Evaluation of Oxygenated Water Treatment

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In order to settle some problems in once-through boilers in all volatile treatment (hereinafter "AVT"), our company researched combined water treatment (hereinafter "CWT"). After we adopted CWT, iron scale changed from magnetite to hematite, and scale generating speed was down to about half of AVT. The optimum condition (pH 8.5-9.0,DO50-100 μg/l) for water quality control in ordinary operation and start-stop has been determined. The criterion of chemical cleaning has been established through research on scale growth predictions and thermal conductivity in CWT. Although the CWT plants have condensate demineralizers to keep the feed water high purity, there might be localized corrosion, especially in the steam concentration area, so it is very important to understand the effects on turbine materials caused by trace impurities.

1. Introduction

AVT is the main method of boiler feed water treatment for once-through boilers in Japan. However, some problems, such as rise in boiler differential pressure due to scale adhesion, have become evident, because supercritical and varia-ble pressure operation for steam condition have been introduced to improve the generating efficiency. In order to settle these problems, our company researched CWT, a kind of oxygenated water treatment for about ten years beginning in 1982, ahead of other electric power companies. Consequently, the good results we expected have been obtained, such as suppression of the rise in boiler differential pressure, reduction of boiler feed water pump driving force, extension of chemical cleaning interval and so on, and at the same time, no particular effect on erosion or corrosion has been recognized, so we successively introduced CWT into 14 plants 10400 MW in total [1].

2. Features of CWT

AVT is the method that keeps dissolved oxygen close to zero and suppresses corrosion.

On the other hand, CWT is the method that keeps traces of the dissolved oxygen (20-200 μg/l) and forms a protective film called hematite (Fe_2O_3).

Hematite particle is fine and dense, so the surface of its protective film is flat, as shown in Fig. 1. The solubility of hematite is extremely small compared to magnetite (Fe_3O_4). Magnetite particle is relatively large, so undulation (wave-shaped) scale is formed on the surface of the metal.

3. Process of introducing CWT

Table 1 shows the actual performance of CWT introduction. Fourteen plants from Chita No.4 to Hekinan No.3 have been changed from AVT to CWT. However, Hekinan No.4 and No.5 were basically designed for CWT and operated on CWT from the commissioning stages.

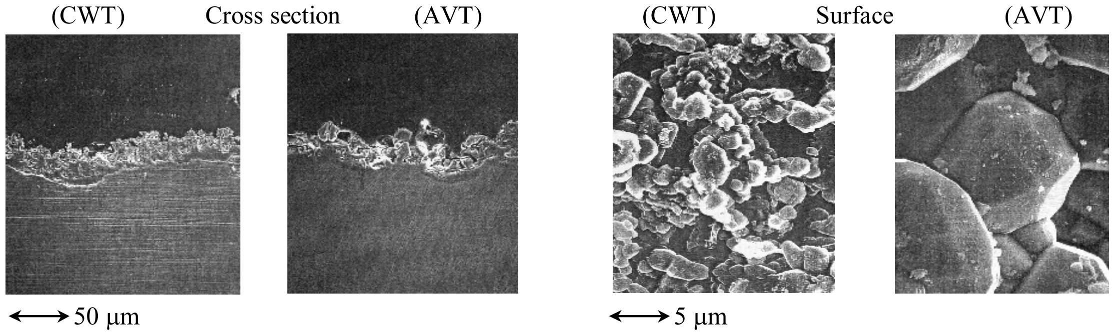

Fig. 1 SEM photomicrograph inside boiler tubes

Table 1 Process of introducing CWT to each plan

	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004
Chita-4 700MW			Installation	Major inspection			Major inspection				
Chita-5 700MW		Installation	Major inspection		Major inspection						
Chita-6 700MW	Installation		Major inspection	Major inspection							
Atsumi-3 700MW		Installation		Major inspection							
Atsumi-4 700MW	Installation	Major inspection	Major inspection								
Chita Second-1 700MW	Full-scale installation	Major inspection									
Chita Second-2 700MW	Installation	Major inspection									
Kawagoe-1 700MW									Installation		
Kawagoe-2 700MW							Installation		Major inspection		
Hekinan-1 700MW							Installation			Major inspection	
Hekinan-2 700MW		Installation		Major inspection							
Hekinan-3 700MW			Installation		Major inspection						
Hekinan-4 1000MW								Test-run		Major inspection	
Hekinan-5 1000MW									Test-run		

