Recent Water Chemistry Strategies on Steam Generator Tube Fouling Mitigation in PWR Secondary Water

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1. Introduction

In secondary system of pressurized water reactors (PWRs), flow accelerated corrosion (FAC) occurring in the feed train of a steam generator (SG) will lead to increase the iron concentration in the feedwater and form the iron oxide on feedwater piping and components [1,2]. After then, the corrosion product particles are transported into the SG from feedwater and deposited on the SG tube free span, top of tube sheet, and tube support plates. This deposition phenomena is generally defined as SG fouling [1].

The SG fouling will form the micro-crevices in which impurities concentrate, potentially forming highly corrosive environments that can lead to stress corrosion cracking (SCC) and eventually SG tube failure and plugging [1]. In addition, the SG fouling also can reduce the heat transfer capability of SGs, lead to thermal-hydraulic instabilities through blockage of tube support plates [1-3].

The SG performance is compromised not only by formation of an insulating scale, but by the tube removal from the service due to corrosion. The occurrence probability for these problems is significantly affected by the characteristics and amount of the SG deposits. Therefore, the reducing the SG fouling is important to improve the SG integrity.

Currently, there are two options employed by utilities for minimizing the SG tube fouling. The first option is to minimize the iron source term (reduce the amount of corrosion products in the feedwater) [1]. To achieve this goal, three methods (chemistry optimization, plant modifications, and deposit removal) are commonly used. The first method uses alternate amines to control the pH in specific locations of the secondary system, thereby minimizing the corrosion of balance of plant metals. The second method requires the removal of metals from the secondary system that are a significant source of corrosion products. The third method utilizes the chemical cleaning or sludge lancing to remove existing deposits from the SGs. Many nuclear power plants have opted for a combination of these methods [1]. The two option is to minimize the deposition rate of corrosion products on SG internal surfaces. The use of online dispersant addition such as polyacrylic acid could prevent the corrosion products from adhering to the SG surfaces [1,4,5]. By inhibiting the deposition of the corrosion products, the dispersant can facilitate more effective removal from the SGs during blowdown [1,4,5]. In addition to dispersants, the SG fouling rate could be reduced through the other water chemistry controls.

Recently, our group newly developed a recirculating loop system for SG tube fouling test (Fig. 1) [6]. Using this loop system, the effects of various water chemistry factors (pH values, pH agents, impurities, and the addition of film forming amine) on the SG tube fouling rate were investigated in Korea Atomic Energy Research Institute (KAERI). This paper summarizes the some researches on water chemistry strategies to reduce SG fouling phenomena and proposes the optimal water chemistry conditions.

Fig. 1. Recirculation secondary loop system for SG tube fouling test developed in KAERI.

2. Methods

2.1 Specimen preparation and film formation by addition of octadecylamine (ODA)

Alloy 690TT tube specimens were cut with length of 500 mm, an inner diameter (ID) of 17.00 mm, an outer diameter (OD) of 19.05 mm, and thickness of 1.025 mm. One side of the specimens was blocked by welding with a cap of diameter of 19.05 and thickness of 2.0 mm. The chemical composition of the SG tube used in this work is presented in Table I. A cartridge heater made by stainless steel 316 was totally covered with magnesium oxide and was directly inserted into the SG tube specimens.

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

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

Fig. 2 shows the film formation on the specimens by ODA addition [7]. SG tube specimen was for fouling test and several piece specimens were for various analyses of organic film. The film forming solution was used in deionized water containing 500 ppm ODA and 25 ppm ethanolamine (ETA) with pH 10.0 at 25 °C. The film was formed on the surface of the specimens in an autoclave at 230 °C for 10 days [7].
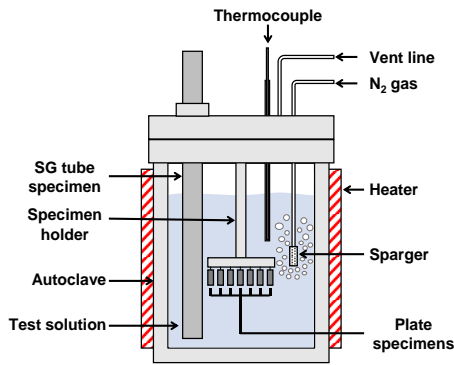

Fig. 2. Schematic of film formation on the specimen by ODA addition.

