Abstract: Ethanolamine (ETA) is widely used to control the pH value in the secondary water of pressurized water reactors. However, it is necessary to consider other advanced amines which can replace ETA due to its serious human hazards and environmental treatment problems. The purpose of this study is to contemplate the effects of three advanced amines (ETA, 3-methoxypropylamine (MPA), and dimethylamine (DMA)) on the magnetite deposition behavior of a thermally treated (TT) Alloy 690 tubes by using a steam generator (SG) tube fouling loop in simulated secondary water. All particles were identified as a magnetite and were polyhedral or spherical in shape. When using ETA, MPA, and DMA, the average porosity of the deposits was about 34.7%, 33.0%, and 24.6%, respectively. The amount of deposits was largest when ETA was added, and it decreased by 41% when adding MPA and 55% when adding DMA. The mechanism of magnetite deposition was discussed in terms of zeta potentials of both the magnetite particles and the Alloy 690TT surface and magnetite solubility depending on the amines. To compare the potential for replacing ETA with other advanced amines, the various factors such as SG integrity, human hazards, and environmental treatment problems were discussed.

Keywords: steam generator tube; water chemistry; advanced amine; ethanolamine; 3-methoxypropylamine; dimethylamine; magnetite deposits; sludge

1. Introduction

The secondary water systems of pressurized water reactors (PWR) inevitably generate the corrosion products that are transported into the SG through the feedwater [1,2]. Most of the corrosion products in SG typically originate from flow accelerated corrosion (FAC) of carbon steel tubing and other carbon steel components. The resulting deposits occur in the form of magnetite [3–5]. In spite of blowdown system operation for the removal of impurities, the magnetite remaining in the final feedwater accumulates on surfaces within the SG shell [6,7]. The magnetite deposits in SGs may result in clogging at the top of the tube support plate (TSP) and in SG tube fouling [1,2].

The magnetite deposition in the SG could cause the following problems to SG integrity [7,8]. First, SG tube fouling forms micro-crevices in which impurities could concentrate, potentially creating the aggressive corrosion environments that could lead to stress corrosion cracking (SCC), pitting corrosion, and eventually SG tube failure and/or plugging [9–11]. Second, SG tube fouling could also lead to less effective SG heat transfer efficiency [1,12]. Third, TSP clogging leads to the high velocity regions and transverse velocity in the secondary water flow, which causes flow-induced vibrations and SG tube cracks or failure [13].

Therefore, many researchers have made a significant effort to reduce the amount of secondary-cycle corrosion product transport to SGs by controlling the water chemistry
parameters such as pH (pH agent replacement and pH value elevation), use of dispersants, and addition of a film-forming amine [4,14]. These efforts have been largely successful in reducing Fe concentrations in feedwater by decreasing the corrosion rate. In particular, many investigations have focused on the effects of water chemistry parameters on the FAC of carbon steel and other structural materials [4,15].

However, there are a few studies on the relationship between water chemistry parameters and SG tube fouling, which is an ongoing concern in the fields. Recently, Lee et al. [16] reported on the effects of pH control agents such as ETA, ammonia, and morpholine on magnetite deposition of SG tubes, using a deposition loop system. Among these pH control agents, ammonia is the most effective in controlling pH for mitigation of SG tube fouling. In addition, the addition of NaCl has the effect of reducing magnetite deposition in Alloy 690TT SG tubes in a secondary water system [17].

In 1986, some investigations were performed using morpholine as an alternate to ammonia for pH control of PWR secondary system [18]. Based on the beneficial morpholine experience, Electric Power Research Institute (EPRI) began an extensive project to evaluate the candidate amines for use as pH control agents [18]. Detailed data such as base strength and volatility were development for about 100 amine compounds [18]. From these studies, the researchers identified several amines qualified for nuclear power plant use and successfully implemented them in secondary system of PWR [18]. These several amines were called as advanced amine. The representative advanced amines are ETA, DMA, MPA, 5-aminopentanol, pyrrolidine. One of them, ETA is widely used to control the pH value in secondary water of PWRs.

In this work, the effects of three advanced amines (ETA, MPA, and DMA) on the magnetite deposition behavior of commercial Alloy 690TT SG tubes were investigated using a simulated secondary system based on an SG tube fouling loop system. In previous studies, various parameters have been reported that can control the deposition behavior of particles. These include thermal-hydraulic factors (heat flux, flow rate, temperature, pressure), water chemistry factors (pH, DO, conductivity, impurities), particle factors (size, concentration, zeta potential, solubility), and substrates (zeta potential, roughness, morphology) [20,21]. In this work, because most of the variables were equally in operation,

Table 1. Basic properties of three advanced amines widely used for control of secondary water chemistry in PWRs.

| pH Control Agent | Chemical Formula | Density (g/cm³) | Boiling Point (°C) | Basicity (pK) | Half-Life Times at 185 °C (min) |
|------------------|-----------------|----------------|-------------------|--------------|-------------------------------|
| ETA              | C₃H₇NO          | 1.01           | 170               | −9.50        | 5                             |
| MPA              | CH₃O(CH₂)₃NH₂    | 0.87           | 135               | −9.88        | 4                             |
| DMA              | (CH₃)₂NH         | 0.67           | 7                 | −10.78       | 35                            |

In this work, the effects of three advanced amines (ETA, MPA, and DMA) on the magnetite deposition behavior of commercial Alloy 690TT SG tubes were investigated using a simulated secondary system based on an SG tube fouling loop system. In previous studies, various parameters have been reported that can control the deposition behavior of particles. These include thermal-hydraulic factors (heat flux, flow rate, temperature, pressure), water chemistry factors (pH, DO, conductivity, impurities), particle factors (size, concentration, zeta potential, solubility), and substrates (zeta potential, roughness, morphology) [20,21]. In this work, because most of the variables were equally in operation,
the main factors affecting the amount of magnetite deposited were two: zeta potential and particle size in relation to the amine used. The magnetite solubility was not considered necessary for this study because the pH of three advanced amines was kept same at 270 °C, the temperature at which the SG tube fouling tests were performed.

After the fouling tests, the magnetite deposit samples were characterized using various analytical techniques and the amount of deposition was also measured. These results were discussed in accordance with the zeta potential of magnetite particles and an Alloy 690TT specimen, particle size, porosity, and magnetite solubility, in relation to which of the advanced amines was used. In addition, to evaluate the possibility of replacing ETA with MPA or DMA, factors such as human hazards and environmental treatment problems were also discussed.