4. Optimum condition

Each plant was primarily tested on a couple of conditions of pH and DO. After the tests, the optimum condition in ordinary operation was judged to be pH 8.5-9.0 and DO 50-100μg/l, considering corrosion. In plants with electromagnetic filters (hereinafter "EMF"), it is better to set the pH close to 9.0 because the place of EMF is before oxygen injection, so iron concentration is relatively high. After the plant had been adopted the optimum conditions, it was confirmed that iron solution was decreased by formation of the protective film hematite. As for the optimum conditions at plant start-stop, it was judged by laboratory corrosion test to remain as it is, not injecting oxygen if the plant is scheduled to stop for under 72 h [2].

5. Results of periodical inspection of equipment

The condition of the equipment was checked at the periodical inspection every two years as well as at monitoring of ordinary operation. In each plant it has been confirmed that iron scale adhering to the equipment and boiler tube has been changed from magnetite to hematite and the adhering amount and thickness have a tendency to decrease. The scale generating speed was down to about half of AVT. It has been further lowered, as shown in Fig. 2.

On the other hand, erosion probably due to selective corrosion has occurred in the Stellite weld metal section of the control valve at some plant.

Taking all things into consideration, we changed the materials to ULTIMET from stainless steel as a measure for the Stellite section and also changed the plating method from chromium to nickel electrolysis as a measure for the BFP rotor sliding section of Hekinan-2 (available from Hitachi), but the measures of other plants (available from Ebara) are taken by replating at the time of periodical inspection.

As for EMF, it can be settled down for differential pressure rise by setting at pH 9.0 or bypassing the EMF. Corrosion and erosion of other parts are evaluated to be slight, so it has been concluded that there is no problem in long term use.

6. Criterion of chemical cleaning

Investigation and research were made into scale growth prediction by getting the periodical change of the scale amount and thickness, and judgment of the time of chemical cleaning by measuring the thermal conductivity in CWT, as shown in Fig. 3.

Results of extrapolation on the thermal load of the actual plant were scattered in a range of 0.4 to 2.0 W/mK, and the average was 0.86 W/mK. Then we established the criterion of chemical cleaning, and set it up about 230 g/m^2 as CWT [3].

Scale growth prediction in CWT is shown in Fig. 4. As a result, chemical cleaning is not required for about 180,000 hours. Sample tubes of CWT scale are not sufficient, so in order to enhance the precision, more tubes must be sampled at periodical inspection.

