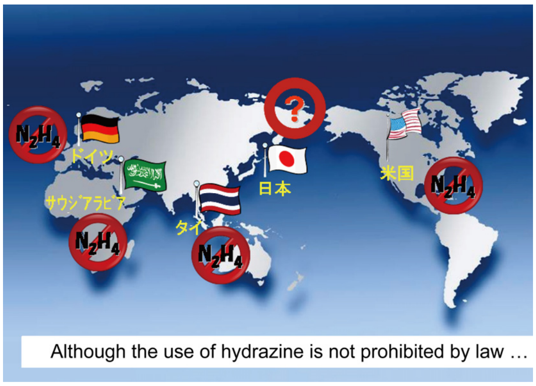
Alternatives to Hydrazine in Water Treatment at Thermal Power Plants



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Hydrazine is generally used as an oxygen scavenger for corrosion control in thermal power plants. Although hydrazine is very effective in this application, it is a genotoxic carcinogen. The use of alternative chemicals such as nontoxic oxygen scavengers and new oxygen scavenger-free water treatment technologies is recommended or required in foreign countries. Even in Japan, such new approaches to water treatment would contribute to environmental protection, increased confidence, and a reduction in power plant operating costs.

1. Introduction

In recent years, our company has received orders for power plants from overseas customers. The specifications for some of these plants prohibit the use of hydrazine, requiring the use of nontoxic alternatives or different methods of water treatment technology without oxygen scavengers. Hydrazine-free water treatment provides the following advantages:

- Reduction in environmental impact and improvement of the work environment;
- Reduction in deposition, which in turn reduces the frequency of chemical cleaning for through-flow boilers;
- Reduction in pipe wall thinning due to flow-accelerated corrosion (FAC); and
- Reduction in startup time and water consumption in the drum boilers and heat recovery steam generator (HRSG) boilers.

In this paper, we introduce our approach to water treatment technologies.

2. Role of Hydrazine in Water Treatment

2.1 What is hydrazine?

There are two types of hydrazine: anhydrous hydrazine (N_2H_4) and hydrazine hydrate ($N_2H_4 \cdot H_2O$).

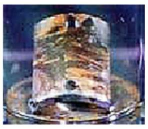
Hydrazine hydrate is mainly used as a raw material for plastic foaming agents, with 28% of hydrazine used in water treatment and pH control.

2.2 Corrosion-control effects of hydrazine

Oxygen dissolved in water causes corrosion. Because hydrazine removes this oxygen via the reaction $N_2H_4 + O_2 \rightarrow N_2 + 2H_2O$, it is useful in preventing corrosion. It decomposes at a temperature of 200°C or more to form ammonia ($3N_2H_4 \rightarrow 4NH_3 + N_2$) , which acts as a pH adjuster.

This scavenging reaction proceeds very slowly near room temperature, and the formation of ammonia by decomposition is not great. However, hydrazine is also used to control corrosion during the storage or cooling of water due to its action as a pH adjuster.

Figure 1 shows an example of corrosion-control tests on metallic material using hydrazine. When the metal was soaked in 100 mg/l hydrazine, no rust was produced even after 500 hours had elapsed.

Test conditions / Soaking time	N_2H_4 20mg/l	N_2H_4 50mg/l	N_2H_4 100mg/l
After 10 hours			
After 100 hours			
After 500 hours			

※No rust was produced in 100 mg/l hydrazine even after 500 hours.

Figure 1 Corrosion reduction using hydrazine

3. Restrictions on the Use of Hydrazine

3.1 Trends in chemical substance management

In recent years, an international framework for the control of chemical substances has been created.

(1) In 1992, the United Nations Conference on Environment and Development adopted "Agenda 21" (Chapter 19), a global action plan for sustainable development in the 21st century.

(2) In 2002, the World Summit on Sustainable Development (WSSD) adopted the "Johannesburg Plan of Implementation" containing guidelines on the management of chemical substances to minimize major adverse effects on human health and the environment by 2020.