2.2 SG tube fouling test

In deposition loop system, the flow rate of the circulating water was controlled at 260 ml/min. The concentration of dissolved oxygen was continuously maintained below 5 ppb during the fouling test. The pH of the circulating water was maintained at 9.0 and 10.0 by injecting diluted solutions of various pH agents (ETA, ammonia, 3-methoxypropylamine (MPA), dimethylamine (DMA)), and the pH value was continuously monitored using an in-situ pH sensor. The pressure of test section was then gradually increased to 60 bar by the back pressure regulator, and the water temperature near the tube surface was maintained at 270 °C to maintain subcooled nucleate boiling conditions by operating the pre-heater, ceramic heaters surrounding the test section, and the internal heater inside the SG tube specimen.

After test conditions were stabilized, iron sources were injected into the test section through the metering pump with a flow rate of 1 ml/min from the source tank. The precursor solution was diluted in the simulated secondary water stream and its final concentration was calculated as 1 ppm iron in the test section. Each fouling test was conducted for 14 days.

2.3 Amount and microstructure analysis of SG tube deposits

After the fouling tests, the SG tube specimens were cut into tubular segments for the measurement of magnetite mass and microstructural analysis of the magnetite. To evaluate the amount of deposits, two tubular segments of about 20 mm in length at different axial locations were immersed separately in ethylenediaminetetraacetic (EDTA)-based solution at 93 °C for 12 hours to selectively dissolve the magnetite only. The dissolved solution was analyzed using an inductively coupled plasma (ICP) analysis to measure the iron concentration. Finally, the amount of magnetite per unit area was calculated by using the measured iron concentration.

The deposits were analyzed by using a focused ion beam (FIB)-SEM to observe closely the cross-section of deposits. The deposit particle morphology, chemical composition, and deposit layer thickness were analyzed using FIB-SEM attached with an energy-dispersive X-ray spectroscopy (EDS).

3. Results and Discussions

3.1 Effect of representative pH agents and values on SG tube fouling

ETA and ammonia are recently used to control pH value in secondary coolant water of PWRs. In addition, the pH of feedwater recently elevated pH of up to 10.0 has been under consideration to decrease flow accelerated corrosion (FAC). Fig. 3 presents the amount of corrosion deposits per unit area deposited onto the SG tube, which indicates that the pH control agents and pH values (9.0 and 10.0) clearly affect the SG fouling behavior. The lowest amount of corrosion deposits was formed when pH was controlled with ammonia at a pH of 10.0. The amount of deposits in the case of ETA at pH 10.0, compared to ammonia, increased about 2.6 times, respectively. Furthermore, under all pH agents, the amount of deposit decreased on the SG tube at pH 10.0 value compared to that on the SG tube at pH 9.0 value. Based on the results, ammonia at pH 10.0 is the most beneficial pH conditions in the viewpoint of SG tube fouling mitigation in SG.
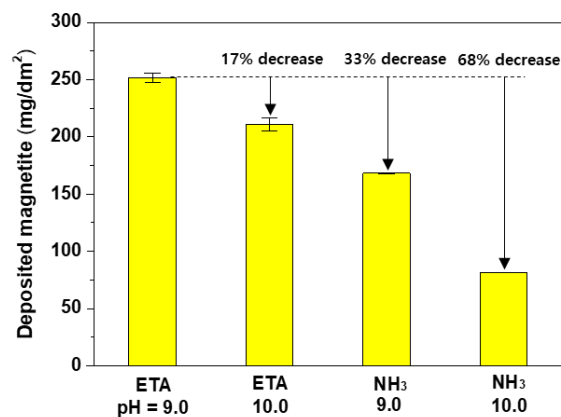

Fig. 3. The amount of magnetite per unit area deposited onto the SG tubes depending on the widely used pH control agents and pH values.

