitoring instruments, operation information (flow rate, pressure and temperature), equipment information (valve opening and equipment differential pressure), etc., to carry out water quality diagnosis. TOMONI Water Quality Diagnosis is basically a cloud service that provides (1) real-time monitoring (automatic diagnosis, 24 hours a day, 365 days a year), (2) regular reports (automatic issue, once a month) and (3) expert diagnosis reports (comprehensive evaluation, twice a year). Items (2) and (3) are optional.

The diagnosis report (3) lists serious potential problems in the future based on the observed water quality abnormality signs and makes recommendations for additional investigations to study countermeasures and inspection items at the next regular inspection.

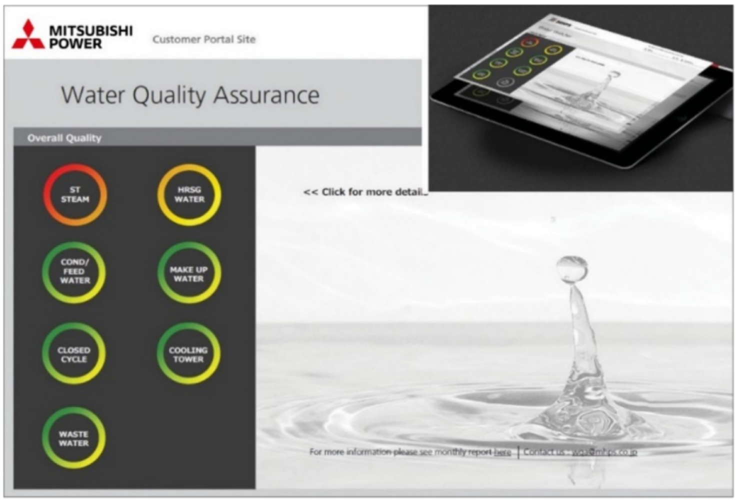


Figure 8 TOMONI Water Quality Diagnosis screenshot

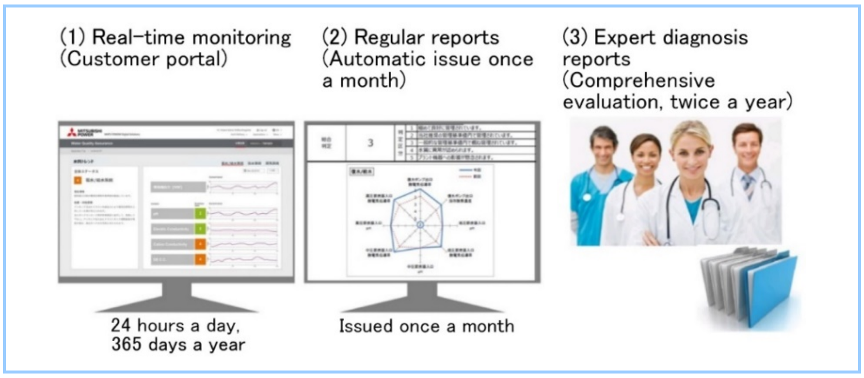


Figure 9 Example of TOMONI Water Quality Diagnosis service content

6. Conclusion

Water treatment technology for thermal power plants is being studied and improved as a countermeasure against damage to equipment such as corrosion and scale adhesion. We developed and are currently providing new technologies such as the elimination of the use of hydrazine, high-temperature filter for iron removal, OT, High-AVT (LO) and TOMONI Water Quality Diagnosis. We will continue to participate in and contribute to new knowledge-based regular revisions of the required water quality for boilers and turbines stipulated by JIS B8223.

We believe that TOMONI Water Quality Diagnosis not only prevents the occurrence of serious problems, but also maintains long-term integrity and performance, reduces the burden on the environment by reducing the amount of chemicals and wastewater used and brings great economic benefits such as shortened plant start-up time and reduced operating costs. We will expand the application range of TOMONI Water Quality Diagnosis.

References

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