

## Dissolution Behavior of Magnetite Deposits Accumulated in a Printed Circuit Steam Generator during an EDTA-Based Chemical Cleaning Process

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### 1. Introduction

A printed circuit steam generator (PCSG) is a plate type of heat exchanger in which flow mini-channels are alternately stacked to form a block. Mini-channels generally have hydraulic diameters ranging from 300  $\mu\text{m}$  to 2 mm [1]. Therefore, PCSGs have excellent heat transfer surface area per unit volume than commercial shell-and-tube steam generators. Because of this advantage, the PCSG has been a growing interest in the development for application to small modular reactors. However, small flow channels can act as a weakness in terms of a fouling phenomenon.

Fouling in a nuclear power plant refers to a phenomenon that magnetite ( $\text{Fe}_3\text{O}_4$ ) deposits are accumulated on the surfaces of steam generator tubes or tube support plates [2,3]. Severe fouling leads to undesirable results such as thermal hydraulic instability, thermal performance degradation, and coast-down operation [4,5]. PCSGs are expected to be much more vulnerable to fouling compared to conventional SGs due to the small flow channel size. Therefore, it is essential to remove magnetite deposits accumulated on the flow channels of PCSGs. Nevertheless, no experimental research on the removal of deposits in PCSGs has been investigated to date.

The purpose of this work is to investigate the dissolution behavior of magnetite deposited on the flow channel surfaces of a PCSG. Additionally, the corrosion of the PCSG material was evaluated under the chemical cleaning condition.

### 2. Experimental Methods

#### 2.1. Preparation of the PCSG

PCSGs were produced through two major processes. First, flow channels were photo-chemically etched into a STS 316L plate with the dimensions of 84 mm x 850 mm x 5 mm as shown in Fig. 2(a). After then, the etched plate was diffusion-bonded without inserting an interlayer with an STS 316L cover plate with the same dimension as the channel plate as shown in Fig. 2(b). After bonding, STS 316L tubes were welded to the ends of both the inlet and outlet of the PCSG, which served as headers.

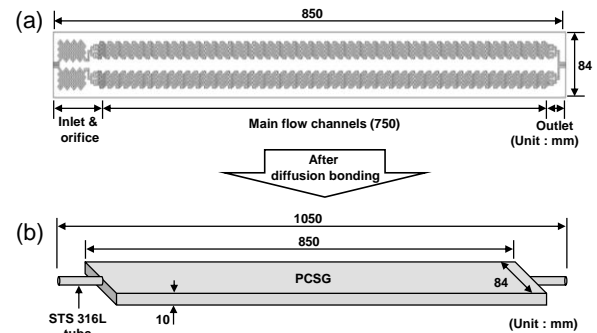


Fig. 2. Manufacturing processes and detailed dimensions of the PCSG: (a) etched plate, (b) after diffusion bonding.

#### 2.2. Fouling test

The fouling tests were performed for 500 h each using two fresh PCSGs under the simulated secondary-side operating condition of a small modular reactor. The  $\text{pH}_{25\text{ }^\circ\text{C}}$  and dissolved oxygen of the feedwater were maintained at about  $9.8 \pm 0.2$  and below 5 ppb, respectively. The feedwater of 230  $^\circ\text{C}$  was fed into the PCSG inlet at a flow rate of 340 mL/min. At this time, heat fluxes were supplied to the PCSG main flow channel surfaces using electric heaters to generate superheated steam of 303.5  $^\circ\text{C}$ . The superheated steam which is effused through the PCSG outlet was transformed to single-phase liquid again through a condenser. Iron acetate was artificially injected as a fouling source into the feedwater, so that the iron concentration of the feedwater flowing into the PCSG inlet was a constant 100  $\mu\text{g/L}$  until the test over.

#### 2.3. Chemical cleaning of deposits within PCSGs

After the fouling test, PCSGs were cleaned using an EDTA-based cleaning solution. The EDTA-based solution is composed of the following chemical compositions: 20 wt.% diammonium ethylenediaminetetraacetic acid ( $(\text{NH}_4)_2\text{EDTA}$ ), 1 wt.% hydrazine ( $\text{N}_2\text{H}_4$ ), 1 wt.% corrosion inhibitor (CCI-801). The pH of the cleaning solution was adjusted to 7.0 at 25  $^\circ\text{C}$  with ammonium hydroxide ( $\text{NH}_4\text{OH}$ ).

One PCSG was bisected along the centerline between the symmetric flow channels, and then each main flow channel region was cut widthwise into ten equal zones.

One symmetrical flow channel was used to identify the deposit characterization. The other channel was used to quantify the amount of deposits removed from the non-circulation and circulation cleaning method. The chemical cleaning was performed in two steps: first, each PCSG segment was immersed in a static reaction cell containing the chemical cleaning solution at 93 °C for 12 h; in the second step, specially made jigs were mounted to both ends of the PCSG segment, so that the cleaning solution could be circulated further for 12 h.

Another PCSG was cleaned without sectioning. The cleaning solution was fed into the PCSG inlet using a pump. The chemical cleaning was performed at 93 °C for a total of 42 h, and sampling was periodically conducted to measure the iron concentrations dissolved in the cleaning solution. After sampling, the cleaning solution was always replaced with a new one.

After the all cleaning processes were terminated, the concentrations of iron ions dissolved in the chemical cleaning solutions were analyzed using inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

#### 2.4. Corrosion behavior of a PCSG material

The corrosion of the PCSG material, which may occur during chemical cleaning, was evaluated from the weight change for 42 h. In addition, the surfaces of corrosion coupons were examined using a scanning electron microscope (SEM) to compare the corrosion behavior before and after the chemical cleaning process.