2. Experimental Methods

2.1. Preparation of Specimens and Test Solutions

The specimens selected for the deposition test were SG tubes made of the commercial Alloy 690TT. They were 500 mm length, had 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 welded with an Alloy 600 cap of diameter 19.05 mm and thickness 2.0 mm. The chemical compositions of the Alloy 690TT tubes used in these experiments are presented in Table 2. After cleaning the outer surface of the specimen with acetone, a stainless steel 316 cartridge heater of 600 mm length and an OD of 16.97 mm (which could simulate the primary water as a heat source) was inserted into the tube specimen. During insertion of the heater into a specimen, MgO was spread to remove the air gap between the heater and the specimen. The heater-inserted specimen was baked in an electric oven at 60 °C for 6 h. Afterwards, the specimen was installed in the test section.

| Cr  | Fe  | Si  | Mn  | Ti  | Al  | Cu  | Co  | C   | Ni  |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 29.3| 10.4| 0.3 | 0.3 | 0.3 | 0.2 | 0.01| 0.01| 0.02| 59.16|

A 100 L tank was filled with deionized (DI) water in which the dissolved oxygen (DO) level (<2 ppb) was continuously maintained by nitrogen gas purging. This DO level was sufficient to satisfy the secondary water chemistry guideline of the EPRI [22]. For the reasons mentioned above we selected ETA, MPA, and DMA in this study.

Fe(II)-acetate was used as the precursor in this work. In previous work, Fe(II)-acetate and Fe(III)-acetate were reported to be widely used to synthesize iron oxide particles [23,24]. In particular, pure nanometer-sized particles could be simply synthesized using Fe(II)-acetate in water under argon gas [22]. Hence, Fe(II)-acetate was chosen as the source for deposit synthesis. In a 50 L tank, 260 ppm Fe(II)-acetate was continuously maintained with a DO level of <2 ppb by nitrogen gas purging.

When conducting a fouling test with an SG tube containing one of the advanced amines, the pH value at the high temperature at which the fouling test was actually performed, was kept the same. This is because a difference in pH could greatly affect the zeta potential and magnetite solubility. It is well-known that the zeta potential is a function of pH, and that magnetite solubility is a function of pH and temperature [25,26]. In previous studies, the magnetite solubility was predicted to decrease with the increase of the pH [25].

To exclude the effect of magnetite solubility on the magnetite deposition, the pH of ETA, MPA, and DMA should be same at 270 °C, the temperature at which the SG tube fouling tests were performed. Before a fouling test, we calculated the variation of the pH of the three advanced amine solutions of ETA, MPA, and DMA as a function of temperature using the MULTEQ code (Figure 1). The ETA, MPA, and DMA solutions were continuously maintained at pH 10.0, 10.2, and 9.74 at 25 °C during the test to reach pH 6.56 at 270 °C,
under which conditions the SG tube fouling tests were conducted, respectively. Hence, it was not necessary to consider magnetite solubility in this study. In addition, the Fe concentration in the test section was maintained at about 1 ppm by supplying the fouling source in excess of its solubility (several ppb) during the entire reaction period. That is, the test section was maintained in a thermodynamically supersaturated state with a sufficient amount of magnetite particles that could adhere to the surface of Alloy 690TT. Thus, the effect of magnetite solubility on deposition behavior seems to be negligible.

![Figure 1](image-url) Figure 1. Calculated pH of ETA, MPA, and DMA solutions as a function of temperature using the MULTEQ code.

The concentration of each of the ETA, MPA, and DMA required to achieve pH 6.56 at 270 °C is 26.0, 43.0, and 2.7 ppm, respectively. During the fouling tests, each of the highly concentrated amine (pH > 11.0 at 25 °C) solutions were injected into the secondary solution tank to maintain pH 6.56 at 270 °C.

2.2. SG Tube Fouling Loop System

Figure 2 shows a schematic diagram of the SG tube fouling loop system under simulated secondary water conditions. As shown in Figure 2, the loop consists of three main parts: (1) Test section, (2) Secondary coolant water tank, and (3) Fouling source tank. Furthermore, the loop system was composed of high-pressure (HP) pumps, a metering pump for injecting the Fe(II)-acetate, micro-filters for removing the remaining magnetite particles and impurities during fouling tests, various sensors (such as for pH, DO, and conductivity), a thermo-couple (T/C), preheaters, coolers, and back-pressure regulators (BPR).

When the loop system was ready to start, the pressure of the test section was gradually increased to 60 bar (above the saturation pressure) using the BPR. After that, the preheater, line heater, band heaters around the test section, and the cartridge heater were sequentially heated to cause the surface of tube specimen to reach 270 °C. These heaters were operated to maintain the subcooled nucleate boiling (SNB) conditions. The heat flux of the cartridge heater was maintained at 30 W/cm². The flow rate of the test solution was 260 mL/min. After the water chemistry parameters (i.e., temperature, pressure, pH, and DO) and the water flow rate of the loop system was stabilized, Fe(II)-acetate solution from the fouling source tank was continuously injected to the bottom of the test section at a system-water flow rate of 1 mL/min. This was done to maintain the Fe concentration in the secondary water near the surface of the tube specimen at 1 ppm. Each of the fouling tests lasted for 14 days.
2.3. Characterization of the Simulated Deposits

After the SG tube fouling test, the specimens were cut using a low-speed diamond saw. As shown in Figure 3, three types of segments were fabricated to conduct various analyses. First, three tubular segments with a 20 mm length were used to measure the amount of deposition. To measure the amounts of deposition, the magnetite deposits were selectively dissolved by immersing them in a chemical cleaning solution (20 wt.% ethylenediaminetetraacetic acid + 1 wt.% N\textsubscript{2}H\textsubscript{4} + 1 wt.% corrosion inhibitor + NH\textsubscript{4}OH) at 93 °C for 12 h. The dissolved solutions were directly analyzed using an inductively coupled plasma atomic emission spectroscope (ICP-AES, Thermo Scientific iCAP 7000, Cambridge, UK) to measure the Fe concentration. It was confirmed that Alloy 690TT tube specimens were not corroded during the chemical cleaning process due to the absence of Ni and Cr in the ICP-AES analysis results. Finally, the amount of deposition in each case was converted to magnetite using the measured Fe concentration, and calculated to determine the per unit area.

