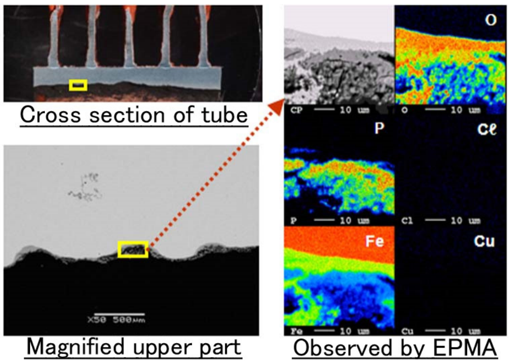
# Advantages and New Technologies of High-AVT Water Treatment in Combined Cycle Plants

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*In today's water treatment using the heat recovery steam generator (HRSG) of combined cycle plants, ammonia and hydrazine are used in the feedwater system and sodium phosphate is used in the boiler system. In recent years, however, corrosion due to phosphate has occurred at some plants, and efforts to realize hydrazine-free water treatment will be needed in the future. To cope with these issues, conversion to high-AVT water treatment is effective, and its actual performance has been well-received and was adopted as the JIS standards revision proposal. Mitsubishi Hitachi Power Systems, Ltd. (MHPS) developed the new technologies for conversion to high-AVT water treatment, specifically neutral room-temperature chemical cleaning and an electrolytic denitrification system for high-pH waste water, which will be introduced below.*

## 1. Introduction

HRSG installed in combined cycle plants uses gas turbine combustion exhaust gas as the heat source. Therefore, the heat load is small, and it has been thought that water quality control is easy. In recent years, however, corrosion problems due to phosphate (caustic corrosion, acid phosphate corrosion) have occurred at some plants. As a countermeasure, conversion to high-AVT water treatment without the use of phosphate is recommended. In conversion, it is necessary to remove scale which may result in the development of corrosion. We have developed neutral/non-heating cleaning technology which has a high degree of safety and requires no heating/circulation. In addition, assuming cases where high-concentration ammonia waste water treatment is required in high-AVT water treatment, we developed a simple ammonia waste water treatment technology. An overview of the technologies will be introduced. The actual performance of High-AVT water treatment has been well-received and it was adopted as the next JIS standards revision proposal.

## 2. Problems caused by water in HRSG and measures

**Fig. 1** shows an overview of conventional water treatment[1] in HRSG. In HRSG, the phosphate treatment is mainly applied, and ammonia and hydrazine are injected in feedwater (condensate pump outlet), and sodium phosphate is injected in boiler water (steam drum or feed-water tube of steam drum inlet). The heat load is small in HRSG, and so it has been thought that water quality control is easy. However, at overseas plants and some domestic plants, the problems described below due to water have occurred.

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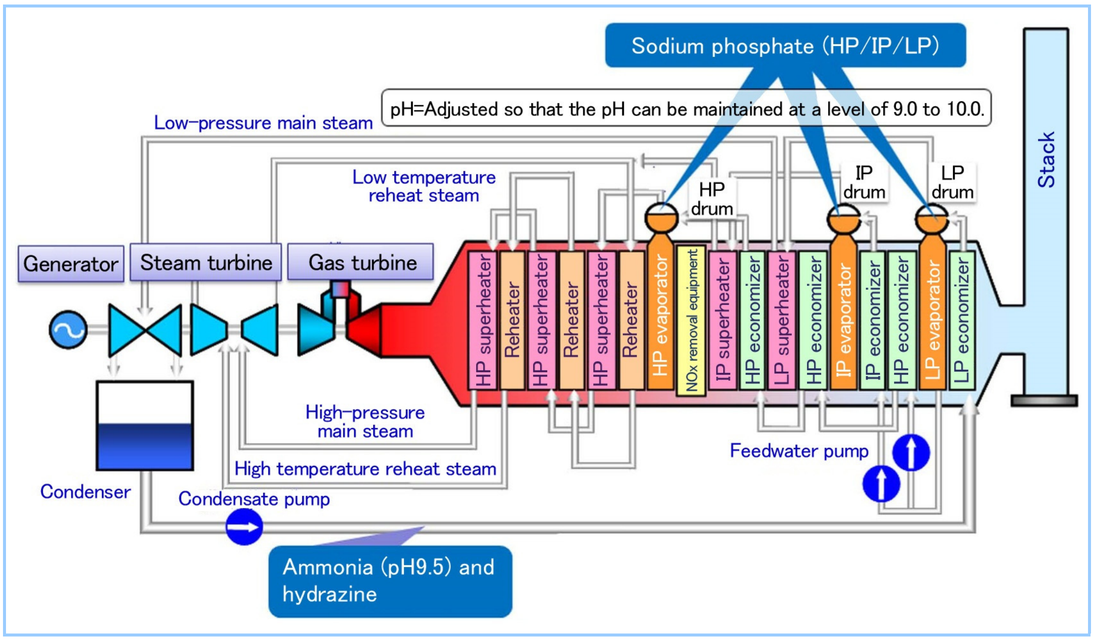


