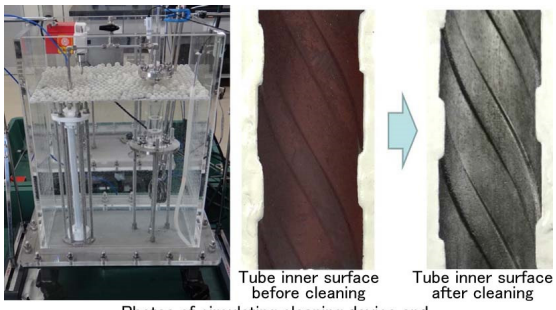
Development of Chemical-Cleaning Technology Effective at Neutral pH and Ambient Temperature Condition enable Safety Improvement and Period Reduction of Maintenance of Power Generation Equipment



Photos of circulating cleaning device and tube inner surface of OT boiler before and after cleaning

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In water systems in power plants, etc., scale adhesion and rust generation may cause problems. As a countermeasure, the periodic chemical cleaning of scale and rust are carried out. Mitsubishi Heavy Industries, Ltd. (MHI) has a developed chemical cleaning technology effective at neutral pH and ambient-temperature featuring high safety and high workability. Currently, we are carrying out cleaning performance evaluation tests and actual equipment cleaning of adhered scale mainly on thermal power plant equipment such as electromagnetic filters, HRSG evaporator pipes (heat recovery boiler), and main steam evaporation pipes (drum type and once-through type), and are promoting the application of the developed technology to after-sales service to realize high safety and the shortening of construction period.

1. Introduction

Problems in power plants caused by water include scale adhesion to the components such as boilers. As one of the countermeasures, the removal and cleaning (chemical cleaning) of scale is performed. Scale removal is generally performed at high-temperature (≧80℃) cleaning with acid. This calls for the prohibition of the use of fire and an independent cleaning process for work operations due to the explosion risk of generated hydrogen, and thus the plant has to stop for a long period of time.

Therefore, we developed chemical cleaning technology effective at neutral pH and ambient-temperature (≤40°C) condition for the purpose of improving the safety of chemical cleaning technology and applied it to the removal and cleaning of scale adhered to plant components. This paper describes the outline, application results, and future development of this developed technology.

2. Neutral chemical cleaning agent

Table 1 compares our developed chemical cleaning method with a general chemical cleaning method. This technology uses the Rust Vulture MK series, which is a neutral scale removal chemical developed by MHI and Kyoeisha Chemical Co., Ltd. In 1991 in order to solve the problems of safety and workability of acid cleaning, as the main agent and can selectively remove just iron oxide scale (rust) by catching iron ions with the use of a chelating reaction and enhancing the scale dissolution reaction. Since this agent has a fundamental property that reacts in the neutral region and in the ambient temperature range, it can improve the working environment and simplify the process and can be applied to a wide range of applications including the removal of rust on equipment generated during storage.

Figure 1 shows the relationship between the scale removal mechanism and the oxidation-reduction potential of the developed chemical cleaning method. The iron oxide dissolution of this technology is related to the oxidation reduction potential of the environment, and

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by controlling the environment to a reducing atmosphere (low potential), iron oxide can be dissolved even in a neutral environment.

Table 1 Comparison of our developed chemical cleaning method with general chemical cleaning method

	General chemical cleaning method	Chemical cleaning method developed by MHI
Base compound	Inorganic acid, Organic acid, Etc.	Chelating agent, Surfactant
Cleaning solution pH	Acidic	Neutral
Dissolution temperature	Heating (up to 90°C)	Ambienttemperature (25 to 40°C)
Cleaning time	Up to 10 hours*	Up to 100 hours*
Hydrogen generation	Generated	Trace amount
Cleaning method	Circulating	Circulating, Pickling, Swinging

*Since the time to completion of cleaning varies depending on the attached amount and properties of the scale, cleaning time is set in advance by the dissolution test.