Second, the two tubular segments 15 mm long were used to analyze the particle morphologies, porosity of deposits, and particle characteristics and distribution. The surface morphologies of the deposits were observed using a scanning electron microscope.
(SEM, FEI Company, Hillsboro, OR, USA). Two-dimensional particle characteristics and
distribution of the deposits was evaluated using an image analyzer (Image J software, 1.52a,
National Institutes of Health, Bethesda, MD, USA). Cross sections of the deposits were
prepared using the focused ion beam (FIB) technique, and three locations per specimen
were observed using FIB-SEM. The two-dimensional porosity of the deposits was also
evaluated using an image analyzer. It was used to analyze four images per location
(i.e., at least 12 images per specimen) for each analysis using a surface SEM images or
cross-sectional SEM images.

Third, four tubular segments 10 mm long were used to identify the particles using an
high resolution X-ray diffractometer (HR-XRD, Rigaku, Tokyo, Japan). After the simulated
deposits were removed from the tube segments, HR-XRD analysis was performed on
deposit material in powder form. Calculate the full-width at half-maximum (FWHM) with
the XRD diffraction patterns. The crystallite size of a deposits is given by Equation (1)
below, according to Sherrer’s formula [27].

\[
D_{hkl} = \frac{K \times \lambda}{\beta \times \cos \theta}
\]

where \( K \) is the unit cell geometry-dependent constant (0.89), \( \lambda \) is the wavelength of the
XRD (0.154056 nm), \( \beta \) is the FWHM value of XRD diffraction patterns, and \( \theta \) is the half
diffraction angle of \( 2\theta \). The average crystallite size is calculated by averaging the sizes of
six representative peaks.

2.4. Zeta Potential Measurement

The zeta potential of magnetite nanoparticles and of the surface of Alloy 690 TT tubes
was measured in simulated secondary water containing ETA, MPA, or DMA at 25 °C.
First, to measure the zeta potential of magnetite nanoparticles, a sample was prepared by
dispersing magnetite nanoparticles with average size of 5 nm at a concentration of 25 mg/L
in a solution adjusted to pH 10.0 at 25 °C using each advanced amine. The prepared
solution shown in Figure 4a was injected into the particle zeta potential measurement
kit. After the stabilization time passed, an electric field was applied through a pair of Pd
electrodes mounted on either side of the cell. At a rate proportional to the electric field
strength and charge, the charged magnetite particles were attracted to the electrode with
opposite charge. The electrophoretic mobility of the particles was measured using the
electrophoretic light scattering (ELS) technique [28]. This technique is well-known to be
the proper method for determining the zeta potential of particles that are fine enough to
remain suspended in the solution. The measured mobility was then converted to the zeta
potential (\( \zeta \)) through Henry’s equation [29], expressed as:

\[
\zeta = \frac{\eta U_E}{\varepsilon_r \varepsilon_0 f(\kappa a)}
\]

\[
f(\kappa a) = \frac{2}{3} \left[ 1 + \frac{1}{2 \left( 1 + \frac{2.5}{\kappa a} \right) } \right] \left[ \frac{1}{2 \left( 1 + \frac{2.5}{\kappa a} \right) } \right] \]

where \( \eta \) is the viscosity of the solution, \( U_E \) is the electrophoretic mobility, \( \varepsilon_r \) is the relative
permittivity of the solution, \( \varepsilon_0 \) is the permittivity of vacuum, \( f(\kappa a) \) is Henry’s function
for a spherical colloidal particle of radius \( a \), and \( \kappa \) is the reciprocal of the Debye length.
The refractive index and absorption of the magnetite particles used were 2.42 and 0.01,
respectively. In this study, \( \kappa a \) was assumed to be sufficiently large; therefore, the \( f(\kappa a) \)
value was set to “1.” During the zeta potential measurement, the magnetite particles
remained thermodynamically stable. When an electric field was applied, the particles in
the suspension became charged and moved under electrophoresis.
Second, the surface zeta potential of metals or alloy steels can be estimated by measuring the electrophoretic mobility at several distances from the specimen surface using a suspended particle tracer. Figure 4b shows a schematic of the surface zeta potential measurement kit. Alloy 690TT was used to make sample plates 5 mm length × 3.5 mm width × 1 mm thickness. Because the state of a specimen surface significantly affects the surface zeta potential [30], the sample surfaces were carefully polished to obtain roughness similar to that of the Alloy 690TT tubes used in the fouling test. The root-mean-square roughness (Rq) of the final sample surface was controlled to ~0.250 μm. The prepared sample was stuck to the specimen holder and immersed in the cuvette solution. This solution was the same as the solution used to measure the zeta potential of magnetite nanoparticles, and the pH was 10.0 at 25 °C. Supplying an electric field through a pair of Pd electrodes started electrophoresis of the tracer particles. Electrical effects of the tracer measurements were conducted at four different distances from the sample surface by rotating a screw to vary the sample height. The surface zeta potential of Alloy 690TT plate was obtained by linear extrapolation.

3. Results and Discussion

3.1. Morphologies of Deposits

Figure 5 presents the surface morphologies of deposits on Alloy 690TT tubes when each of the three advanced amines was contained. Figure 5a,e shows the outer surface of Alloy 690TT tube before the deposition test. The surface of Alloy 690TT was generally flat and smooth. Various sized particles within the range of about 100 nm to 2 μm were present in all three amines. As shown in Figure 5b–d, the deposit layers were observed to be uneven in form. In particular, more relatively large particles (about 1.5–2.0 μm) were observed in the case of ETA than with MPA and DMA. The number of pores between the particles were also observed. As shown in Figure 5f–h, all of the deposit particles are polyhedral or spherical in shape regardless of the amine used.

Figure 6 presents the various parameters such as aspect ratio and mean diameter of simulated deposit particles evaluated using an image analyzer. Here, the aspect ratio is defined as the ratio of the largest axis of a particle to the smallest axis of the particle. When using DMA and MPA, the aspect ratio of particles is smaller than those of particles when using ETA (Figure 6a). The aspect ratio of all particles is in the range from 0.96 to 1.12. This result indicates that the particles in all three advanced amines formed as spheres. As can be seen from Figure 6b, the mean diameter of the deposited particles is largest (0.474 μm) when using ETA. In contrast, when using MPA and DMA, they are 0.292 and 0.189 μm, respectively.
Figure 5. SEM images of surface morphologies of simulated deposits on Alloy 690TT tubes using three advanced amines: low magnification (a) Alloy 690 before the test, (b) ETA, (c) MPA, and (d) DMA and high magnification (e) Alloy 690 before the test, (f) ETA, (g) MPA, and (h) DMA.