(3) The International Conference on Chemicals Management in 2006 adopted the "Strategic Approach to International Chemicals Management (SAICM)" designed to implement the Johannesburg Plan.

In 2007, the European Union implemented the Regulation on Registration, Evaluation, Authorization, and Restriction of Chemicals to achieve the WSSD goals by 2020. Studies on the SAICM-related approach are also under way in Japan.

3.2 Recent development of the use of hydrazine from Pollutant Release and Transfer Register data

Starting in 2002, Japanese business enterprises handling more than 1 ton of chemicals subject to the Pollutant Release and Transfer Register in a year were obligated to report environmental emissions. Hydrazine is among these chemicals.

According to data published in 2007, 222 Japanese companies used more than 1 ton of hydrazine. Companies using a water treatment (combined water and oxygen treatment) process that does not rely on hydrazine tended to use the chemical in smaller quantities. Some power companies have no facilities that are subject to the hydrazine emission reporting requirement.

3.3 Guidelines on the prevention of health problems caused by hydrazine

In March 2006, the Japanese Ministry of Health, Labor and Welfare issued "Guidelines on Prevention of Health Problems." These guidelines cover the renovation of facilities to convert them to closed-type facilities, safety and health education, maintenance of records during the periods when chemicals subject to the guidelines are handled, and maintenance of such records to reduce the exposure to chemicals by workers who handle them on-site. All establishments using hydrazine are subject to these guidelines regardless of the quantity used.

Figure 2 shows an example of measures to be taken to reduce the exposure to hydrazine during the renovation of a facility according to the guidelines. Conversion to a closed tank, installation of local ventilation, securing the supply transfer pump, and other measures are necessary. Hydrazine is not a banned substance. It is, however, recognized as requiring "understanding of its risk by notification," "reduction of exposure," and "voluntary reduction" in Japan.

We consider it necessary to take measures to reduce the use of hydrazine without delay in view of the trend in restricting chemicals overseas.

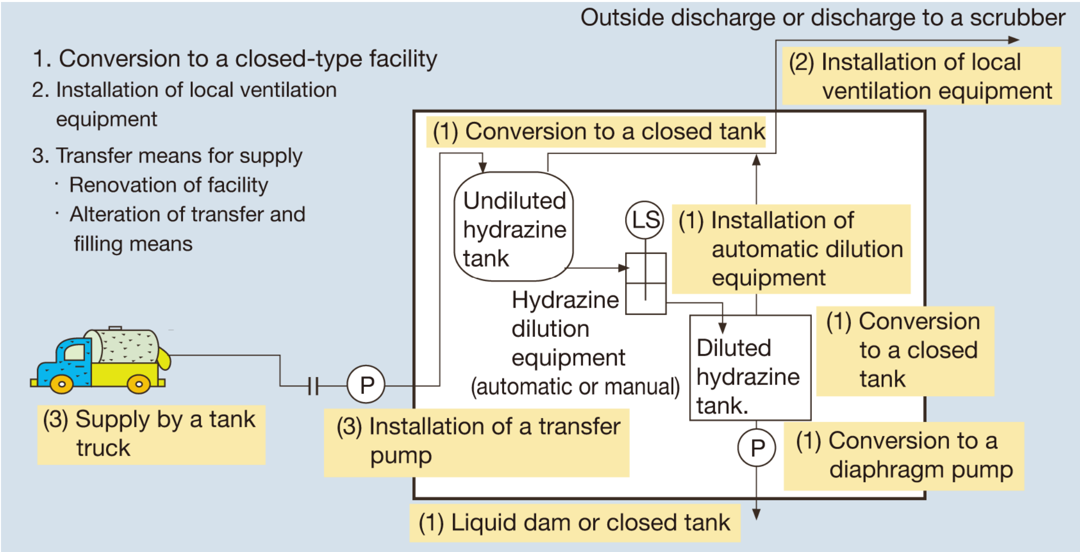


Figure 2 Measures to reduce exposure to hydrazine when renovating a facility.

