Effects of Advanced Amines on SG tube Fouling of Alloy 690TT Tube in Simulated Secondary Water of PWRs

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1. Introduction

In pressurized water reactors (PWRs), pH conditions such as pH control agents and pH values is very important water chemistry parameters to affect the steam generator (SG) tube fouling. Unfortunately, there are a few studies on the relationship between the pH control agents and SG tube fouling, which is an ongoing concern in the nuclear industry.

Ethanolamine (ETA) is widely used to control the pH value in secondary coolant water of PWRs [1]. Meanwhile, it is necessary to compare the other advanced amines which can replace ETA owing to its serious human hazards and environmental treatment costs. Among the various pH control agents, dimethylamine (DMA) and 3-methoxypropylamine (MPA) generally known to be less harmful to the workers in NPPs [2].

In this study, the effects of three advanced amines (ETA, MPA, and DMA) on the SG tube fouling of commercial 690TT tubes were evaluated in the simulated secondary system using a recirculation deposition loop. After the fouling tests, the deposit samples were characterized by using various analysis techniques and the amount of deposits was also measured by chemical cleaning process and inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis. The results were discussed in accordance with zeta potential of magnetite particles and Alloy 690TT specimen, particle size, deposit porosity, and magnetite solubility depending on the advanced amine agents. In addition, to compare the potential for replacing ETA with other advanced amines, a variety of factors, such as SG integrity and human hazard are also discussed.

2. Experimental procedure

2.1 Preparation of specimens

The tube specimens for fouling tests were prepared from the commercial Alloy 690TT tubes with a length of 500 mm, an outer diameter (OD) of 19.05 mm, and thickness of 1.025 mm. One side of the tube was perfectly welded with an Alloy 600 cap. The chemical composition of the Alloy 690TT tubes is presented in Table 1. After the ultrasonic cleaning the outer surface of the specimen with acetone, a stainless steel 316 cartridge heater of 600 mm length and an OD of 16.97 mm, which could simulate the primary water as a heat source was inserted into the tube specimen. During the inserting of the heater into the specimen, magnesium oxide (MgO) was spread to remove the air gap between the heater and the specimen.

Table I: Chemical composition of Alloy 690TT (wt. %).

Cr	Fe	Si	Mn	Ti	Al	C	Ni
29.3	10.4	0.3	0.3	0.3	0.2	0.02	Bal.

2.2 Preparation of test solution and fouling sources

In this study, we selected the ETA, MPA, and DMA as three representative advanced amine agents for use in the secondary water. To exclude the effect of magnetite solubility on the SG tube fouling, the pH value of amines should be same at 270 °C, the temperature at which the SG tube fouling tests were performed. Before a fouling test, we calculated the variation of the pH value of the three advanced amine solutions of ETA, MPA and DMA as a function of temperature using the MULTEQ code. The pH of ETA, MPA, and DMA was continuously maintained to be pH 10.0, 10.2, and 9.74 at 25 °C during the test to reach pH 6.56 at 270 °C under which conditions the SG tube fouling tests were conducted. Fe(II)-acetate was used as the fouling source in this study because Fe(II)-acetate was widely used to synthesize magnetite particles [3].

2.3 SG tube fouling loop system

Fig. 1 shows a schematic of the SG tube fouling loop system under simulated secondary water conditions. As shown in Fig. 1, the loop consists of three main parts: 1) a test section, 2) a secondary coolant water tank, and 3) the fouling source tank. Dissolved oxygen (DO) level of the loop system was maintained less than 2 ppb by N_2 gas purging. This was satisfied with the secondary water chemistry guideline of the Electric Power Research Institute (EPRI) [4]. When the loop system was ready to start, the pressure of the test section gradually was increased to 60 bar (above saturated pressure) using a back pressure regulator (BPR). After that, the preheater, line heater, band heaters around the test section, and the