**Figure 1 Conventional water treatment of HRSG (phosphate treatment)**

## 2.1 Flow accelerated corrosion

**Figure 2** shows an example of the thinning of pipe walls caused by flow accelerated corrosion of HRSG that occurred at an overseas combined cycle plant. In this case, a leak was found at the bend portion of the low-pressure evaporator two years after the start of operation. The probable cause of the leak was that an insufficient concentration of phosphate injected into the boiler resulted in the pH of the low-pressure drum water being controlled to lower levels.

In addition, when a large amount of scale is deposited in the HRSG evaporator tube due to an increase of the iron level in the feedwater through FAC, heat transfer obstruction and corrosion caused by phosphate (caustic corrosion, acid phosphate corrosion)may occur in the interior of scale.

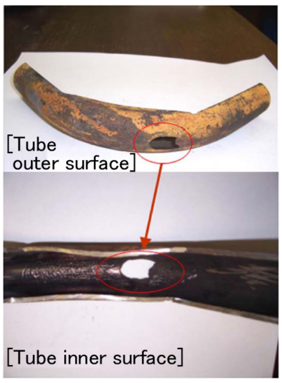


**Figure 2 FAC example**

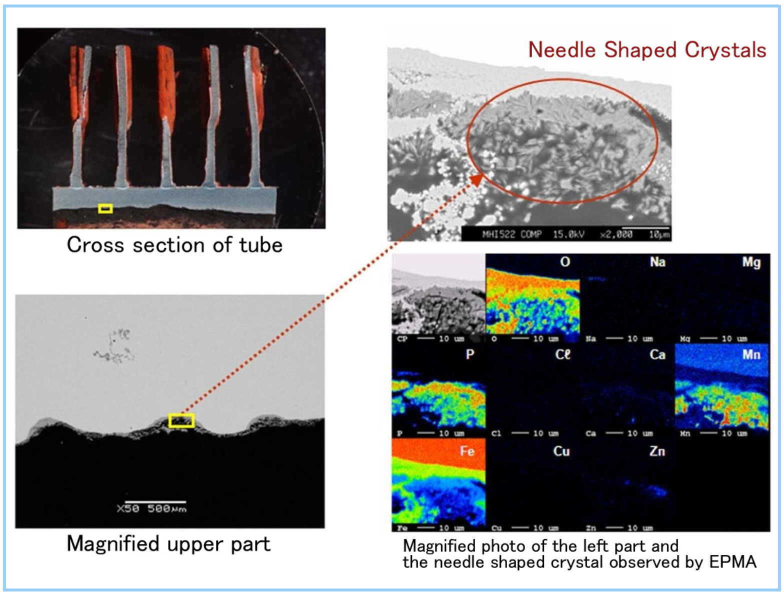


**Figure 3 Example of corrosion caused by phosphate**

## 2.2 Corrosion caused by phosphate

**Figure 3** shows an example of corrosion caused by phosphate in HRSG that occurred at an overseas combined cycle plant. There are few corrosion problems occurring in normal water quality control, but in cases where (1) structurally stagnant or local overheating portions exist, (2) abnormal scale has been formed due to impurities carried in from outside the plant or (3) phosphate is excessively added, and there is a possibility of the occurrence of corrosion. If a change in the concentration of phosphate (hide-out phenomena) as shown in **Figure 4** is observed, it is recommended to check for the occurrence of corrosion due to phosphate.