4. Avoidance of hydrazine use

4.1 Alternative chemicals

Chemical alternatives to hydrazine are currently being used in the boiler plants of some domestic industries based on the manufacturers' recommendations for long-term operation. However, the use of such alternative chemicals by power utilities only occurs overseas, and their application to domestic power plants is still under investigation.

4.2 Oxygen treatment

As a power plant manufacturer, our company promotes the avoidance of hydrazine with a proposed new water treatment system. Specifically, we recommend the following two treatment methods to eliminate the use of hydrazine:

- Combined water treatment (CWT) or oxygen treatment for through-flow boilers
- AVT(O)+High-AVT (treatment by a volatile substance with a high pH value without using hydrazine) (see 4.3 below) for drum boilers and combined cycle plants

Figure 3 shows the difference in the deposits on the inner surface of boiler tubes when AVT (conventional water treatment using hydrazine) and CWT (oxygen treatment without hydrazine) are used. Hematite is formed over the surface of the deposit on the inner surface when a trace amount of oxygen is supplied, and the elution of iron and adhesion of deposits can be significantly reduced due to the effect of corrosion inhibition.

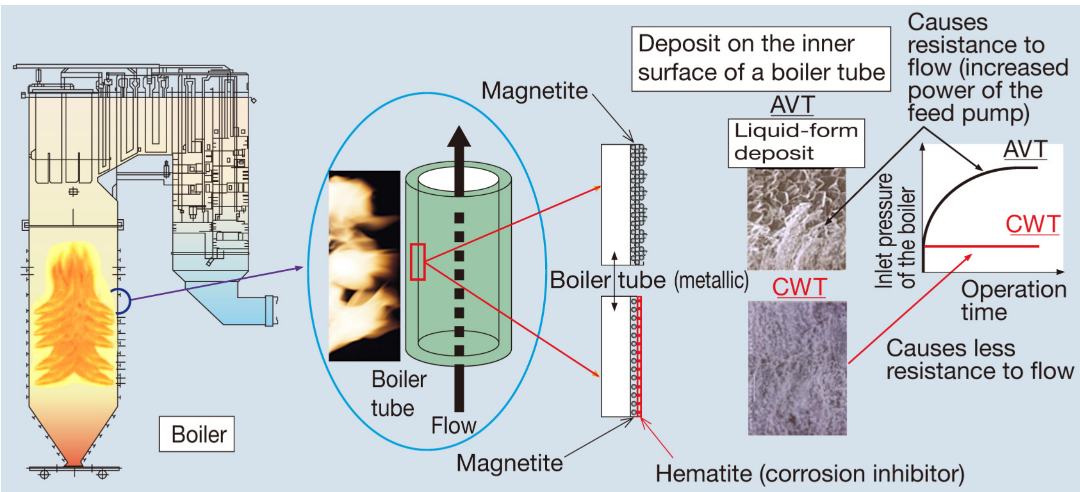


Figure 3 Comparison of the deposits on the inner surface of boiler tubes provided with All-Volatile Treatment (AVT) and oxygen treatment (CWT)

CWT is currently used in 50 boilers in domestic utility plants. The application is restricted to through-flow boilers equipped with a condensate demineralizer.

4.3 Treatment by a volatile substance with high pH value without using hydrazine (AVT(O)+High-AVT)

What is AVT(O)+High-AVT?

- All-Volatile Treatment (Oxidizing) (AVT(O)): No oxygen scavenger such as hydrazine is used.
- High-AVT: Water treatment incorporating high-pH all-volatile treatment in which the pH of the supplied water is set higher than that JIS standard requires.