cartridge heater are sequentially heated to reach the outer surface of tube specimen at 270 °C. The heat flux of the cartridge heater is controlled at 30 W/cm^2. The flow rate of the test solution was 260 ml/min. After the system was finally stabilized: temperature, pressure, pH, DO (< 2 ppb) and water flow rate, the Fe-acetate solution in the tank was continuously injected into the bottom of the test section with simulated secondary water at a flow rate of 1 ml/min for the control Fe concentration at 1 ppm in the test solution near the surface of tube specimen. Each of the fouling tests lasted 14 days.
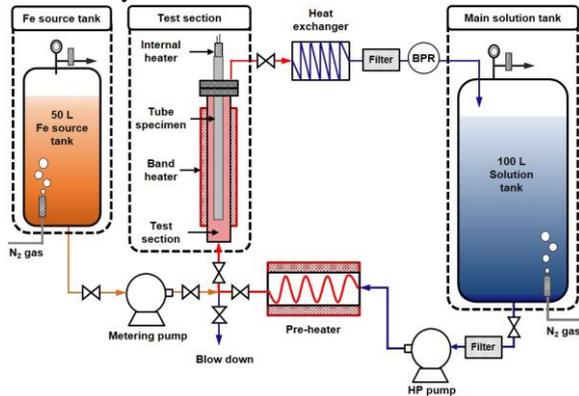

Fig. 1. A schematic diagram of the SG tube fouling loop system under simulated secondary water conditions.

2.4 Analysis of simulated deposits

The surface morphologies of the deposits were observed using a scanning electron microscope (SEM). The cross-sections of the deposits were prepared using the focused ion beam (FIB) technique, and 3 positions per specimen were observed by FIB-SEM. The two-dimensional porosity of the deposits was evaluated by an image analyzer. After the deposits were removed from the segments using a cutter, XRD analyses were performed to identify the structure of the deposits.

To measure the amount of deposits, the deposits were selectively dissolved by immersing in the chemical cleaning solution. After the chemical cleaning, dissolved solutions were directly analyzed using an ICP-AES analysis to measure Fe concentrations. It was confirmed that Alloy 690TT tube specimen was not corroded during the chemical cleaning process through the absence of Ni and Cr in results of ICP-AES analysis. Finally, the total amount of deposits per unit area was obtained by converting the weight of identified phase (pure magnetite in this work) using the measured Fe concentration.

3. Results and discussion

3.1 Characterization of deposits

Fig. 2 presents the surface morphologies of simulated deposits on Alloy 690TT tube when each of advanced

amines was contained. Various sized-particles in the range of about 100 nm~2 μm existed under all advanced amines. These deposit particles were the iron oxide formed on the outer surface of Alloy 690TT tube by synthetization of Fe(II) acetate. A number of pores between the deposit particles were also observed. The deposit particles are all polyhedral or spherical in shape regardless of advanced amine agents.
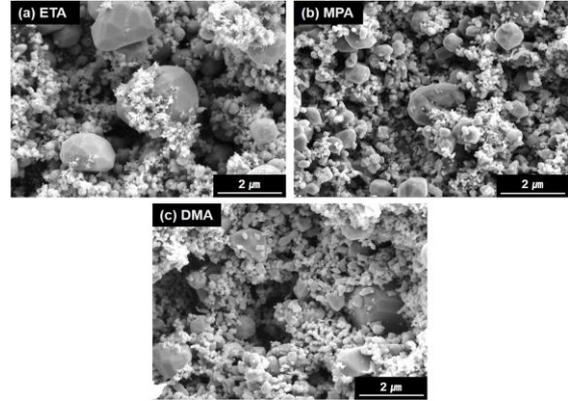

Fig. 2. SEM image of surface morphologies of simulated deposits on Alloy 690TT tubes under three advanced amine agents: (a) ETA, (b) MPA, and (c) DMA.

Fig. 3 presents the XRD patterns of the simulated deposits depending on the three advanced amines for comparison, the patterns of SG tube deposits taken from an operating PWR are also superimposed. The XRD diffraction patterns under all advanced amines were well matched with the pure magnetite XRD data (PDF No. 88-0866). In addition, XRD peaks of the real SG tube deposits show that the deposits were crystalline in nature and all the peak locations also corresponded to pure magnetite (PDF No. 88-0866) because the actual SG tube deposits mainly consisted of magnetite (about 95~96%) [5]. Based on the XRD results, the deposits produced by using the SG fouling loop system were well simulated the actual SG tube deposits.
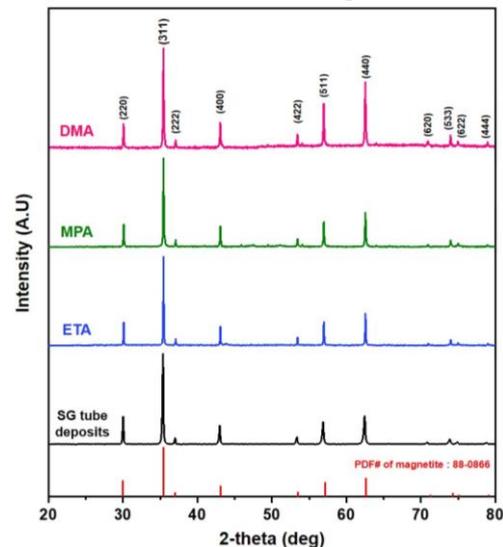