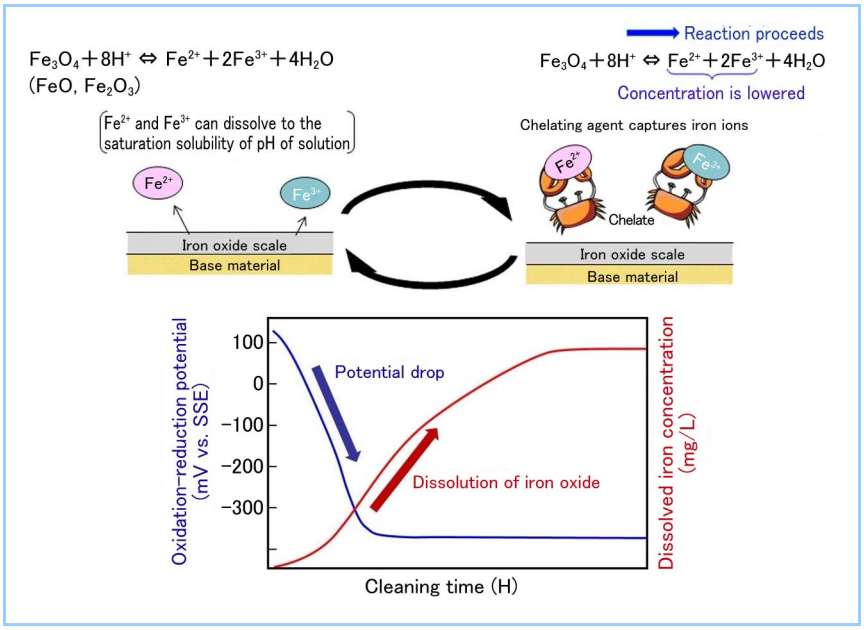

Figure 1 Relationship between scale removal mechanism and oxidation-reduction potential of developed chemical cleaning method

3. Actual cleaning achievements and efforts

Table 2 lists application examples of the new chemical cleaning technology to rust and scale removal. Since its development, this technology has been applied to various kinds of cleaning cases, such as the cleaning, removal, and flushing of rust generated and scale adhered mainly on the surfaces of thermal power plant components. Currently, the technology is being developed further aiming at application to chemical cleaning of boiler evaporation tubes on actual equipment. Case examples of chemical cleaning of scale on electromagnetic filters and industrial drum boiler evaporation pipes, as well as the progress of development aiming at cleaning of scale on evaporation pipes of HRSG and oxygen treatment once-through boilers, are reported below.

Table 2 Application examples of new chemical cleaning technology to rust and scale removal

Target		Purpose
Spiral fin tube		Removal of rust generated on the outer surface due to salt damage
Feedwater flow regulating valve VRT plate		Removal of scale adhered in the hole
Steam turbine oil piping		Removal of foreign matter by chemical flushing, Cleaning of the inner surface
High-pressure feedwater heater		Removal of scale adhered to the heat transfer surface
Cooling water piping		Removal of rust and scale adhered in the pipes
Electromagnetic filter		Removal of scale collected in the filter
Drum boiler		Removal of scale adhered to the inner surface of the evaporation tubes
In development	HRSG	Removal of scale adhered to the inner surface of the evaporation pipes (including phosphoric acid component)
	Once-through boiler	Removal of scale adhered to the inner surface of the evaporation pipes (including hematite and auto-oxidation scale)

3.1 Results of cleaning of electromagnetic filter on actual equipment

When the operation of a plant includes many start-ups and shutdowns such as on weekends and at night, the suspended substances (mainly iron oxide and hydroxide) in the system increase, causing equipment problems such as scale adhesion. Therefore, a filter is installed as a condensate treatment device at the outlet of the condensate pump to improve the quality of the water supply. An electromagnetic filter is one of the components of the filter, and magnetic coils are used to magnetize the filter element in the electromagnetic filter to capture the magnetic particles contained in the fluid. Nonmagnetic particles that penetrate and adhere inside the filter element cannot be removed by reverse cleaning with pure water at the time of plant stop. For this reason, chemical cleaning and physical cleaning (jet cleaning) of the filter element were performed by opening the equipment during periodic inspections.

As a new cleaning method for the electromagnetic filter, cleaning with the developed agent was carried out. **Table 3** compares this cleaning method with the conventional one. Due to cleaning with a swing blow method where the cleaning liquid is prepared in a chemical liquid container, pumped to the filter tower for impregnating and filling, and then pumped back to the chemical liquid container after a certain period of time, the opening of equipment, removal and reinstallation of the filter element, chemical cleaning, and jet cleaning, which are required by the conventional method, are no longer required, and the work period has been greatly shortened from 10 to 20 days in the past to 2 to 3 days. In addition, a cleaning cost reduction of 30% or more was achieved. **Figure 2** indicates the results of this cleaning method.

