

# Interfacial electrokinetic properties of magnetite particles and steam generator tube surfaces

Ji-Min Lee<sup>a</sup>, Yong-Beom Lee<sup>a,b</sup>, Soon-Hyeok Jeon<sup>a</sup>, Do Haeng Hur<sup>a,\*</sup>

<sup>a</sup> Materials Safety Technology Development Division, Korea Atomic Energy Research Institute, Daejeon, Korea

<sup>b</sup> Department of Materials Science and Engineering, Chungnam National University, Daejeon, Korea

\*Corresponding author: dhhur@kaeri.re.kr

## 1. Introduction

Magnetite particles deposited on the secondary side of steam generator (SG) tubes not only reduce the heat transfer but also accelerate the corrosion of the SG tube materials, leading to integrity degradation of the SG in pressurized water reactors (PWRs) [1]. Fig. 1 shows a typical morphology of the magnetite deposits on SG tubes [2]. Therefore, inhibiting such magnetite deposition is a critical goal of secondary water chemistry control for reliable PWR operation.

To achieve this goal, it is necessary to understand interfacial electrokinetic properties of magnetite particles and SG tube materials, which can be evaluated by the zeta potential.

In this study, when the pH was controlled with ammonia, morpholine, or ETA, the pH-dependent zeta potentials of magnetite particles were measured. Additionally, the surface zeta potentials of Ni-based Alloy 690 were measured, which is the SG tube material commonly used in PWRs.

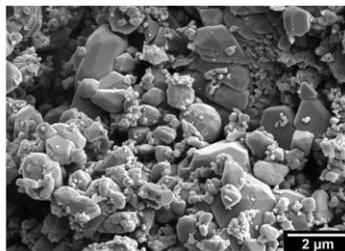


Fig. 1. Morphology of the magnetite deposits on SG tubes at water side. Reprinted from Ref. [2].

## 2. Experimental

### 2.1 Zeta Potential Measurement

Fig. 2 shows a schematic of the zeta potential measurement system. Most of all, a sample solution was prepared with dispersing magnetite nanoparticles in deionized water. An average size of the particles was 5 nm and a concentration was 25 mg/L. A diluted alkaline solution that is made of ammonia, morpholine, or ETA was also prepared. The small amount of alkaline solution was injected into the sample solution using a micro-pump to titrate the pH value. After the pH reaches the target value, the sample was automatically transferred to a measurement cell. After stabilized, an electric field was applied via electrodes attached to the side of the cell. The charged magnetite nanoparticles were then attracted to electrode with opposite charges. Subsequently, particles

velocity per applied electric field, i.e., electrophoretic mobility, could be measured. More details of the measurement principle are presented in Ref. [3]. Furthermore, the measured mobility was then converted to the zeta potential from Henry's equation [4], which is given below:

$$\zeta = \frac{\eta U_E}{\varepsilon_r \varepsilon_0 f(\kappa a)} \quad (1)$$

where,  $\eta$  is the viscosity of the solution,  $U_E$  is the electrophoretic mobility,  $\varepsilon_r \varepsilon_0$  is the permittivity of solution, and  $f(\kappa a)$  is Henry's function. After the measurement was finished, the solution in the cell was automatically returned to the sample solution container. The zeta potential measurement is repeated by increasing the pH value from 9.0 to 10.0.

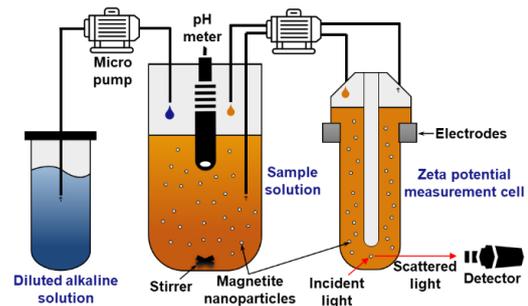


Fig. 2. Schematic of zeta potential measurement system.

### 2.2 Surface Zeta Potential Measurement

Fig. 3 shows a schematic of the surface zeta potential measurement kit. Rectangular samples of Alloy 690 were prepared ( $5 \times 4 \times 1 \text{ mm}^3$ ). The sample was attached to a sample holder and immersed in a solution in a cuvette. The solution was the same as that used to measure the zeta potential of magnetite nanoparticles as described in section 2.1, and the pH was either 9.0 or 10.0. When an electric field is applied via a pair of Pd electrodes, the electrophoresis of tracer particles begins. We measured the apparent tracer electrophoretic mobility at four different distances from the sample surface by rotating a screw for adjusting the sample height. The surface zeta potential of Alloy 690 was then derived by the linear extrapolation method. More details have been described elsewhere [5].