Figure 6. Particle characteristics of magnetite particles using an image analyzer: (a) aspect ratio and (b) mean diameter.

As shown in Figure 7, the particle size distribution is also different. In the case of DMA, about 92% of all particles have a diameter <0.35 µm, and there are a few particles with diameter exceeding 0.95 µm (about 0.75%). However, with ETA, approximately 50% of the particles have a diameter of <0.35 µm and about 14.3% of the particles have a diameter >0.95 µm. Based on the Figures 6b and 7, the particle size decreases when MPA and DMA are used, compared to the case using ETA.

Figure 8 shows the pores of various sizes between the simulated deposit particles on the Alloy 690TT tubes when each of the three advanced amines was contained. Under all amine conditions, many pores of sizes in the range of about 0.1–5 µm were observed. Varrin [20] observed the SG tube sludge taken from real operating PWRs and reported that the pores between the deposit particles could be divided into typical two types: (1) steam chimneys and (2) fluid micro-pores). A steam chimney is a large pore (about 5–10 µm) and a fluid micro-pore is a small one (0.1–1 µm). Steam chimneys of more than 10 µm, in particular, have a detrimental effect on the heat transfer efficiency of SG tubes [20]. Moreover, this steam chimney could promote the concentration of impurities close to the tube surface, a phenomenon which results in SCC, pitting corrosion, and corrosion acceleration [11,20].
Figure 7. Particle size distribution of magnetite particles using an image analyzer: (a) ETA, (b) MPA, and (c) DMA.

Figure 8. SEM image of steam chimney and fluid micro-pores between magnetite particles on the Alloy 690TT tubes depending on which of the three advanced amines was used: (a) ETA, (b) MPA, and (c) DMA.

Figure 9 shows the cross-sectional SEM images of simulated deposits in Alloy 690TT tubes depending on which of the three advanced amines was used. Numerous micro-pores were clearly observed in the deposits with all the amines. The pores form when steam bubbles escape from a heated metal surface [20,31] and serve as a site for the accumulation of various chemical impurities [32–34]. The chemical impurities concentrated in the pores could adversely affect the SG integrity. First, impurities such as Zn, Ca, Al, and Si form a new phase within the pores and result in the consolidation of SG deposits. Turner et al. [9,10] reported that Zn and Ca could affect deposit consolidation by forming new phases such as willemite (Zn$_2$SiO$_4$) and calcium sulfate. Beal et al. [15] also showed
that Si combined with Al or Al alone could form chemical compounds such as kaolinite (Al$_2$Si$_2$O$_7$(OH)$_4$) or boehmite (AlO(OH)) (an Al oxide), and that these compounds have an important role in the promotion of sludge formation and in the consolidation of hard sludge. Second, metallic impurities like Cu and Pb particles concentrate within the micro-pores, where they can electrically contact the surface of the SG tube and thus affect the galvanic acceleration of an SG tube because Cu and Pb particles act as cathodes of a galvanic couple [11]. In addition, Na, Cl, and S impurities concentrated within the micro-pores of SG tube deposits can cause various corrosion phenomena such as pitting corrosion and chloride-induced stress corrosion cracking [12,35,36]. One notable fact was that the deposit thickness was not constant. In other words, the thickness should vary according to being in different positions, in spite of being the same specimen. Accordingly, the amount of simulated deposition for each condition is shown in Section 3.3.

Figure 9. Cross-sectional SEM images of magnetite deposits on Alloy 690TT tubes depending on which of the three advanced amines was used: (a) ETA, (b) MPA, and (c) DMA.

Figure 10 shows the two-dimensional porosity of simulated deposits using an image analyzer, in relation to the pH agent used. When using the advanced amines, the average porosity is about 34.7%, 33.0%, and 24.6%, respectively, and when using DMA, magnetite deposits were the densest. The reason for this is that, as shown in Figures 5–7, when using DMA, the average particle size is smaller than with the others, so the particles are densely distributed. Generally, the lower the porosity of a deposit, the higher its thermal conductivity [37,38]. Based on the porosity results, if the same amount of corrosion product is deposited on a SG tube, the thermal conductivity of a SG tube using ETA will be lower than that if using DMA.
3.2. Identification of Simulated Deposits

Figure 11 presents HR-XRD patterns of the simulated deposits depending on the advanced amine used, and of real SG tube deposits. The XRD diffraction patterns with all the advanced amines matched well those with pure magnetite, according to XRD data (PDF No. 88-0866). In addition, HR-XRD peaks of the real SG tube deposits show that the deposits are crystalline and that all the peak locations also correspond to pure magnetite (PDF No. 88-0866). This is because the actual SG tube deposits mainly consisted of magnetite (about 95–96%) [39]. These results mean that the deposit specimens produced using the loop systems are good simulations of the actual SG tube deposits.
In addition, the peak broadening of XRD pattern indicates that the crystallite size is small. The crystallite size could be calculated by the Sherrer’s formula. The crystallite sizes of the simulated deposits depending on the advanced amine used are given in Table 3. The crystallite size of the deposits in the case of MPA and DMA, compared to ETA, was approximately 17% and 24% less, respectively.

Table 3. Crystallite size using three advanced amines calculated by JADE9 software 9 (Materials Data, Inc., Livermore, CA, USA) and Sherrer’s formula (µm).

| Peaks  | ETA | MPA | DMA |
|--------|-----|-----|-----|
| D_{220} | 1.019 | 0.863 | 0.746 |
| D_{311} | 1.022 | 0.862 | 0.733 |
| D_{400} | 1.021 | 0.858 | 0.742 |
| D_{422} | 0.990 | 0.772 | 0.839 |
| D_{511} | 0.901 | 0.784 | 0.696 |
| D_{440} | 0.929 | 0.759 | 0.715 |
| Average | 0.980 | 0.816 | 0.745 |

Figure 12 shows the chemical composition of the particles of various size deposited on the Alloy 690TT tubes used in the test with three advanced amines, as determined by SEM energy-dispersive X-ray spectrometer (EDS) analysis. Under all advanced amine conditions, site 1 is the location of a tiny particle (about 0.25 µm) and shows a magnetite particle consisting of the 56.48~58.56 at.% O and 41.44~43.52 at.% Fe. Site 2 is a large particle (about 2.3~9.5 µm) and also represents a magnetite particle because it was composed of 55.91~58.01 at.% O and 41.99~44.09 at.% Fe. These results showed that all the deposited particles under three advanced amine conditions were identified as magnetite regardless of the particle size.