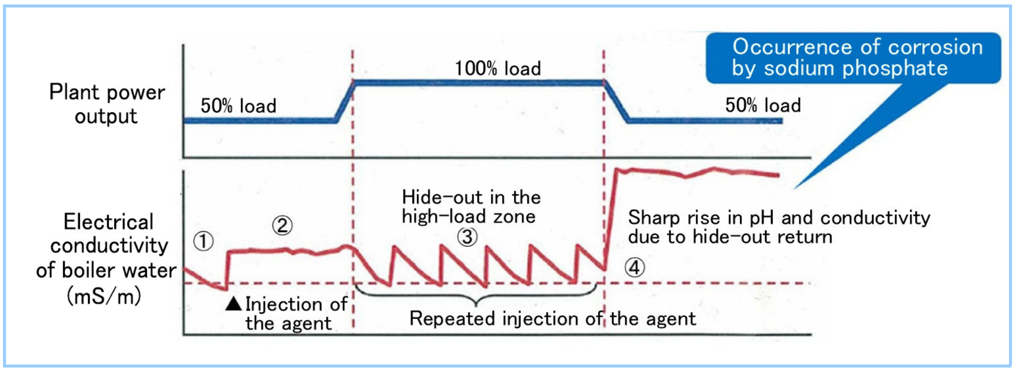


**Figure 4 Phosphate hide-out phenomenon**

The corrosion phenomena are classified as caustic corrosion in which free alkali (NaOH) is locally concentrated and as acid phosphate corrosion in which compounds (acid) with a low Na/PO4 molar ratio are formed inside the deposits produced through the introduction of impurities or local heating, but there are many cases that are indistinguishable from each other.

To prevent corrosion caused by phosphate (caustic corrosion, acid phosphate corrosion), scale in which alkali or acid phosphate concentrates must be removed first. Conversion to phosphate-free high-AVT water treatment after the removal of scale is also an effective measure.

## 3. High-AVT water treatment[2]

High-AVT water treatment is an all-volatile treatment method for feedwater with a high pH level exceeding the Japanese feedwater quality control standards (upper limit: pH 9.7) provided by JIS B8223 (2006), and the 2013 JIS Revision Committee, in which MHPS has participated, promoted its standardization and decided to adopt it as a revision proposal.

**Table 1** shows a comparison between the conventional phosphate treatment and high-AVT water treatment. In high-AVT water treatment, the pH of feedwater can be set at a level higher than that of the conventional JIS standard, and the use of hydrazine and sodium phosphate can be stopped.

The Global Plan of Action in the Strategic Approach to International Chemicals Management (SAICM) indicates "Toward 2016-2020, alternative substances to carcinogenic or mutagenic substances (hydrazine, etc.) shall be identified and used." Therefore, high-AVT water treatment is considered as an effective hydrazine-free alternative option.

**Table 1 Comparison between phosphate treatment and high-AVT water treatment**

| | Chemical agents used | | | pH of feedwater |
|---|---|---|---|---|
| | Feedwater | | Boiler water | |
| | Ammonia | Hydrazine | Sodium phosphate | |
| Phosphate treatment | ○ | ○ | ○ | 8.5~9.7 (JIS standard) |
| High-AVT | ○ | × | × | 9.8~10.3 (JIS revision proposal) |

○ : Use × : Non-use

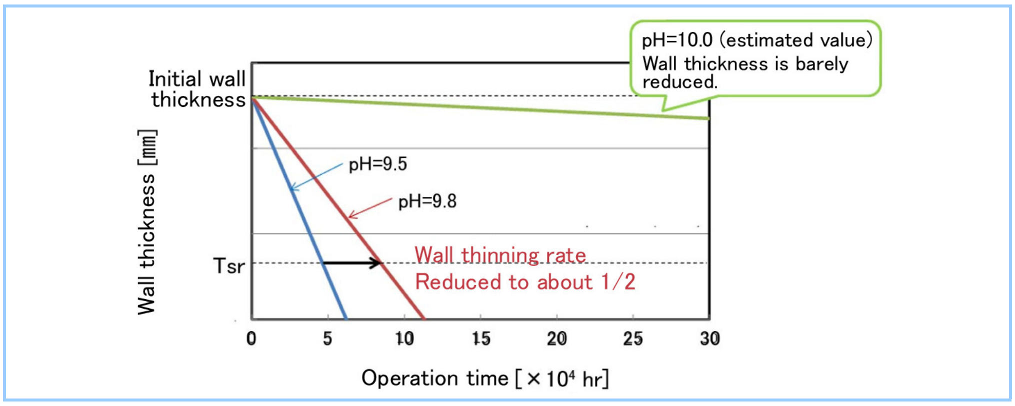


**Figure 5 Relationship between pH and FAC thinning rate (High-pressure economizer)**

It has been verified that higher pH levels decrease the rate of flow accelerated corrosion (FAC)[3], and the thinning of pipe walls caused by FAC is expected to be suppressed. **Figure 5** shows the relationship between pH levels and the FAC rate. It has actually been measured that an increase of the pH of feedwater from 9.5 to 9.8 reduces the rate of the thinning of pipe walls by half, and at a pH level of 10, the rate of the thinning of pipe walls is expected to be further reduced.