Table 3 Comparison with conventional cleaning method of electromagnetic filter

	Process	Conventional cleaning method	Cleaning with developed by MHI
Cleaning procedure	1. Opening of equipment (using a crane)	●	—
	2. Removal of filter element	●	—
	3. Chemical cleaning	●	●
	4. Jet cleaning	●	—
	5. Assembly of equipment (using a crane)	●	—
	6. Washing with water	●	●
Number of working days (days)		10 to 20	2 to 3

●: Required

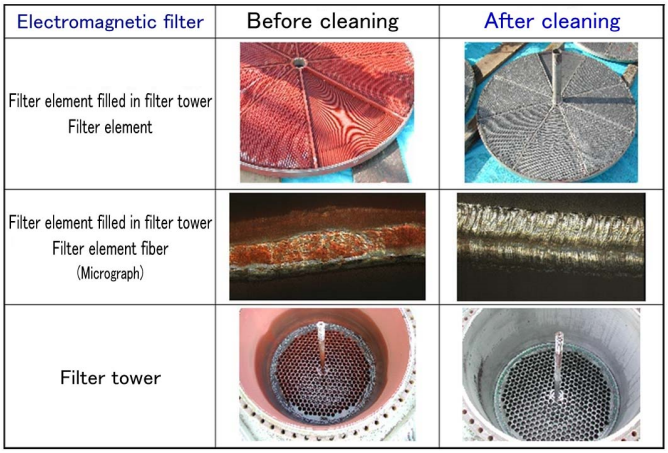

Figure 2 Results of cleaning of electromagnetic filter (opened to confirm effectiveness)

3.2 Results of cleaning of industrial drum boiler on actual equipment

The new chemical cleaning method was applied to chemical cleaning of the main boiler (evaporation amount: MCR 78 t/h) at the Yamaguchi Plant of Taiyo Oil Co., Ltd., to verify the application of the method to cleaning of scale adhered to the boiler evaporation pipes of actual equipment. **Table 4** shows the specifications of the target unit. Since the scale component of the target boiler included copper scale that cannot be dissolved and removed by the new chemical cleaning alone, the new chemical cleaning was performed for 24 hours, and acid washing with a copper dissolver added was performed for 6 hours for chemical cleaning of the actual equipment. **Figure 3** gives the results of the chemical cleaning test. **Figure 4** indicates the results of hydrogen measurement during chemical cleaning. The appearance of the tube after the application of the new chemical cleaning method confirms that the scale on the outside of the furnace with less adhesion

of copper could be completely removed by the new chemical cleaning method alone. The generation of hydrogen during the application of the new chemical cleaning method was lower than the detection limit (0.05%). On the other hand, it was confirmed that hydrogen gas with a concentration of 2% or more was generated during acid cleaning that was subsequently performed. As a result, it was verified that chemical cleaning can be carried out in an environment where fire is used for work operations and where other work operations are performed in parallel. The internal inspection at the end of cleaning resulted in just several kilograms of sludge remaining in the water drum and no sludge deposition in the steam drum. A significant reduction in the amount of sludge, compared with cases where acid cleaning is carried out independently, was confirmed.

Table 4 Specifications of target unit

Target		Yamaguchi Plant of Taiyo Oil Co., Ltd. Main boiler
Boiler specifications	Type	MB-EBR boiler (outdoor type)
	Evaporation amount	MCR 78 t/h
	Steam pressure	Maximum operating pressure 11.18MPa
	Steam temperature	Superheater outlet 500°C
	Fuel	Heavy oil and off gas
	Operation commencement	1993
	Cleaning history	No cleaning
Amount of adhered scale	Inside furnace	88 mg/cm^2
	Inside casing	35 mg/cm^2
Cleaning work (actual results)	New low-temperature boiler chemical cleaning	September 14 to 15, 2016 (40°C - 24 hours)
	Conventional cleaning (with hydrochloric acid)	September 16 to 17, 2016 (60°C - 6 hours)
	Internal check	September 18, 2016

