Influence of film forming amine on fouling behavior of steam generator tube in PWR secondary water at 270 ºC

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1. Introduction

Film forming amine (FFA) addition in nuclear power plants (NPPs) was considered as an alternative corrosion inhibition method for the inorganic inhibitors. In general, FFA are defined by the general formula R_1-[NH-(R_2)-]n-NH_2, where n is an integer between 0 and 7, R_1 is an unbranched alkyl chain with 12 to 18 carbon atoms and R_2 is a short-chain alkyl group that usually contains 1 to 4 carbon atoms [1].

The addition of FFA can produce a protective hydrophobic film on exposed surface of secondary structural components, thereby isolating the surfaces from corrosive environments and reducing the corrosion rate of components [2]. Among of various FFA, octadecylamine (ODA) has been applied to reduce the amount of the corrosion products at Almaraz Unit 1 and 2 (PWR Units) in Spain during plant operation since 2011 and at Embalse (PHWR Unit) in Argentina during layup period in 2015 [3].

To expand FFA injection to the secondary system of NPPs, the effect of FFA addition should be considered not only for corrosion behavior of carbon steel piping but also for fouling behavior on steam generator (SG) tube. However, there are few studies on the effect of the FFA addition on the fouling behavior of SG tube in secondary water of PWRs.

In this study, the influence of FFA addition on the fouling behavior of Alloy 690 SG tube in secondary water of PWR was investigated using a newly designed deposition loop system. ODA was selected in this study because it is widely used in NPPs. The effect of organic film-formed surface on fouling behavior is discussed from the viewpoint of wettability and electrochemical properties.

2. Experimental procedure

2.1 Specimen preparation and film formation

SG tube specimens were selected the Alloy 690 SG tube 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 Alloy 690 tube used in this study 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 690 (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. 1 is a schematic of film formation on the specimens by addition of ODA. Two types of specimens were hanged to specimen holder. One tube specimen was for magnetite deposition test and seven plate specimens were for various analyses of organic film. The film forming solution was used in deionized water containing 25 ppm ethanolamine (ETA) and 500 ppm ODA with pH 10.0 at 25 ºC. The organic film was formed three times on the surface of the specimens in an autoclave at 230 ℃ for 10 days.

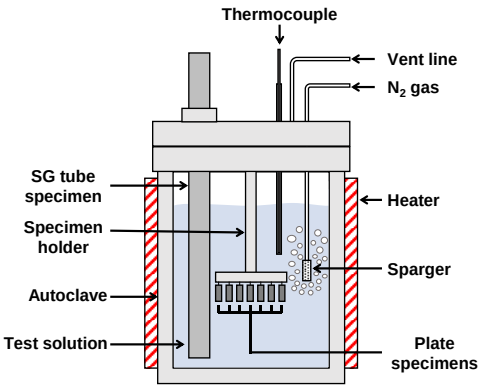


Fig. 1. Schematic of film formation on the specimen by ODA addition.

2.2 Analyses of the film formed on SG tube

The surface roughness of the film-formed and as-received specimens was measured using a non-contacting surface profiler. In addition, wettability of both specimens was measured using the contact angle between the surface of the specimen and the water droplet. Surface morphology and chemical composition of the film was observed by using scanning electron microscope energy dispersive X-ray spectroscope (SEM-EDS). To measure the electrochemical properties of film formed on Alloy 690 tube, electrochemical impedance spectroscopy (EIS) and zeta potential measurement were performed.

2.3 SG tube fouling loop system

The loop consists of three main parts: 1) the test section, 2) the secondary coolant water tank, and 3) the Fe ion source tank. DO level of a loop system was maintained less than 2 ppb by nitrogen gas purging. That 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 using the BPR. After that, the preheater, line heater, band heaters around the test section, and the cartridge heater are sequentially heated to reach the surface of tube specimen at 270 °C. The heat flux of the cartridge heater is maintained 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 source tank was continuously added into the bottom region of the test section with system water at a flow rate of 1 ml/min for the maintaining Fe concentration at 1 ppm in the secondary water near the surface of tube specimen. The fouling tests were conducted for 14 days.