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## 4. New technologies at introduction of high-AVT water treatment

### 4.1 Removal of scale in neutral/non-heating conditions[4]

For the prevention of corrosion caused by phosphate, scale must be removed before the application of high-AVT water treatment. **Table 2** shows the properties of the neutral rust removing agent developed by Mitsubishi Heavy Industries, Ltd. (MHI) and Kyoeisha Chemical Co., Ltd., and **Figure 6** shows the mechanism (conceptual image) of the removal of scale using the neutral rust removing agent. The cleaning component in the neutral rust removing agent (chelating agent) does not contain any substances that actually corrode materials, and the chelating agent is used to collect iron ions. As it causes a reaction in the neutral region, at room temperature or in the state of being immersed, the safety of cleaning work and the simplification of equipment and processes can be expected.

**Table 2 Properties of neutral rust removing agent**

| Item | Neutral rust removing agent | Conventional chemical agent (hydrochloric acid) |
|---|---|---|
| Appearance | Pale yellow clear liquid | Clear and colorless |
| Specific gravity (20°C) | 1.2 | 1 |
| pH | 6.0 (undiluted solution) | < 1 |
| COD (0.1%) (Chemical Oxygen Demand) | 160 ppm | 60 to 300 ppm |
| Major components | Chelating agent Surface-active agent | Hydrochloric acid, inhibitor, reducing agent |
| Use condition | Room temperature (20 to 30°C) | Room temperature to 60°C |

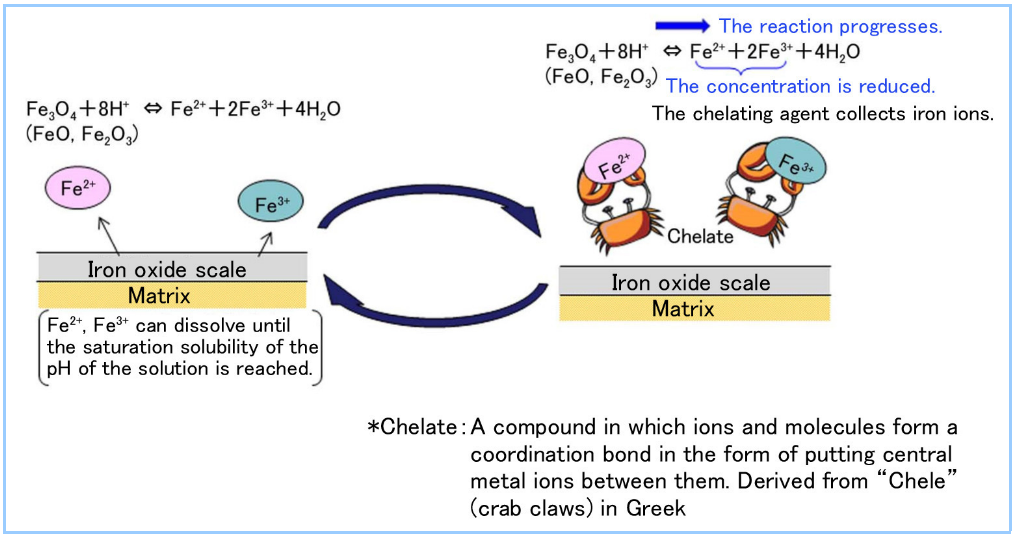


**Figure 6 Mechanism (conceptual image) of removal of scale using neutral rust removing agent (chelating agent)**

**Figure 7** shows the states of the sample tube inner surface before and after the scale removal test and the change in iron level at the scale removal test. With the neutral rust removing agent, the dissolution of iron progresses slowly in comparison with other cleaning agents. Accordingly, it was verified that an increase of the concentration and setting of a longer cleaning time enable the removal of scale under a non-heating (room temperature) condition.

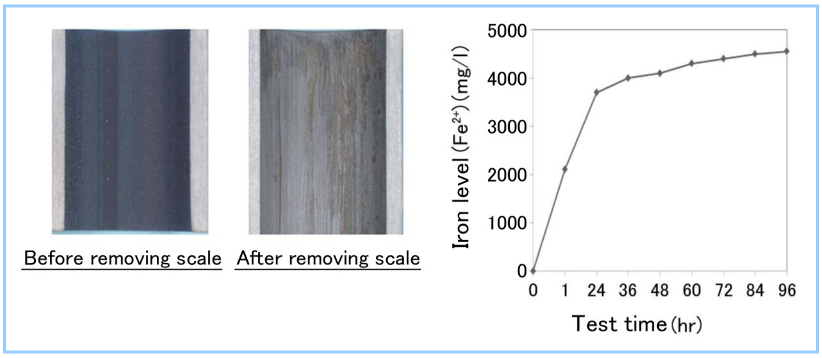


**Figure 7 States of sample tube inner surface before and after scale removal test**

### 4.2 Simplified ammonia waste water treatment[5]

In high-AVT water treatment, the ammonia levels in feedwater are more than approximately 10 times higher than in the conventional JIS method. Therefore, strict waste water standards are set for total nitrogen (T-N), and it is difficult to apply high-AVT water treatment at plants without nitrogen waste water equipment. As a simplified ammonia waste water treatment method, MHI and Mitsubishi Heavy Industries Environmental & Chemical Engineering Co., Ltd. developed a low-cost ammonia waste water treatment system, in which the electrolytic chlorine generator being used as an anti-biofouling measure was applied.