3.2 Effect of advanced amines on SG tube fouling

Recently, in spite of the many advantages of using ETA in secondary water of PWRs, the nuclear industry has developed interest in other advanced amines that could replace ETA [8]. This is because ETA is very harmful to the human body and is problematic when treating it in the environment. Among the various amines, MPA and DMA are well known to be less harmful to the human body than ETA. ETA is known to be more toxic than MPA and DMA to the human body, so ETA is disadvantageous in maintenance and storage. For these reasons, we selected these advanced amines (MPA and DMA) to see if they might be used to replace ETA in the secondary system of PWRs.

Fig. 4 shows the amount of magnetite deposited per unit area on Alloy 690TT tubes depending on the amine used. As seen in the figure, the largest deposits were formed when ETA (approximately 209.83 mg/dm^2) was added to the secondary water. The amount of magnetite deposited in the case of MPA and DMA, compared to ETA, was about 41 and 55% less, respectively. These results indicate that the choice of advanced amine clearly positively affects the SG fouling rate [8].
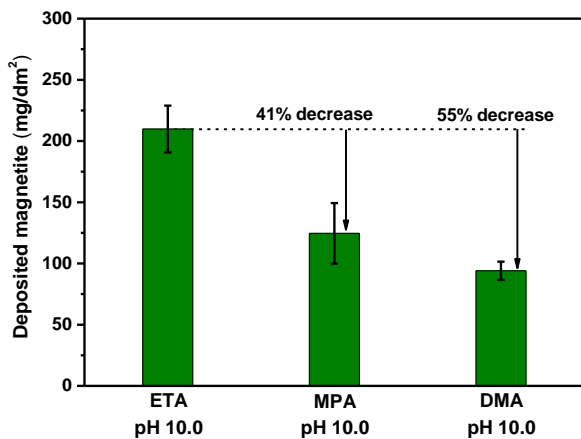

Fig. 4. The amount of magnetite per unit area deposited onto the SG tubes depending on the three advanced amines.

3.3 Effect of film forming amine on SG tube fouling

Film forming amine in PWRs was recently applied to reduce the corrosion rate of carbon steel and low alloy steel. However, there have been few studies on the effect of film forming amine addition on the SG tube fouling in the secondary system of PWRs. Therefore, the effect of film forming amine on the SG tube fouling behavior in secondary water of PWR was investigated.

Fig. 5 shows the amount of the deposits of both specimens. The amount of deposits of the film-formed specimen decreased approximately 58% compared to that of the as-received specimen. This indicates that SG fouling behavior was heavily dependent on the surface states of the SG tube [8].
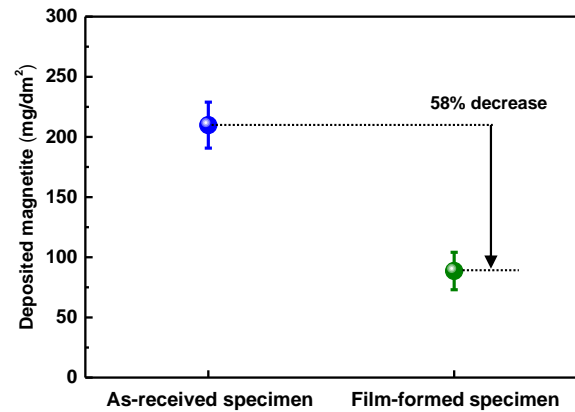

Fig. 5. The amount of magnetite per unit area deposited onto the SG tubes depending on film formation.

In order to elucidate the mechanism on effect of water chemistry factors on SG tube fouling behavior, zeta potential of corrosion product particles and surface zeta potential of SG tube should be measured. The results of zeta potential and microstructure data of deposits will be presented at the oral presentation. In addition, the optimal water chemistry condition for SG tube fouling mitigation will also discussed at the presentation.

4. Conclusions

1) In real operating pH condition of PWRs, ammonia at pH 10.0 is the most beneficial pH condition in the viewpoint of SG tube fouling mitigation in SGs.

2) Compared to ETA, DMA has many advantages in terms of SG tube fouling mitigation, human safety, and environmental treatment cost. Hence, it is worth considering DMA as an alternative pH control agent to replace ETA.

3) Based on the SG fouling results, we think that the application of film forming amine could be considered as a potential strategy to reduce the fouling problem of SG tube.

ACKNOWLEDGEMENTS

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