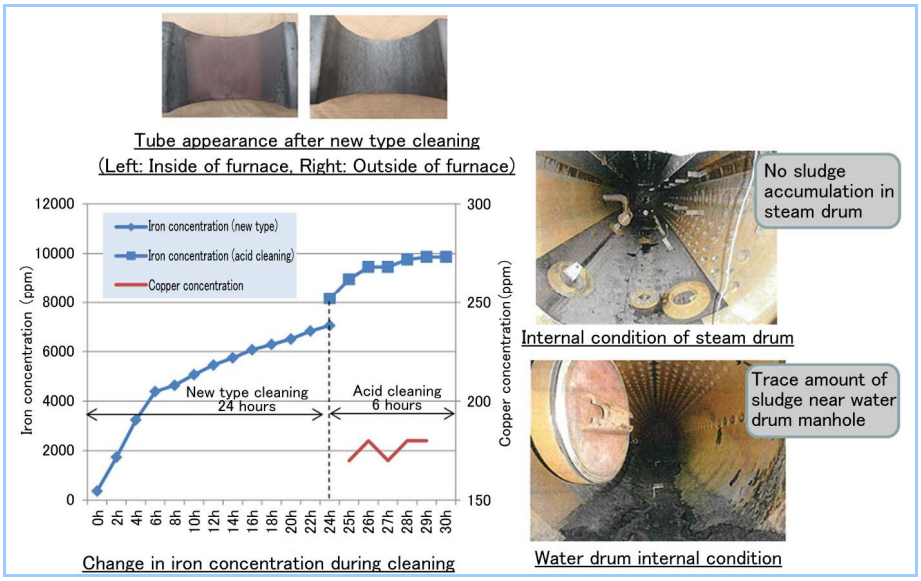

Figure 3 Results of new low-temperature boiler chemical cleaning

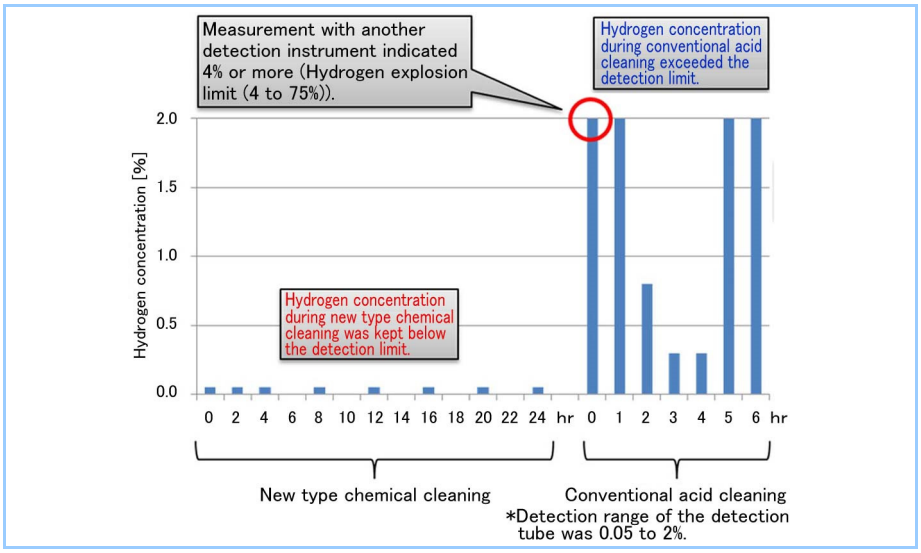

Figure 4 Results of hydrogen measurement during boiler chemical cleaning

3.3 Results of application of developed cleaning method to HRSG chemical cleaning

Since HRSG has a smaller heat load than a conventional drum boiler, it was thought that chemical cleaning is not required. However, because leakage problems due to water treatment incompatibility (phosphate corrosion) occurred, the removal of corrosive scale by chemical cleaning is considered to be one of the countermeasures. **Figure 5** shows an example case of corrosion caused by a boiler compound considered to remain in scale observed in an overseas plant. In this case, the phosphate hide-out phenomenon (phosphate is not detected even though injected) was confirmed during trial operation, so the injection of phosphate was stopped. However, leakage occurred 10 years or more after the injections were stopped. The cause is thought to be the development of phosphate corrosion due to the phosphorus component remaining in the scale. This led to the determination that the removal of corrosive scale is necessary.

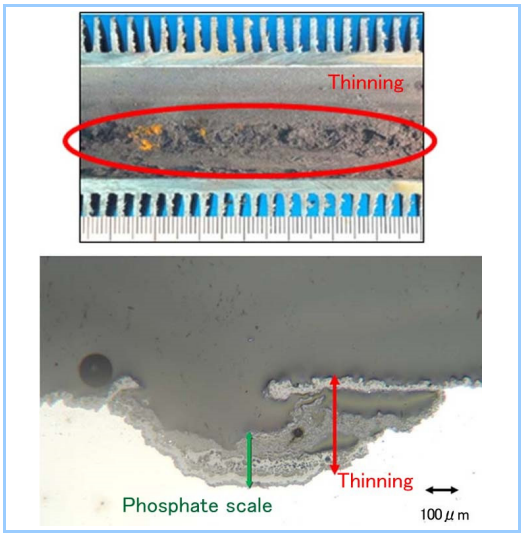

Figure 5 Example of problem with HRSG (phosphate corrosion)