Figure 4 shows an example of pipe wall thinning due to FAC that occurred in an overseas HRSG. The wall thinned by 1.2 mm after 3 years of operation. FAC frequently appears in an orange peel-like pattern over the part of pipe where wall thinning occurs, and this corrosion pattern is thus referred to as “orange peel corrosion.” Control of the flow rate, material, temperature, oxygen, and pH are the key factors in reducing FAC. CWT using oxygen and High-AVT using raised pH both have a remarkable effect in reducing the solubility of iron and have thus attracted much attention as effective countermeasures to pipe wall thinning due to FAC.

The FAC-reducing effect of High-AVT is demonstrated by the results of the experiment shown in **Figure 5**. The effect of the pH on the thinning rate due to FAC is significant. Reduction of the thinning rate is promising using High-AVT (pH 9.8–10.5) in place of conventional AVT (pH 9.0–9.6). High-AVT has been used in five overseas combined cycle thermal power plants delivered by our company. There have been no reports of troubles related to water since 2001.

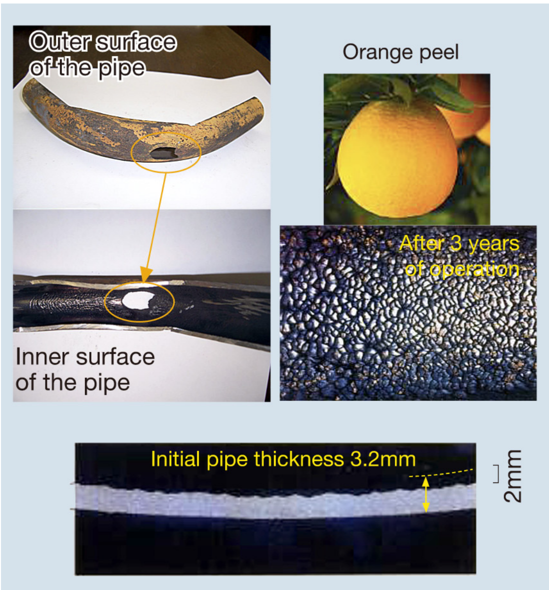


Figure 4 FAC example.

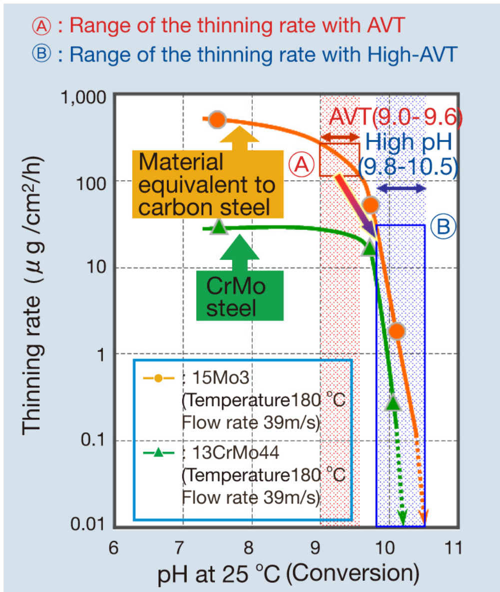


Figure 5 Effect of pH on the pipe wall thinning rate due to FAC.

Another advantage of High-AVT is that the effect of corrosion inhibition can be preserved without changing the water. **Figure 6** shows the results of a maintenance test using ammonia alone. When the pH was raised to 10.5, no rust could be detected after a lapse of 4 weeks (672 hours) in the absence of hydrazine. In other words, the application of High-AVT enabled treatment with ammonia alone, without requiring hydrazine or changing the water during either operation or maintenance.

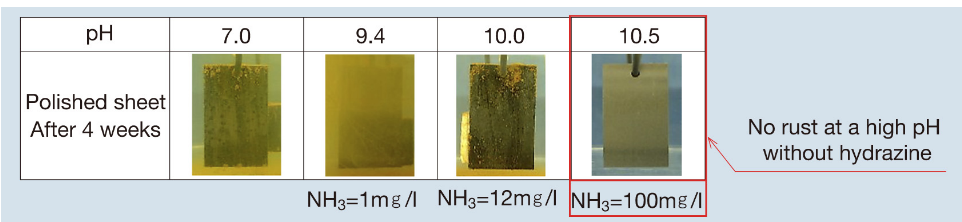


Figure 6 Results after 4 weeks of maintenance test using ammonia.