### 3. Results and Discussion

#### 3.1. Characteristic of the deposits

Fig. 3 shows the scanning transmission electron microscope (STEM) image and energy dispersive spectroscopy (EDS) analysis results of deposits attached on the flow channel surfaces after the fouling test. The results of the EDS point analyses revealed that the chemical composition of the deposit particles had a stoichiometry corresponding to that of magnetite. Therefore, the above results provided a solid basis for the selection of the EDTA-based chemical cleaning solution.

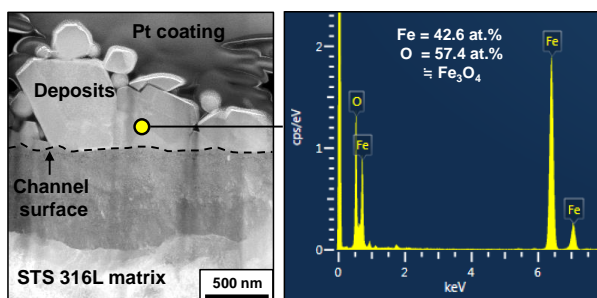


Fig. 3. STEM image and EDS spectra of deposits accumulated on the channel surfaces.

#### 3.2. Dissolution behavior of magnetite deposits

Fig. 4 shows the dissolved iron concentration in the cleaning solution after cleaning two PCSGs in different cleaning methods. The blue solid squares in Fig. 4 show the magnetite dissolution behavior of the full-length PCSG under the circulation cleaning condition. The magnetite dissolution reaction proceeded rapidly in the early stage of chemical cleaning. The dissolved iron concentration was no longer increased after a cumulative cleaning time of 30 h, indicating the magnetite deposits were completely dissolved within 30 h.

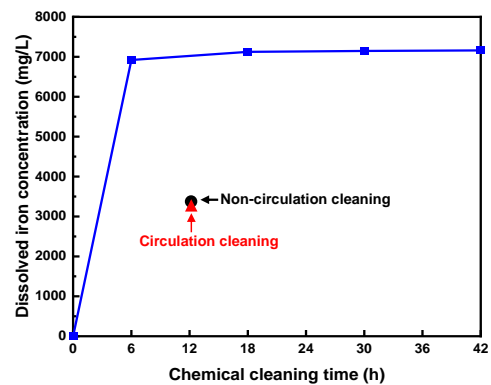


Fig. 4. STEM image and EDS spectra of the deposits accumulated on the channel surfaces.

Black circle and red triangle symbols in Fig. 4 indicate the total dissolved iron concentration when ten PCSG zones were cleaned with circulation and non-circulation method, respectively. At first glance, these values may lead to misjudgment that the dissolution kinetics of deposits are similar to each other in each step. The dissolved iron concentration in the non-circulation method is not even half of what it is expected from the full-length circulation cleaning for the same time. However, the circulation of the cleaning solution facilitates not only the supply of the fresh solution inside the small and complex channels but also the removal of the iron-EDTA chelates from the channels, thereby resulting in a faster dissolution of deposits than under the static immersion cleaning condition. As a result, it is expected that the deposits remained after the non-circulation cleaning step had already been dissolved before the circulation cleaning step was terminated. This inference can also be supported by the result that the most of deposits were dissolved in 6 h during the full-length circulation cleaning.

#### 3.3. Corrosion behavior of a PCSG material

Fig. 5 shows SEM images of the STS 316L coupons before and after the corrosion tests in the EDTA-based solution for 42 h. Grinding marks produced by SiC paper during the specimen preparation were intact after the exposure to the solution. Additionally, localized corrosion such as pitting was not observed. This result indicates that the corrosion rate of STS 316L is significantly slow during the chemical cleaning process. Thus, the EDTA-based cleaning solutions can be applied to fouled PCSGs without concern for the base metal corrosion.

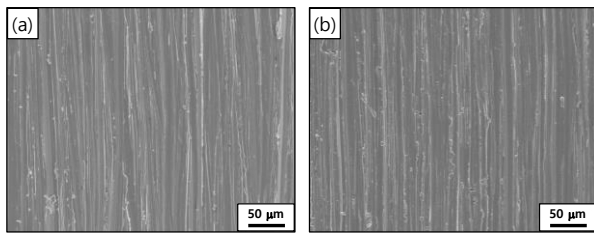


Fig. 5. SEM images of the corrosion coupons surface: (a) before test, (b) after the test for 42 h.

#### 4. Conclusions

The dissolution behavior of magnetite deposits within PCSGs and the corrosion of PCSG material were investigated when chemical cleaning was performed with an EDTA-based solution, and the obtained conclusions were as follows.

- (1) The deposits accumulated on the PCSG channel surfaces had a stoichiometry corresponding to that of magnetite. This result provided a solid basis for selecting the EDTA-based chemical cleaning process.
- (2) The magnetite deposits accumulated on the channel surfaces of the PCSGs were easily removed by the 20 % EDTA-based chemical cleaning solution. Especially, most of the magnetite deposits were dissolved in the early stage of the full-length circulation cleaning.
- (3) The surfaces of the STS 316L coupons were uniform even after the 42 h corrosion tests in the EDTA-based solution. This indicates that the fouling layer within PCSGs can be effectively removed by the EDTA-based chemical cleaning process without concern about base metal corrosion.

#### ACKNOWLEDGEMENTS

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