The fin tubes used for HRSG have a larger heat dissipation effect than general tubes, so it is expected that maintaining the cleaning temperature is difficult. For this reason, a chemical cleaning test under a non-heating condition was carried out in a laboratory to confirm the phosphate scale removal capability, which is the cause of corrosion. **Figure 6** gives the results of the scale dissolution test. **Figure 7** shows the schematic system and process of chemical cleaning for the removal of scale adhered to the inner surface of HRSG, which was studied based on these test results. Since there is no need for a heating source and the risk of hydrogen gas generation during cleaning is low, it is considered that safety can be ensured, and cleaning can be performed in parallel with other work in the case of actual equipment.

Test conditions
(new low-temperature boiler chemical cleaning)

Item	Condition
Sample	HRSG evaporation pipe (high-pressure evaporator)
Test solution	Neutral rust removal agent (Rust Vulture) Reduction agent, Corrosion inhibitor
Specific solution volume to specimen surface area	1 ml/cm^2
Test temperature	Ambient temperature (25°C)
Cleaning method	Standing and swinging (alternating every 12 hours)
Test time	96 hours (4 days)
Water cleaning method	Hydrazine 100 mg/L × 2 times

Test results
(sample tube appearance, cross section)

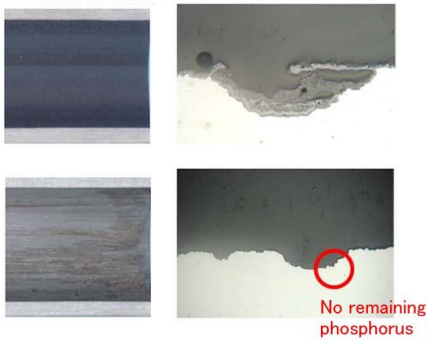

Figure 6 Results of scale dissolution test of HRSG on actual sample equipment

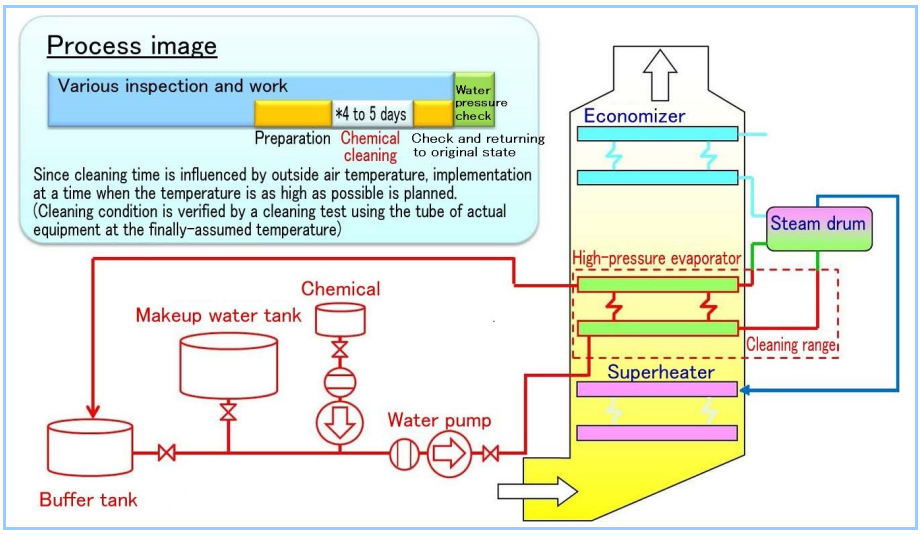

Figure 7 Schematic of system and process of new low-temperature boiler chemical cleaning method for HRSG

3.4 Efforts toward application of developed cleaning method to once-through boiler cleaning for oxygen treatment

For oxygen treatment (OT), which is the main water treatment of once-through boilers, cases of poorly soluble powder scale (the chief component of which is hematite) adhered and created on the scale surface were reported. Therefore, in conventional chemical cleaning based on an acid solution, magnetite scale on the inner surface is melted and peeled off, and then discharged by conveying with liquid flow.

Figure 8 depicts the residual sludge of a once-through boiler after chemical cleaning (organic acid is applied). Most of the hematite (over 90%) remains un-melted as sludge and cannot be sufficiently discharged by cleaning with water. It has been reported that such sludge clogged a pipe after the boiler started and caused a leak. For this reason, it is necessary to collect sludge by installing a filter in the system during cleaning, and to cut an inspection hole in the header and jet-clean the remaining sludge in the boiler.