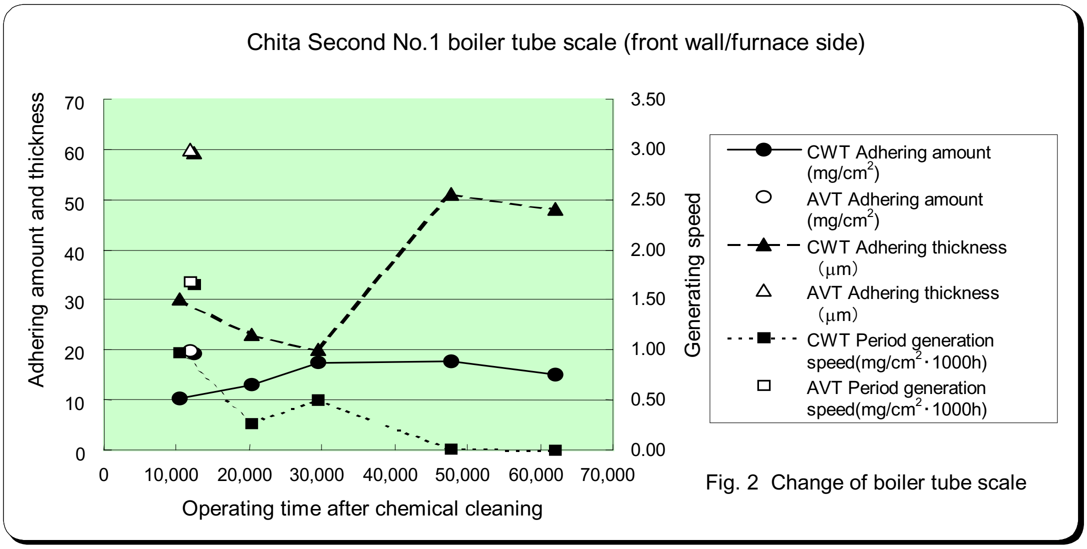

Fig. 2 Change of boiler tube scale

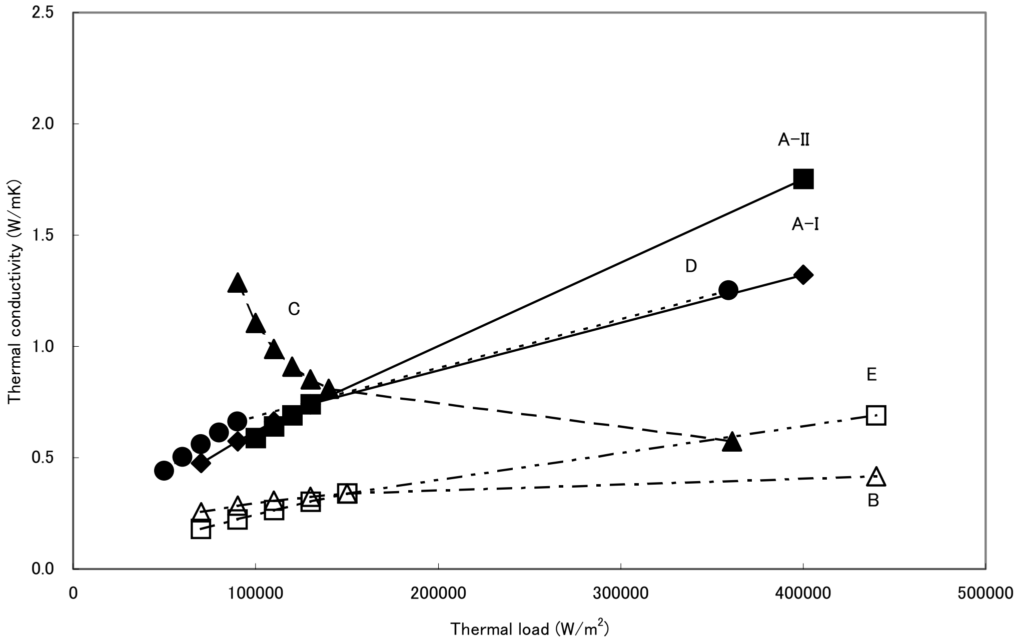

Fig. 3 Relation between thermal load and thermal conductivity
(A-I was sampled in October 1997, and A-II in September 1999.)