Figure 12. Chemical composition of particles deposited on an Alloy 690TT tube in the test using Three advanced amine, according to SEM-EDS analysis (at.%): (a) ETA, (b) MPA, and (c) DMA.
3.3. Amount of Magnetite Deposits

Figure 13 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 simulated secondary water. The amount of magnetite deposited in the case of MPA and DMA, compared to ETA, was approximately 41% and 55% less, respectively. This indicates that the choice of advanced amine clearly affects the amount of magnetite deposited.

![Figure 13. Amount of magnetite deposited on Alloy 690TT tubes depending on which of the three advanced amines was used (pH$_{270^\circ C} = 6.56$).](image)

Figure 14 shows the zeta potentials of both magnetite nanoparticles and the surface of Alloy 690TT plate in conjunction with one of three advanced amines at 25 °C. The samples were prepared by dispersing magnetite nanoparticles in a solution adjusted to pH 10.0 at 25 °C using one advanced amine. As shown in Figure 14, with all three amines, both the particles and plate surfaces were negatively charged, confirming that the force that worked between them was a repulsive force, and not an attractive force. The zeta potential of magnetite particles dispersed in secondary water when controlled using either ETA, MPA, or DMA was $-$33.0, $-$33.7, or $-$37.9 mV, respectively. That is, DMA has higher repulsion between magnetite nanoparticles than other advanced amines, resulting in higher dispersion stability. Meanwhile, the surface zeta potential values of Alloy 690TT plate, which was controlled using ETA, MPA, and DMA, were measured and found to be $-$39.4, $-$42.9, and $-$52.6 mV, respectively. As a result, the difference in zeta potentials between the particle and the surface of Alloy 690TT plate ($\Delta$ZP, repulsive force works with all three amines) was 6.4 mV for ETA, 9.2 mV for MPA, and 14.7 mV for DMA. The smallest $\Delta$ZP is in ETA and the largest is in DMA. In the initial stage of magnetite deposition, the amount of magnetite deposited on the specimen surface decreased due to the larger difference in zeta potential between the particle and the plate surface when using DMA, compared to other advanced amines.

Figure 15 presents the schematic diagram of the magnetite deposition behavior on Alloy 690TT tube at the initial stage and the following stage. As shown in Figure 15a, in the initial stages, the difference in zeta potential between the magnetite particles and the bare surface of metal or alloy steel is an electrostatic driving force that affects these stages [21,40]. As the initial magnetite deposition progressed, the effect of the surface zeta potential of Alloy 690TT on magnetite deposition behavior was reduced and finally no longer affected subsequent magnetite deposition. In this stage of deposition process, the electrostatic force between the already deposited magnetite on surface of Alloy 690TT tube and magnetite particles in the fluid is a major factor in the mechanism of driving deposit growth, which could be explained by the zeta potential of each magnetite particle (Figure 15b). As shown in Figure 14, the electrostatic repulsive force between the magnetite nanoparticles was the lowest in the ETA solution. Therefore, the degree of coalescence of the particles with
already deposited magnetite would have increased, resulting in the maximum amount of magnetite deposits. In addition, the repulsive force between the magnetite nanoparticles was highest in the DMA solution, whereas the amount of magnetite deposited in DMA was smaller than that deposited in the ETA and MPA solutions.

Figure 14. Zeta potentials at 25 °C of the surface of Alloy 690TT plate and magnetite nanoparticles depending on which of the three advanced amines was used.

Figure 15. Schematic diagram of the magnetite deposition behavior on Alloy 690TT tube: (a) initial stage and (b) the following stage.

However, because all the zeta potential values presented in this study were measured at 25 °C, there may be some limitations in understanding the mechanism of magnetite deposition behavior in secondary water at the more typical temperatures in SGs (inlet and outlet saturation temperature of an SG is about 227 and 277 °C, respectively). It is well-known that the zeta potentials of magnetite powder increase in the positive direction with increasing temperature [41]. Nevertheless, the zeta potential of magnetite particles is still negatively charged at temperatures up to 320 °C [41]. However, their results considered only the zeta potentials of magnetite particles, not the zeta potential of the metal or alloy steel surface at high temperatures. Thus, their results are not applicable to the evaluation of the electrostatic driving force for the deposition of particles on a bare surface at high temperature. In spite of some analytical limitations, based on the currently evaluated amount of magnetite deposits on Alloy 690TT shown in Figure 13, it seems that the three advanced amine-dependent zeta potentials at 25 °C (shown in Figure 14) are still valid and reliable at 270 °C, as indicated by testing in this work.
3.4. Consideration of the Possibility of Using Alternative Advanced Amines Instead of ETA

In spite of the many advantages of ETA, which is widely used in secondary systems of PWRs, the nuclear industry has interest in finding other advanced amines that could replace ETA because ETA is very harmful to on-site plant workers and is expensive to deal with as environmental pollution. In this study, we selected two advanced amines (MPA and DMA) and investigated their effects on magnetite deposition behavior on SG tubes. To compare the possibility of replacing ETA with MPA or DMA, various factors were considered, including such as environmental treatment costs, integrity of SGs (corrosion, magnetite deposits, heat transfer efficiency of SG), and human hazard. Table 4 shows the basic properties and important factors from the viewpoint of using another advanced amine in place of ETA.