Development toward the application of the new chemical cleaning technology – which is highly capable of dissolving hematite – to actual equipment is being promoted. **Figure 9** shows the results of the scale dissolution test using hematite reagent. **Figure 10** is a schematic representation of the periodic inspection period shortening effect expected by the application of this technology. While a reduction of plant downtime is desired, the inspection period can be shortened by about one week by establishing this technology.

Figure 8 Residual sludge of once-through boiler after chemical cleaning (organic acid is applied)

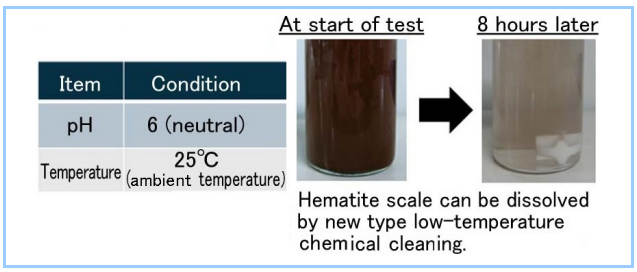

Figure 9 Results of scale dissolution test using hematite reagent

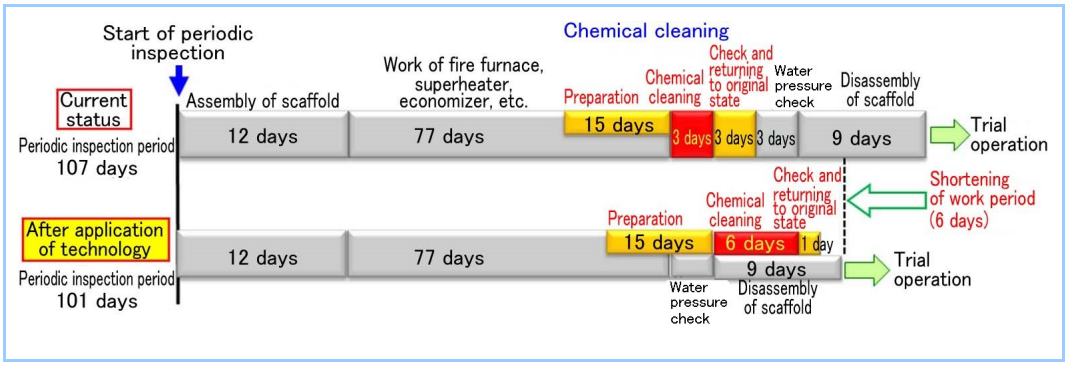

Figure 10 Periodic inspection period shortening effect due to application of new chemical cleaning technology

4. Conclusion

In order to improve safety, shorten the work operation period, and reduce the cost of chemical cleaning by optimizing processes, which is implemented as one of the measures against water-related problems in plants, etc., we developed an ambient-temperature and neutral chemical cleaning technology that can be substituted for general high-temperature and acidic cleaning, and we are working on its application to cleaning work. This paper presented the results of the application of the new chemical cleaning technology to plant components, HRSG and industrial drum boilers, and explained the application situation to once-through boilers. In the future, we will expand the application of this technology to actual equipment and further advance it. The technology introduced above is applicable to not only power generation equipment, but also the iron piping of chemical plants, marine boilers, etc., as a technique to remove the scale and rust produced and adhered therein. We intend to expand the application of this technology.

References

1. Tsubakizaki, S. et al., Scale removing technology by neutral neutral rust removal chemical, The piping engineering (Apr. 2012)
2. Uchida, Y. et al., Introduction to Electromagnetic Filter Cleaning by Neutral Rust Removal Chemical, The thermal and nuclear power, Vol. 63 No.4 (2012)
3. Shimoda, S. et al., Application of Neutral and Non-Heating Scale Removal Method in Combined Cycle Plant, The thermal and nuclear power, Vol. 66 No.2 (2015)
4. Tsubakizaki, S. et al., Advantages and New Technologies of High-AVT Water Treatment in Combined Cycle Plants, Mitsubishi Heavy Industries Technical Review Vol. 52 No. 2 (2015)
5. Tsubakizaki, S. et al., Advanced Water Treatment Technologies (High-AVT) for HRSG Corrosion Control corresponding to New JIS B8223 (Japanese Industrial Standards), Mitsubishi Heavy Industries Technical Review Vol. 54 No. 3 (2017)