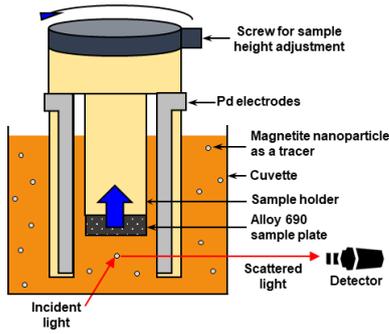


Fig. 3. Schematic of surface zeta potential measurement kit.

### 3. Results

Fig. 4 shows the zeta potentials of magnetite nanoparticles as a function of pH value that is controlled with ETA, ammonia, or morpholine at 25 °C. The solid lines in Fig. 4 show the linear regression fits of the measured data in the solution of each pH agent. The pH-dependent zeta potentials of the particles can be expressed by the following empirical equations:

$$\zeta_E = -9.0 \times \text{pH} + 57.5 \quad (2a)$$

$$\zeta_A = -10.2 \times \text{pH} + 61.9 \quad (2b)$$

$$\zeta_M = -12.3 \times \text{pH} + 77.8 \quad (2c)$$

where  $\zeta_E$ ,  $\zeta_A$ , and  $\zeta_M$  are for the solutions of ETA, ammonia, and morpholine, respectively. These equations are valid at pH values ranging from 9.0 to 10.0. Regardless of the pH agent, when the pH value increased from 9.0 to 10.0, the zeta potentials of the particles increased in the negative direction. At the same pH value, the absolute value of the zeta potential was the lowest when using ETA and the highest when using morpholine.

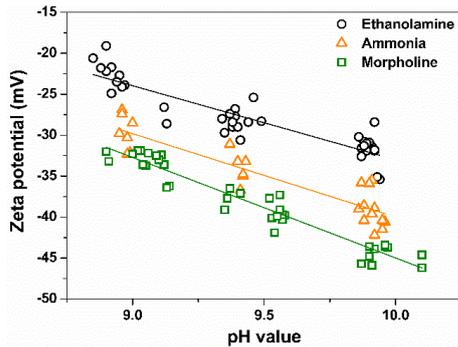


Fig. 4. Measured zeta potentials of magnetite nanoparticles.

Fig. 5 shows the relationship between the zeta potentials of magnetite nanoparticles and Alloy 690 surfaces, depending on the pH agent, at 25 °C. The differences in the zeta potentials between the magnetite nanoparticles and Alloy 690 surfaces ( $\Delta ZP$ ) could be calculated. When the pH increased from 9.0 to 10.0,  $\Delta ZP$  increased regardless of the pH agent. At the same pH value,  $\Delta ZP$  was the smallest in the ETA solution and the largest in the ammonia solution.

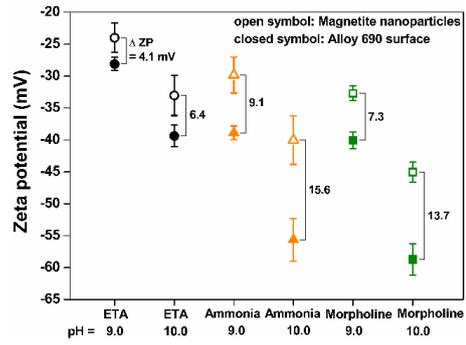


Fig. 5. The differences in the zeta potentials between the magnetite nanoparticles and Alloy 690 surfaces.

### 4. Summary and Future studies

- (1) The zeta potentials of magnetite nanoparticles and Alloy 690 SG surfaces were dependent on the pH value and pH agent.
- (2) The zeta potentials of the magnetite particles increased in the negative direction as the pH increased from 9.0 to 10.0, regardless of the pH agent. At the same pH value, the absolute value of the zeta potential increased in the order: ETA < ammonia < Morpholine.
- (3) The difference in the zeta potentials between the magnetite nanoparticles and Alloy 690 surfaces increased with increasing pH from 9.0 to 10.0, regardless of the pH agent. At the same pH value, the difference was the smallest in ETA and the largest in ammonia.
- (4) Considering the measured zeta potentials, the agglomeration and size of the particles will be studied. Additionally, the magnetite deposition behavior will be explored by comparing the measured zeta potentials of magnetite particles and Alloy 690 surfaces.

### 5. Acknowledgements

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