Table 4. Analysis of the possibility of substituting other advanced amines (MPA or DMA) in place of ETA, an amine widely used in the secondary water of PWRs.

| pH Agent | Environmental Problem | Integrity of SG | Human Hazard |
|----------|-----------------------|----------------|--------------|
|          | Basicity (pK)         | Amount of Deposits (mg/dm²) | Porosity of Deposits (%) | Concentration of Exposed in Air (mg/m³·h) |
|          | Number of Atoms of C, N | 25 °C | 275 °C | RV | |
| ETA      | C:2, N:1              | −9.50 | −5.25 | <1 | 209.83 | 34.7 | 75 |
| MPA      | C:4, N:1              | −9.88 | −5.16 | =1 | 124.01 | 33.0 | 150 |
| DMA      | C:2, N:1              | −10.78 | −6.25 | >1 | 94.01  | 24.6 | 460 |

First, we consider the environmental impact of the amine used, based on its chemical formula and basicity in the secondary water system of PWRs. Regarding a chemical formula, a large number of C and N atoms can increase the chemical oxygen demand (COD) and total nitrogen (T-N). COD is a water quality indicator of organic matter pollution, and refers to the amount of oxygen (ppm) required by organic matter decomposing in water, as indicated with an oxidizing agent such as potassium permanganate (KMnO₄). T-N is the total amount of nitrogen compounds in water and includes all nitrogen components (i.e., organic, ammonia, nitrite, and nitrate). Changes in T-N occur during the natural circulation of nitrogen in water and increases in T-N can be due to artificial inflows such as wastewater or domestic sewage. Increase of COD and T-N indicates adverse effects on the environment and incurs additional cost to solve this environmental problem. As presented in Table 4, ETA, MPA, and DMA have 2, 4, and 2 C atoms per molecule, respectively. In addition, each advanced amine has the same number of N atoms. If there was the same concentration of each amine in the secondary water of a PWR, it would be expected that the environmental impact of ETA and DMA would be similar, and both better than that of MPA. However, we should consider not only the chemical formula but also the basicity of amine. Basicity is defined as the ability of an amine to increase the pH of a solution. The higher the basicity value (pK, pK = −log₁₀K), the higher the pH can be maintained with similar molar concentration. As presented in Table 4, DMA (with its high basicity) is the most effective amine from the viewpoint of operating and maintaining a higher pH in secondary water. That is, because the concentration of DMA is the lowest needed to maintain the target pH in secondary water, using it would result in the least amounts of C and N decomposition products in the secondary system. Considering both the degree of basicity and values of COD and T-N, ETA is less suitable than DMA in terms of environmental treatment problems because ETA would require higher cost to decrease COD and T-N values.

Second, PWR integrity factors such as corrosion, magnetite deposition behavior, and heat transfer efficiency of an SG were considered. In such a secondary system, most of the corrosion products transported into the SG originated from two-phase (water-steam) transition regions such as a moisture separator re-heater (MSR). To mitigate the corrosion products transported into an SG, it is very important to maintain a target pH in the sections where the water-steam phase transition occurs. In general, relative volatility (RV) is defined...
as a measure comparing the vapor pressures of the components in a liquid mixture of chemicals. The RV of an amine refers to the rate at which the water-steam phases are distributed as water or steam when they are present together (i.e., where water-steam phase transition occurs). Hence, RV is an important factor among those related to FAC in the two-phase region. An RV value is classified in relation to the value “1”: if the RV is less than “1” (like ETA), the amine will be distributed as a water phase rather than a steam phase, and if it is greater than “1” (like DMA), it will be distributed as the steam phase rather than the water phase (Table 4). The RV of MPA is close to “1” with temperatures >175 °C, and thus is distributed about equally in steam and water phases. From the viewpoint of mitigating corrosion in two-phase regions, the use of ETA is more suitable than the use of DMA. Based on the ICP-AES results in this work, the amount of magnetite deposits with MPA and DMA (relative to that of ETA), were less by approximately 41 and 55%, respectively. In addition, when using ETA, MPA, and DMA, the average porosity was approximately 34.7%, 33.0%, and 24.6%, respectively. Large pores have a negative effect on the heat transfer efficiency of SGs. The reduction in heat transfer efficiency of an SG is expected to be the lowest when DMA is used. In terms of SG tube fouling, ETA would be less suitable than DMA or MPA.

Finally, we consider the effect of amines on the human bodies of workers in nuclear power plants (NPPs). It is well-known that all amines may be exposed to the air during work on-site, and that most amines have deleterious effects on the human body. Among the various amines, ETA is known to have seriously deleterious effects on the human body. The hazards to humans of each advanced amine were investigated and specified in the Support Document to Technical Guide 230, which was reported by the U.S. Army Public Health Command (USAPHC) [42]. According to this document, when the human body is exposed to these three amines in air, the amount of ETA, MPA, and DMA able to cause critical deleterious effect is 75, 150, and 460 mg/m³ per hour, respectively. That is, compared to the other amines, ETA would be the most harmful to workers in NPPs, DMA the least harmful.

From these comparative analyses of the possibility of using MPA or DMA in place of ETA, we concluded that DMA is more suitable than MPA to replace ETA. Although DMA has a negative effect on the FAC in two-phase transition regions, it was superior to ETA and MPA in terms of human toxicity, cost of solving environmental problems, magnetite deposition behavior, and degradation of the heat transfer efficiency of SGs. However, several issues such as amine cost, stability, and decomposition products of other substances should be considered before applying DMA as an alternative to ETA in real NPPs [43].

4. Conclusions

(1) The deposited magnetite particles were polyhedral or spherical, ranging in size from tens of nanometers to several micrometers with all three amines. The average porosity when using ETA, MPA, and DMA was approximately 34.7%, 33.0%, and 24.6%, respectively. Compared to ETA, the amount of magnetite deposited with MPA and DMA was significantly less (by about 41% and 55%, respectively).

(2) Based on the particle characteristic data, the particle size decreases when MPA and DMA are used, compared to the case using ETA. The mean diameter of the deposited particles is largest (0.474 µm) when using ETA. In contrast, when using MPA and DMA, they are 0.292 and 0.189 µm, respectively.

(3) In the initial stage of magnetite deposition, the deposition mechanism could be explained by the difference in the zeta potential of magnetite particles and the surface of the Alloy 690TT tubes. When using DMA, the difference in zeta potential was largest, so the greatest electrostatic repulsion occurs between the magnetite particles and the surface of Alloy 690TT tubes during the deposition. As magnetite deposition proceeds, the electrostatic force between the already deposited magnetite and magnetite particles in secondary water would be a major factor in the mechanism of deposit
growth. The repulsive force between the magnetite nanoparticles was highest in the DMA solution, resulting in the minimum amount of magnetite deposition.