2.4 Analysis of simulated deposits

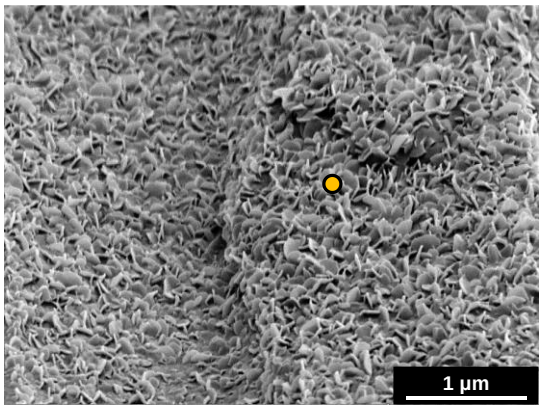
The surface morphologies and chemical composition of the SG tube deposits were observed using a SEM-EDS. The cross-sections of the deposits were observed by focus ion beam (FIB)-SEM. To measure the amounts of SG tube deposits, the deposits were selectively dissolved by immersing in chemical cleaning solution. The dissolved solutions were directly analyzed to an inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis to measure the Fe concentration. Finally, the amount of deposits was converted to magnetite using the measured Fe concentration and calculated to per unit area.

3. Results and Discussion

3.1 Surface characteristics of the film

The surface roughness on the both specimens were 0.246 μm for the as-received specimen and 0.252 μm for the film-formed specimen. This result indicates that the film formation by addition of ODA does not greatly affect the surface roughness of specimens. The surface of as-received specimen had the contact angle of 77 ± 1°, whereas the surface of film-formed specimen had the contact angle of 110 ± 2°. The contact angle is a measure of the wettability of the surface, i.e., whether the surface is hydrophobic or hydrophilic properties. A high contact angle corresponds to a lower surface wettability.

Fig. 2 shows the surface morphology and a chemical composition of the film formed on the Alloy 690 tube by SEM-EDS analysis. The film had a petal-like morphology and was uniformly distributed on the tube surface. It was mainly composed of C, N and O. The metallic elements such as Cr, Ni, and Fe were rarely detected.



Element	C	N	O	Cr	Fe	Ni
at. %	89.85	5.66	3.49	0.58	0.09	0.33

Fig. 2. Surface morphology and a chemical composition of the film formed on the tube.

The value of the zeta potential of the magnetite nano-particles was -33.0 mV. Meanwhile, the surface zeta potential of as-received and film-formed plate specimens were measured to be -39.4 and -41.0 mV, respectively.

Fig 3 shows the EIS measurement results of the both specimens. The radius of Nyquist arc of as-received specimen is smaller than that of film-formed specimen. The measured EIS data were analyzed in more detail by fitting them to the EEC shown in Fig. 4. It is composed of a parallel combination of the electric double layer (EDL) and passivation film. The EIS data were fitted using the GAMRY software. The R_{ct} of the film-formed specimen was about 3.1 times higher than that of as-received specimen. In addition, the R_f of the film-formed specimen was slightly higher than that of as-received specimen.

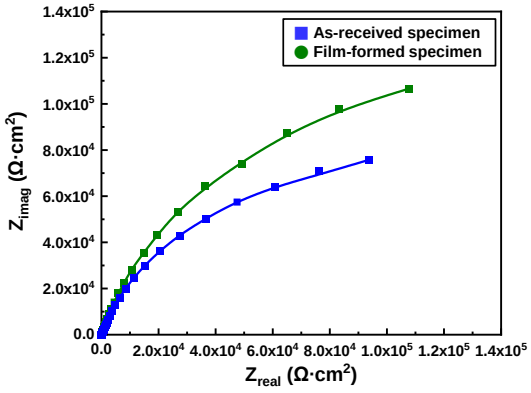


Fig. 3 EIS measurement results of the both specimens.