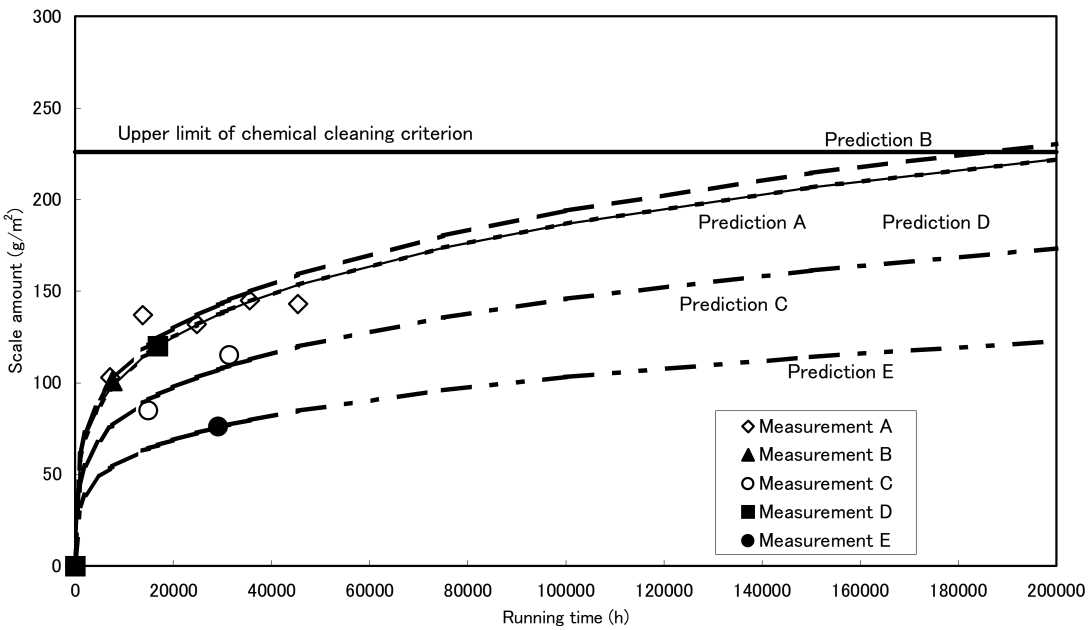

Fig. 4 Scale growth Prediction in CWT
(biquadratic rule)

7. Effects on turbine material by trace impurities

The CWT plant keeps the boiler feed water high purity. However, there might be localized corrosion by trace impurities in the steam concentration area of low-pressure turbines, so it is extremely important for water quality control to carry out tests under corrosive conditions simulating the wet-dry alternatiion and to understand the effects on turbine material.

Species prepared by turbine constituent material were inserted into an autoclave test container, simulating water adjusted to CWT water quality was allowed to flow, and a corrosion test was carried out under wet-dry alternating conditions.

The material that includes more chromium has superior corrosion resistance, and correlation is recognized between chromium content and corrosion amount, and corrosion effects on material by trace impurities generally tend to increase in the order of sulfate ion > sodium ion > chlorine ion, and effects on rotor material are more outstanding than on blade material, as shown in Fig. 5.

As for effects by dissolved oxygen, the corrosion amount of blade material is small, regardless of dissolved oxygen concentration, but the corrosion amount of rotor material tends to increase in proportion to the dissolved oxygen concentration even if there is no clearance, as shown in Fig. 6 [4-6].