(4) Compared to ETA, DMA has many advantages in terms of SG fouling control, human safety, and environmental treatment cost, so it is worth considering DMA as an alternative pH control agent to replace ETA, which is currently widely used for this purpose in PWRs. However, several issues such as amine cost, stability, and decomposition products of other substances should be considered to before applying DMA as an alternative to ETA in real NPPs.

**Author Contributions:** Designed study, Y.-B.L.; methodology, J.-M.L.; software, Y.-B.L. and J.-M.L.; analysis, Y.-B.L.; investigation, Y.-B.L. and J.-M.L.; writing—original draft preparation, Y.-B.L.; writing—review and editing, J.-H.L., D.-H.H. and S.-H.J.; supervision, S.-H.J. All authors have read and agreed to the published version of the manuscript.

**Funding:** This work was supported by the National Research Foundation (NRF) grant of the Republic of Korea funded by the Korean government (NRF-2017M2A8A4015159).

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** Not applicable.

**Conflicts of Interest:** The authors declare no conflict of interest.

**Abbreviations**

- BPR: Back-pressure regulator
- COD: Chemical oxygen demand
- DI: Deionized
- DMA: Dimethylamine
- DO: Dissolved oxygen
- EDS: Energy-dispersive X-ray spectrometer
- ELS: Electrophoretic light scattering
- EPRI: Electric Power Research Institute
- ETA: Ethanolamine
- FAC: Flow accelerated corrosion
- FIB: Focused ion beam
- FWHM: Full-width at half-maximum
- HP: High-pressure
- HR-XRD: High resolution X-ray diffractometer
- ICP-AES: Inductively coupled plasma atomic emission spectroscope
- ID: Inner diameter
- MPA: 3-methoxypropylamine
- MSR: Moisture separator re-heater
- NPP: Nuclear power plants
- OD: Outer diameter
- PWR: Pressurized water reactor
- RV: Relative volatility
- SCC: Stress corrosion cracking
- SEM: Scanning electron microscope
- SG: Steam generator
- SNB: Subcooled nucleate boiling
- T/C: Thermo-couple
- T-N: Total nitrogen
- TSP: Tube support plate
- TT: Thermally treated
- USAPHC: U.S. Army Public Health Command
References

1. Prince, A.A.M.; Velmurugan, S.; Narasimhan, S.V.; Ramesh, C.; Murugesan, N.; Raghavan, P.S.; Gopalan, R.J. Dissolution behaviour of magnetite film formed over carbon steel in dilute organic acid media. J. Nucl. Mater. 2001, 289, 281–290. [CrossRef]
2. Ramesh, C.; Murugesan, N.; Prince, A.A.M.; Velmurugan, S.; Narasimhan, S.V.; Ganesan, V. Applied of polymer electrolyte based hydrogen sensor to study corrosion of carbon steel in acid medium. Corros. Sci. 2001, 43, 1865–1875.
3. Bignold, G.J.; Garbett, K.; Garnsey, R.; Woolsey, I.S. Erosion corrosion of nuclear steam generators, water chemistry of nuclear reactor systems 2. Br. Nucl. Energy Soc. 1981, 1, 5–18.
4. Marks, C. Steam Generator Management Program: Effects of Different pH Control Agents on Pressurized Water Reactor Plant Systems and Components; EPRI: Palo Alto, CA, USA, 2009.
5. Vepsäläinen, M.; Saario, T. Magnetite Dissolution and Deposition in NPP Secondary Circuit; VTT Technical Research Centre of Finland (VTT): Espoo, Finland, 2010.
6. Robert, D.V., Jr. Deposit accumulation in PWR steam generators. In Steam Generators for Nuclear Power Plants; Woodhead Publishing: Cambridge, UK, 2017; Volume 11, pp. 323–363.
7. Turner, C.W.; Khumsa-Ang, K. Corrosion product transport and fouling in nuclear steam generators. In Steam Generators for Nuclear Power Plants; Woodhead Publishing: Cambridge, UK, 2017; Volume 9, pp. 215–271.
8. Wolfe, R. Steam Generator Management Program: Steam Generator Deposit Removal Strategies Sourcebook; EPRI: Palo Alto, CA, USA, 2015.
9. Turner, C.W.; Shamsuzzaman, K.; Tapping, R.L. Factors Affecting the Consolidation of Steam Generator Sludge; AECL-10759; AECL: Chalk River, ON, Canada, 1993.
10. Turner, C.W.; Brimkie, M.E.; Lavoie, P.A. Physical and Chemical Factors Affecting Sludge Consolidation; AECL-611674; AECL: Chalk River, ON, Canada, 1997.
11. Jeon, S.-H.; Song, G.D.; Hur, D.H. Micro-galvanic corrosion of steam generator materials within pores of magnetite flakes in alkaline solutions. Metals 2018, 8, 899. [CrossRef]
12. Jeon, S.-H.; Shim, H.-S.; Lee, J.-M.; Han, J.O.; Hur, D.H. Simulation of porous magnetite deposits on steam generator tubes in circulating water at 270 °C. Crystals 2020, 10, 107486. [CrossRef]
13. Yang, G.; Pointeau, E.; Tevissen, E.; Chagnes, A. A review on clogging of recirculating steam generators in pressurized-water reactors. Prog. Nucl. Energy 2017, 97, 182–196. [CrossRef]
14. Tyapkov, V.F.; Erpyleva, S.F. Erpyleva. Water chemistry of the secondary circuit at a nuclear power station with a VVER power reactor. Thermal Eng. 2017, 64, 357–363. [CrossRef]
15. Beal, K.; Million-Picallion, L.; Lefèvre, G.; Berger, G.; Delaunay, S.; Goujon, C.; Breitelle, J.-L. Formation and Consolidation of Hard Sludge under Secondary Circuit Conditions. In Proceedings of the 20th NPC International Conference, Brighton, UK, 2–7 October 2016; p. 138.
16. Lee, J.-M.; Jeon, S.-H.; Kim, K.-S.; Han, J.O.; Hur, D.H. Effects of pH control agents on magnetite deposition on steam generator tubes. Ann. Nucl. Energy 2020, 143, 729.
17. Lee, J.-M.; Jeon, S.-H.; Han, J.O.; Hur, D.H. Effects of NaCl on magnetite deposition on the outer surfaces of steam generator tubes. Ann. Nucl. Energy 2021, 151, 107886. [CrossRef]
18. Millett, P. PWR Advanced Amine Application Guidelines—Revision 2; TR-102952-R2; EPRI: Palo Alto, CA, USA, 1997.
19. Turner, C. Identification and Testing of Amines for Steam Generator Chemistry and Deposit Control; EPRI: Palo Alto, CA, USA, 2002.
20. Varrin, R. Characterization of PWR Steam Generator Deposits; TR-106048; EPRI: Palo Alto, CA, USA, 1996.
21. Fruzzetti, K. Multivariable Assessment of Flow Accelerated Corrosion and Steam Generator Fouling, Literature Review; EPRI: Palo Alto, CA, USA, 2003.
22. Fruzzetti, K. Pressurized Water Reactor Secondary Water Chemistry Guidelines—Revision 8; EPRI: Palo Alto, CA, USA, 2017.
23. Vijayakumar, R.; Koltypin, Y.; Felner, I.; Gedanken, A. Gedanken. Sonochemical synthesis and characterization of pure nanometer-sized Fe3O4 particles. Mater. Sci. Eng. A. 2000, 286, 101–105. [CrossRef]
24. Gotić, M.; Musić, S. Synthesis of nanocrystalline iron oxide particles in the iron(III) acetate/alkohol/acetic acid system. Eur. J. Inorg. Chem 2008, 6, 966–973. [CrossRef]
25. Fruzzetti, K. Multivariable Assessment of Flow Accelerated Corrosion and Steam Generator Fouling, Loop Tests to Investigate the Role of Dissolved Iron in Steam Generator Fouling; EPRI: Palo Alto, CA, USA, 2006.
26. Dooley, R.B. Flow-accelerated corrosion in fossil and combined cycle/HRSG plants. Powerpl. Chem. 2008, 10, 68–89.
27. Cullity, B.D. Elements of X-Ray Diffraction; Addision-Wesley: Reading, MA, USA, 1978.
28. Carlson, J.J.; Kawatra, S.K. Factors affecting zeta potential of iron oxides. Miner. Process. Extr. Metall. 2013, 34, 299–303. [CrossRef]
29. Ohshima, H. Zeta potential. In Encyclopedia of Colloid and Interface Science; Tadros, T., Ed.; Publisher: Berlin/Heidelberg, Germany, 2013; pp. 1423–1436.
30. Shim, H.-S.; Park, M.-S.; Baek, S.H.; Hur, D.H. Effect of aluminum oxide coated on fuel cladding surface on crud deposition in simulated PWR primary water. Ann. Nucl. Energy 2018, 121, 607–614. [CrossRef]
31. Choi, W.-I.; Song, G.D.; Jeon, S.-H.; Kim, S.J.; Hur, D.H. Magnetite-accelerated stress corrosion cracking of alloy 600 in water containing 100 ppm lead oxide at 315 °C. J. Nucl. Mater. 2019, 522, 54–63. [CrossRef]
32. Millet, P.J.; Fenton, J.M. A Detailed Model of Localized Concentration Processes in Porous Deposits of SGs. In Proceedings of the 5th International Symposium on Environmental Degradation of Materials in Nuclear Power Systems-Water Reactors, Monterey, CA, USA, 25–29 August 1991; pp. 745–751.