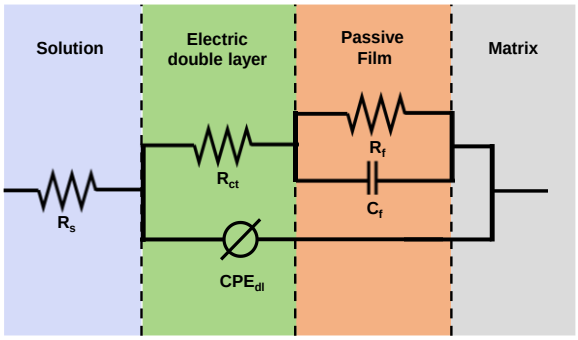
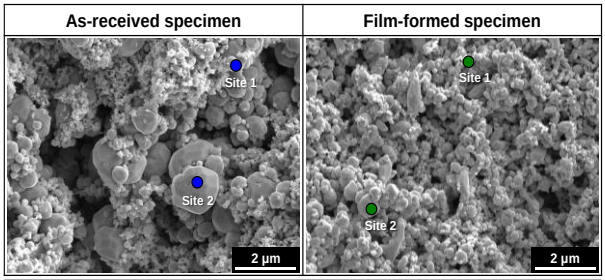


Fig. 4. Electrical equivalent circuit used to fit the EIS result.

3.2 Morphology and chemical composition of the simulated deposits

Fig. 5 shows the surface morphologies and chemical composition of the simulated deposits of both specimens. All deposit particles are polyhedral or spherical in shape regardless of film formation. Various sized particles within the range of approximately 50 nm to 2 μm were observed in both specimens. In particular, the size of particle formed on as-received specimen was larger than that of film-formed specimen. Based on the SEM-EDS results, it was concluded that all simulated particles were identified as magnetite regardless of particle size and film presence.



	As-received specimen		Film-formed specimen	
Element	Site 1	Site 2	Site 1	Site 2
O (at.%)	56.5	57.5	57.0	57.7
Fe (at.%)	43.5	42.5	43.0	42.3

Fig. 5. SEM-EDS analysis of the simulated SG tube deposits.

3.3 Amount of the simulated deposits

Fig. 6 shows the amount of the simulated deposits of both specimens. The amount of magnetite deposited on the as-received and film-formed specimens were about 209.8 mg/dm^2 and 88.6 mg/dm^2, respectively. The amount of deposits of the film-formed specimen decreased approximately 58% compared to that of the as-received specimen. This indicates that magnetite deposition was heavily dependent on the surface states of the SG tube.

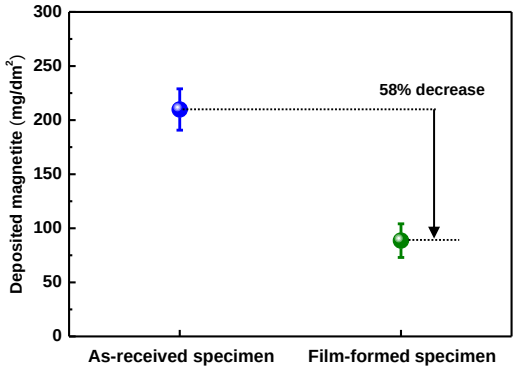


Fig. 6. Amount of the simulated SG tube deposits.

In this study, because most of the factors were carefully controlled in our deposition tests, we considered the four parameters such as the surface roughness, wettability, zeta potential and EDL resistance. Although the surface roughness of both specimens was similar, the film-formed surface has a more hydrophobic property than the as-received surface. Therefore, it is expected that the amount of magnetite deposits of film-formed specimen will increase compare to that of as-received specimen. The difference in the zeta potentials between the magnetite particles and the tube surface slightly increased by the film formation. In addition, the charge transfer resistance of the filmed surface in the double layer was also greater by about 3.1 times than that of the as-received surface. Hence, the amount of magnetite deposits on film-formed tube will decrease compare to that of as-received specimen.

As shown in Fig. 6, the amount of deposits of the film-formed specimen decreased approximately 58% compared to that of the as-received specimen. The reason why the amount of magnetite deposit on film-formed SG tube decreased is that the reduction effect by difference of zeta potential and EDL resistance was greater than the acceleration effect by difference in SNB with wettability change.

In future work, we plant to perform the experiment with film formation and magnetite deposition at same time through equipment modification.

4. Conclusions

1) The organic film formed on the specimen had a petal-like morphology and mainly consisted of C, N and O. The filmed-surface turned more hydrophobic with little change in surface roughness.

2) The deposition tests revealed that the amount of magnetite deposits on the filmed tube decreased by about 58% compared to that on the as-received tube due to the change of zeta potential and EDL resistance.

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

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