## On the Wrong Use of Sodium Hydroxide as a Chemical Impurity Concentrated in Nuclear Steam Generator Crevices

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## 1. Introduction

During the manufacturing process of a nuclear steam generator (SG), narrow crevices are inevitably created around SG tubes expanded in the tubesheet and tubes supported by the tube support plates. As a result, aggressive chemical impurities in the SG feedwater can be concentrated into the narrow-heated crevices, thereby inducing corrosion damage of the SG materials.

Although the feedwater is strictly controlled during the operation of SGs, it would transiently be contaminated by some sources [1]: seawater influx due to condenser leakage, unwanted discharge from ion exchange resins, and impurity ingress during maintenance processes. Accordingly, numerous studies have been performed to evaluate the integrity of SG materials in solutions containing sodium, chloride, sulfur, lead, silica [2-5]. Among them, sodium hydroxide (NaOH) solution has been most frequently used to simulate corrosive crevice environments.

This study aimed to investigate the adequacy of using concentrated NaOH solutions to simulate the crevice environments of SGs. To this end, we examined the immersion corrosion behavior of deposit flakes taken from the tubes of an operating SG in 0.4 wt.% NaOH solution at 300 °C. The thermodynamic stability of magnetite was also investigated at various NaOH concentrations.

## 2. Experimental Methods

The corrosion test of SG tube deposits was carried out using deposit flakes taken from an operating SG of a domestic pressurized water reactor. The deposits were mostly composed of magnetite (Fe<sub>3</sub>O<sub>4</sub>) and contained small amounts of trevorite (NiFe<sub>2</sub>O<sub>4</sub>), jacobsite (MnFe<sub>2</sub>O<sub>4</sub>), and metallic copper. The porosity of the deposits was measured to be approximately 9.8 %. The detailed characteristics of the deposits are given elsewhere [6].

The dissolution behavior of the deposit flakes was investigated under two different water chemistry conditions listed in Table I. The reference condition simulates a normal bulk water chemistry with a  $pH_{25^{\circ}C}$  of 9.5. The caustic condition represents a simulated crevice environment of an SG, which contains 0.4 wt.% NaOH. The test solution was deaerated by bubbling argon gas into the solution after the closure of the autoclave at a rate of 300 mL/min before heating. The

tests were interrupted to examine the morphology change of the flake samples after 20 and 30 days. The morphology of the samples was observed using an optical microscope and a scanning electron microscope (SEM).

Table I: Experimental conditions for the dissolution tests of the SG tube deposits

Test condition	NaOH concentration (wt.%)	pH <sub>25</sub> ℃
Reference condition	1.075 x 10 <sup>-4</sup>	9.5
Caustic condition	0.40	13.1

#### 3. Results and Discussion

## 3.1 Dissolution Behavior of the SG Deposit Flakes

Fig. 1 shows the optical images of the SG deposit flake samples exposed to the two different water chemistry conditions at 300 °C. In the reference solution, there was no change in the surface morphology of the sample up to 30 days. However, the sample immersed in the caustic solution was rapidly dissolved and only a certain amount of the flake was left after the 30-day immersion.



Fig. 1. Optical images of the SG deposit flake samples exposed to the two different water chemistry conditions.

The surface morphologies of the samples exposed to the solutions were further examined using SEM. As shown in Figs. 2a and 2b, the size and shape of the particles of the deposit flakes did not change after exposure in the reference solution for 30 days. However, comparing Fig. 2c with 2a, the size of the particles was significantly decreased, and the shape tended to have more rounded edges, indicating that the deposit particles were dissolved in the caustic solution.

# 3.2 Thermodynamics for the Dissolution of the SG Deposit Flakes

The SG deposits used in this study can be assumed to be magnetite because they are mostly composed of magnetite [6]. Therefore, the stability of the magnetite deposits can be inferred using a potential-pH diagram. Fig. 3 shows the potential-pH equilibrium diagram for an iron-water system at 300 °C [7]. pH values at 300 °C in various environments were calculated using the MULTEQ code and presented in the diagram.

It can be deduced that the SG magnetite deposits were formed within the stable domain of magnetite, which is shown in the red box. Similarly, the lack of dissolution of the deposit flakes immersed in the reference solution indicates that the deposits are still located in the stable area of magnetite during the immersion tests.

Now, let us consider the following electrochemical reaction (1):

$$3HFeO_2^- + H^+ = Fe_3O_4 + 2H_2O + 2e$$
(1)

The equilibrium of this reaction is expressed by line  $\mathbb{O}$  in Fig. 3. The equilibrium potential (*E*) of reaction (1) at 300 °C can be calculated using the following Nernst equation (2):

$$E = -1.819 + 0.0568 \text{pH} - 0.1706 \log a_{HFeO_2^-}$$
(2)

For 0.4 wt.% NaOH solution, since magnetite is dissolved, the potentials at which the HFeO<sub>2</sub><sup>-</sup> species (dihypoferrite ion) is stable are in the range of -1.239 to -1.395 V<sub>SHE</sub> shown in Fig. 3. From Eq. (2), these values correspond to an  $a_{HFeO_2^-}$  of 0.73 to 6.0. Consequently, these calculations provide evidence that magnetite is thermodynamically unstable in 0.4 wt.% NaOH solution, leading to a dissolution to HFeO<sub>2</sub><sup>-</sup> ions. In a similar manner, we can predict that magnetite is no more stable in a caustic solution containing NaOH over 0.1 wt.% under the reducing environments of SGs.

Corio reported for the first time in the world that stress corrosion cracking of Alloy 600 SG tube material can occur in deoxygenated pure water [8], while Copson failed to reproduce such attack [9]. The essential reason is that Copson used boiling MgCl<sub>2</sub> solutions as accelerated test conditions, which are not relevant to nuclear environments. Therefore, the results obtained in this work indicate that concentrated NaOH solutions are not relevant to the real crevice environments of SGs.



Fig. 2. SEM micrographs showing the surface morphology of the SG deposit samples exposed to the two different water chemistry conditions at 300 °C for 30 days.



Fig. 3. Potential-pH diagram for the iron-water system at  $300 \text{ }^{\circ}\text{C}$  [7]. pH values at  $300 \text{ }^{\circ}\text{C}$  in various environments were calculated using the MULTEQ code and superimposed in the diagram.

## 4. Conclusions

The magnetite deposits formed in an operating PWR SG were rapidly dissolved in 0.4 wt.% NaOH solution. This result is consistent with the thermodynamic calculation that magnetite is not stable in a solution containing NaOH over 0.1 wt.%, resulting in the dissolution of magnetite to dihypoferrite ions. These results indicate that concentrated NaOH conditions are not applicable in simulating the real crevice environments of SGs. Therefore, the research results obtained in concentrated NaOH solutions may be misleading and not suitable for evaluating the corrosion behavior of SG tubing materials.

#### Acknowledgements

This study was supported by the National Research Foundation (NRF) grant funded by the government of the Republic of Korea (NRF-2017M2A8A4015159, RS-2022-00143316).

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