33. Paine, J.P.N.; Hobart, S.A.; Sawochka, S.G. Predicting Steam Generator Crevice Chemistry. In Proceedings of the 5th International Symposium on Environmental Degradation of Materials in Nuclear Power Systems-Water Reactors, Monterey, CA, USA, 25–29 August 1991; pp. 739–744.

34. Plonski, I.J. Effect of bare metal surface on the dissolution in aqueous citrate solutions of magnetite films on carbon steel. J. Appl. Electrochem. 1997, 27, 1184–1192. [CrossRef]

35. Song, G.D.; Jeon, S.-H.; Kim, J.G.; Hur, D.H. Synergistic effect of chloride ions and magnetite on the corrosion of Alloy 690 in alkaline solutions. Corros. Sci. 2017, 131, 71–80.

36. Xia, D.-H.; Behnamian, Y.; Luo, J.-L. Review—Factors influencing sulfur induced corrosion on the secondary side in pressurized water reactors (PWRs). J. The Electrochem. Soc. 2019, 166, C49–C64. [CrossRef]

37. Turner, C.W.; Klimas, S.J.; Brideau, M.G. Thermal resistance of steam-generator tube deposits under single-phase forced convection and flow-boiling heat transfer. Can. J. Chem. Eng. 2000, 78, 53–60.

38. Smith, D.S.; Alzina, A.; Bourret, J.; Nait-Ali, B.; Pennec, F.; Tessier-Doyen, N.; Otsu, K.; Matsubara, H.; Elser, P.; Gonzenbach, U.T. Thermal conductivity of porous materials. J. Mater. Res. 2013, 28, 2260–2272. [CrossRef]

39. Jeon, S.-H.; Hong, S.; Kwon, H.-C.; Hur, D.H. Characteristics of steam generator tube deposits in an operating pressurized water reactor. J. Nucl. Mater. 2018, 507, 371–380. [CrossRef]

40. Essi, J.; Konsta, S.; Timo, S. Determining Zeta Potential of Magnetite Particles in PWR Secondary Side Water Treated with Ammonia or Ethanolamine by Using Streaming Potential Technique. In Proceedings of the 20th NPC International Conference, Brighton, UK, 2–7 October 2016; p. 151.

41. Vidojkovic, S.M.; Rakin, M.P. Surface properties of magnetite in high temperature aqueous electrolyte solutions: A review. Adv. Colloid Interface Sci. 2017, 245, 108–129. [CrossRef]

42. Matthew, M.A. Methodology for Developing Chemical Exposure Guidelines for Deployed Military Personnel; USAPHC: Palo Alto, CA, USA, 2009.

43. Klimas, S.J.; Fruzzetti, K.; Turner, C.W.; Balakrishnan, P.V.; Strati, G.L.; Tapping, R.L. Identification and testing of amines for steam generator corrosion and fouling control. In Proceedings of the ECI Conference on Heat Exchanger Fouling and Cleaning: Fundamentals and Applications, Santa Fe, NM, USA, 18–22 May 2003.