Currently, when boilers undergo maintenance for more than 3 days, boiler water is replaced with a high concentration of hydrazine, and the hydrazine is blown off before start-up. When using High-AVT, one may skip the processes for blowoff, water filling for maintenance, blowoff of maintenance water, and water filling for start-up (**Figure 7**). This also reduces the quantity of pure water used.

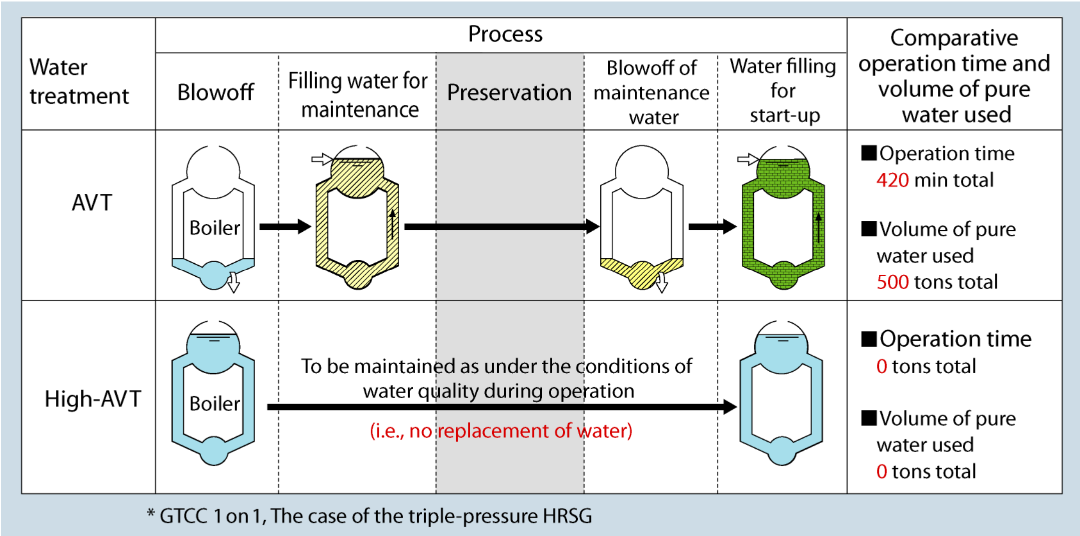


Figure 7 Difference in the long-term preservation process of plants using AVT and High-AVT.

5. Conclusion

Hydrazine is recognized as a mutagenic chemical substance. The alternatives to hydrazine used in overseas locations were investigated to reduce the impact of hydrazine on the environment. Some countries are ahead of Japan in adopting alternative chemicals and new water treatment techniques. From the standpoint of labor safety in particular, a policy of not using toxic oxygen scavengers has been adopted in certain cases. This is also the basis of the Electric Power Research Institute's measures in the United States to counter pipe wall thinning due to FAC as a means of improving plant reliability. The use of hydrazine alternatives does not require the development of new techniques. Since the behavior during the implementation of AVT(O) or High-AVT may be different from plant to plant, now is the time to apply these techniques in an actual plant demonstration to demonstrate their advantages in domestic plants.

References

(1) Mizuno, Water Treatment Agent Present situation of Alternatives to Hydrazine, Year Book of Boilers, 2006 Edition

(2) Tsubakizaki, S., Mawatari, K., Anai, T., Application of High-AVT to Combined Cycle Power Plant, Electrical Chemistry Congress in Autumn 2005,The University of Chiba, 2005

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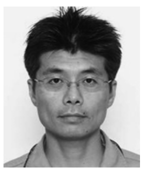

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