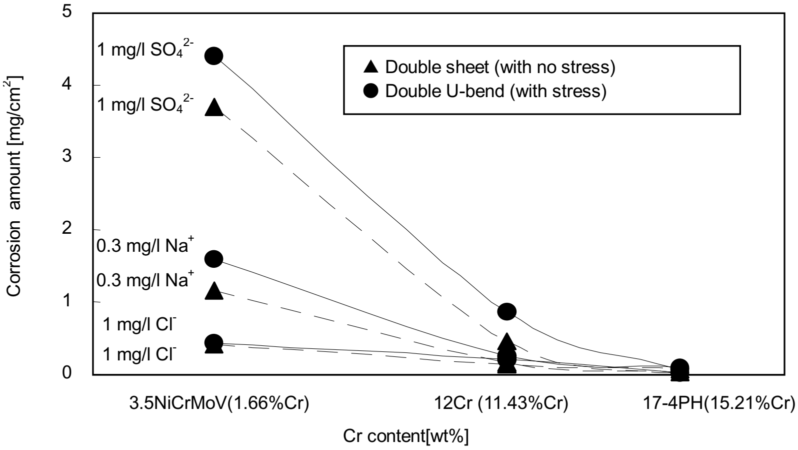

Fig. 5 Relation between corrosion rate and Cr content

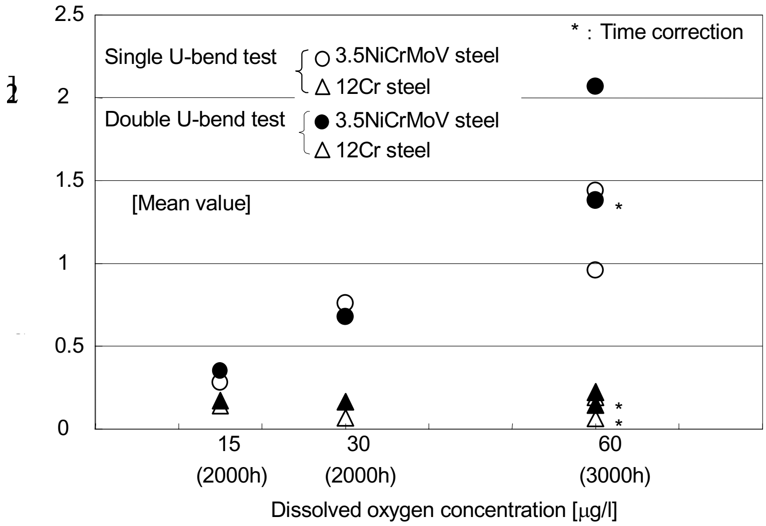

Fig. 6 Relation between dissolved oxygen concentration and corrosion amount (with stress)

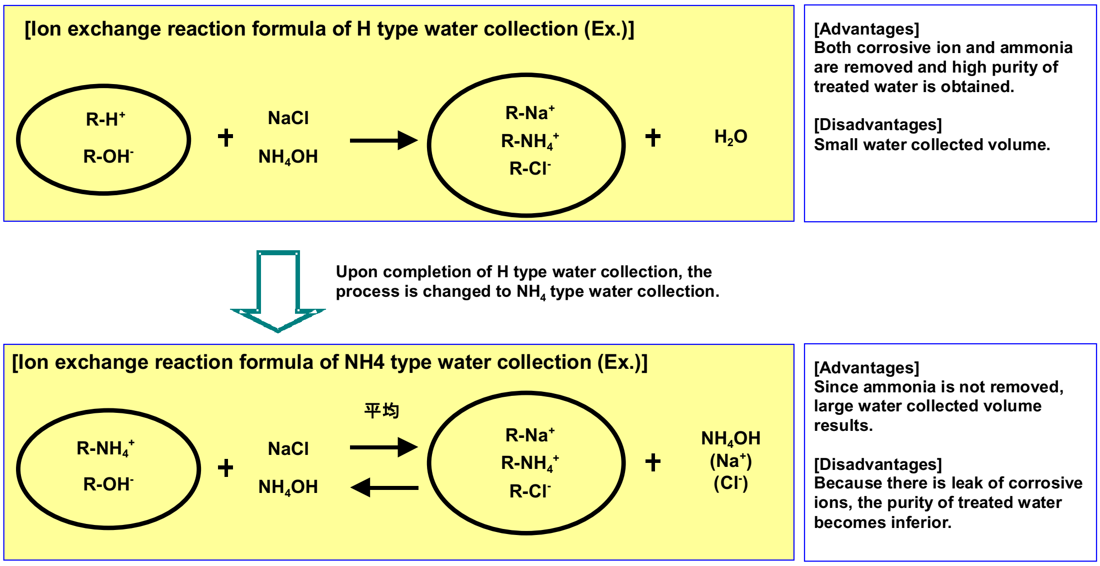

Fig. 7 Water collecting system and features of condensate demineralizer

8. Operating method of condensate demineralizer

Condensate demineralizer is necessary for a CWT plant. Figure 7 shows the ion exchange reaction scheme. There are two types for water collection, H-type and NH_4-type. H-type has higher perform-ance in removing corrosive ions than NH_4-type, so usually four H-type demineralizers are operated in a CWT plant. However, H-type has a smaller water collection volume than NH4-type. So the regener-ation time of ion exchange resin increased.

So we had to cut costs and wastewater volume. We carried out research to settle these problems by adopting NH_4-type water collection. After the long-term investigation, there were no problems in demineralizer performance, so we have come to the conclusion that one NH_4-type water collection out of four demineralizers is optimum operation [7].

9. Conclusions

The operation loss of each plant can be reduced 20-95% by adopting CWT, and approximately one billion yen/year can be estimated as the total cost saving amount. In addition, chemical cleaning of boilers is no longer required and nitrogen coming from regeneration wastewater of condensate demine-ralizer, which is regulated in 2004, decreases, so it can be said that CWT is environmental-friendly feed water treatment [8]. We'll continue to evaluate the long-term effects in the future, too.

Acknowledgements

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References and Notes

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