**Figure 8** shows the principle of ammonia treatment using the electrolytic chlorine generator, and **Figure 9** shows an overview of the electrolytic denitrification system. Hypochlorous acid solution and waste water are mixed in a mixing vessel for the oxidative destruction of ammonia. Seawater is used for the production of hypochlorous acid to be used in the reaction. It is characterized in that no solid waste or waste liquid that requires separate treatment is discharged, the equipment is compact, and the operation is easy.

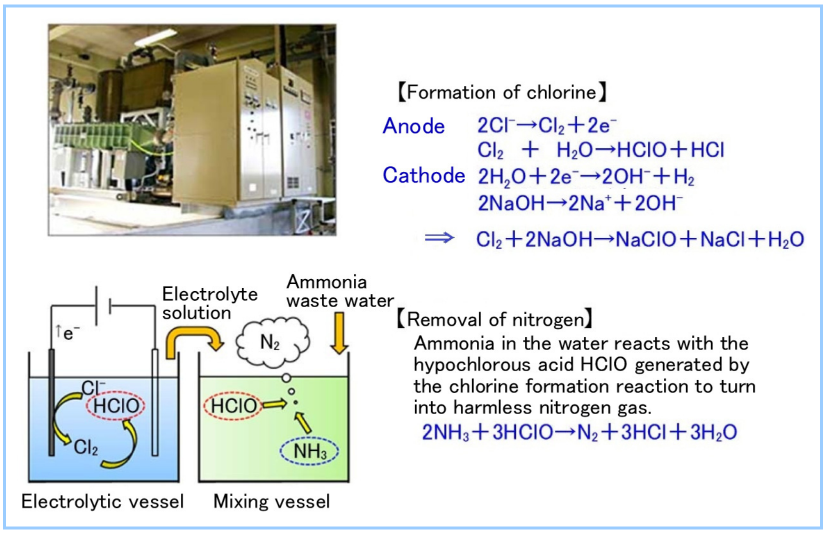


**Figure 8 Ammonia treatment by electrolytic chlorine generator**

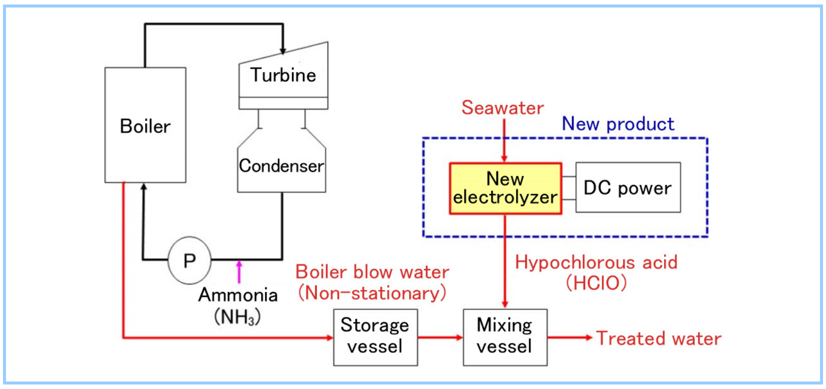


**Figure 9 Overview of electrolytic denitrification system**

## 5. Conclusions

High-AVT water treatment in combined cycle plant HRSG has been adopted as the next JIS standards revision proposal, because its actual operation results were well-received. In addition, problems due to corrosion caused by phosphate (caustic corrosion, acid phosphate corrosion) have occurred, and to prevent corrosion, it is recommended that high-AVT water treatment should be adopted as an alternative method, and that scale on tube inner surfaces, which may cause the progression of corrosion, be removed in advance.

It is assumed that in addition to the occurrence of problems with water quality control such as the excessive phosphate addition, when the heat load of HRSG increases along with a rise in gas turbine exhaust gas temperature, the occurrence of similar phenomena may increase in the future. High-AVT water treatment is expected to be increasingly adopted as a hydrazine-free measure.

## Reference

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