Fig. 3. XRD patterns of the simulated deposits depending on the three advanced amines and real SG tube deposits.

3.2 Consideration of the possibility of using alternative advanced amines instead of ETA

In spite of the many advantages of ETA, which is widely used in secondary systems of PWRs, the nuclear industry has interest in finding other advanced amines that could replace ETA because ETA is very harmful to on-site plant workers. Hence, the various factors such as SG integrity and human hazards were considered.

Fig. 4 shows the amount of magnetite deposits per unit area depending on the three advanced amine agents. The largest amount of deposits was formed when ETA was used in the secondary water (about 209.83 mg/dm^2). The amount of magnetite deposits in the case of MPA and DMA, compared to ETA, greatly decreased by approximately 41% and 55%, respectively. It represents that the different advanced amine agents greatly affect the magnetite deposition behavior of SG tube.

The amount of deposits has a negative effect on the heat transfer efficiency of the SGs. It is judged that the best heat transfer efficiency of SG is when DMA is used. In terms of SG integrity, DMA would be appropriate than that of the cases using ETA or MPA.
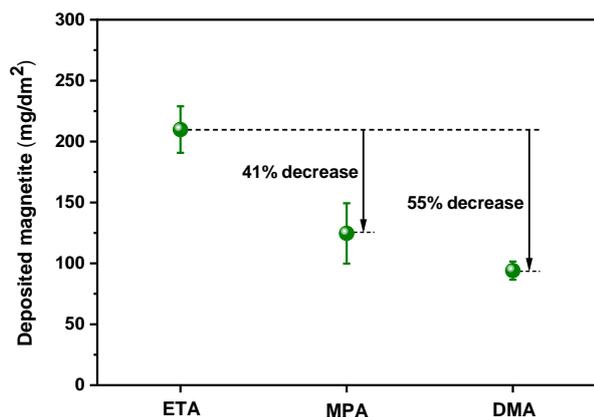

Fig. 4. The amount of magnetite deposits of Alloy 690TT tube depending on the three advanced amine agents.

In addition, we surveyed that the effect of various amine agents on the human body in NPPs. It is well known that all amine agents would be exposed to the atmosphere during work on-sites, and that most amines have deleterious effects on the human body. Among the various amines, ETA is known to have seriously deleterious effects on the human body. In U.S. Army Public Health Command (USAPHC), the human hazards of various amine agents were studied and reported in the Support Document to Technical Guide 230 [2]. According to this document, when the human was exposed to the amines in air, the critical amount of ETA, MPA, and DMA that could cause the deleterious effects to human body is 75, 150, and 460 mg/m^3 per hour, respectively. That is, compared to the MPA and DMA, ETA would be the most harmful to workers in NPP sites.

By comparative analyses about alternative possibility of MPA and DMA for ETA, it is concluded that DMA is the more proper advanced amine than MPA to replace ETA because DMA was superior to ETA and MPA in terms of human toxicity and heat transfer efficiency of SGs.

In the future, the zeta potential of magnetite and surface zeta potential of SG tubes and porosity of magnetite deposits will be analyzed soon. These results will be present at the oral presentation.

4. Conclusions

1) The deposited magnetite particles were polyhedral or spherical under all amine agents. Compared to ETA, the amount of magnetite deposited with MPA and DMA significantly decreased by about 41% and 55%, respectively.

2) Compared to ETA, DMA has many advantages in terms of SG fouling control and human safety, so it is worth considering DMA as an alternative pH control agent to replace ETA, which is currently widely used for this purpose in PWRs.

ACKNOWLEDGEMENTS

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