THEORETICAL ESTIMATION OF HIGH TEMPERATURE WATER CHEMISTRY IN NUCLEAR POWER PLANTS

Hyeeun Jeong, Dayu Fajrul Falaakh, Chi Bum Bahn*
School of Mechanical Engineering, Pusan National University
Busan, 46241, Republic of Korea
** E-mail: bahn@pusan.ac.kr*

ABSTRACT

This study focuses on theoretical pH calculation in secondary system of nuclear power plants, including in the two-phases environment. It uses ionization reactions, equilibrium constants, and distribution coefficients to model how substances partition between phases. This theoretical approach can be a base to develop a full secondary simulation code for enhancing corrosion control and system reliability.

KEY WORDS

Nuclear plant chemistry, pH, Distribution coefficient

1. INTRODUCTION

The secondary system of a nuclear power plant is a circulation system that converts thermal energy generated in the reactor into steam to drive the turbine, thereby producing electricity. The objective of secondary side water chemistry control is to reduce corrosion of components so as to improve the reliability and maximize the availability and operating life of major components, including the steam generator and turbine.

To mitigate corrosion, nuclear power plants in Korea have applied all-volatile treatment (AVT) since the early 1980s. This involves the injection of hydrazine to remove dissolved oxygen and the use of ammonia for pH control. It maintains a pH range 9.0 to 10.0 at room temperature. Since the early 2000s, ethanolamine (ETA) has been used as a pH control agent, which is effective in mitigating flow-accelerated corrosion (FAC). Under nuclear power plant conditions, ETA decomposes to form ammonia with up to approximately one-third decomposition. [1] As a result, when a significant amount of amine is injected, ammonia is consistently present in the system water. Hydrazine also thermally decomposes to produce ammonia, depending on the temperature and pH conditions. [2] Ammonia has a high volatility in each system. This makes the pH in the two-phase wet steam increase, while the pH in the single-phase liquid decrease. [3]

In the secondary system, the fluid circulates through the steam cycle, experiencing continuous changes in pressure, temperature and state. While the pH of the fluid is stable at room temperature, it changes under operating conditions due to temperature and steam quality variations. Since pH is a critical factor in corrosion, it is essential to accurately determine the pH in both single-phase and two-phase regions to ensure effective corrosion management and reliable system operation. Earlier studies calculated the pH of ETA and ammonia, respectively, but did not consider the ammonia produced from the decomposition of ETA and hydrazine. [1,4] Additionally, there are several commercial software programs for calculating pH at high temperatures, but they are not accessible for public use.

This study examines three substances used in the secondary water chemistry-hydrazine, ETA and ammonia-and includes theoretical aspects of pH calculation, especially within the two-phase region.

2. CALCULATION METHODS

2.1 pH in Secondary System

The ionization reaction of water is given by Eq. (1), and the pH can be calculated as follows:

$$H_2O \overset{K_W}{\rightleftharpoons} H^+ + OH^- \tag{1}$$

$$pH = -\log(a_{H^+}) \tag{2}$$

in which K_W is the water dissociation constant and a_{H^+} is the activity of hydrogen ion. When the water is pure, the concentration of hydrogen ions is equal to the concentration of hydroxide ion. The pH can be determined by Eq. (3).

$$pH(T) = -\log\left(\sqrt{K_W(T)}\right) = pK_W/2 \tag{3}$$

When ETA and hydrazine are added to water, both substances and water start to ionize as shown in Eq. (4) and (5).

$$C_2H_7NO + H_2O \overset{K_1}{\rightleftharpoons} C_2H_7NH^+ + OH^- \tag{4}$$

$$N_2H_4 + H_2O \overset{K_2}{\rightleftharpoons} N_2H_5^+ + OH^- \tag{5}$$

The reactions for ammonia formation from ETA and hydrazine is as follows.

$$C_2H_7NO \overset{Q_1}{\rightleftharpoons} NH_3 + C_2H_4O \tag{6}$$

$$2N_2H_4 \overset{Q_2}{\rightleftharpoons} 2NH_3 + N_2 + H_2 \tag{7}$$

The ionization of ammonia is represented by Eq. (8):

$$NH_3 + H_2O \overset{K_3}{\rightleftharpoons} NH_4^+ + OH^- \qquad (8)$$

in which K_i is the base strength expressed as an equilibrium constant. The equilibrium constant for each chemical reaction can be expressed as:

$$K_W = \frac{a_{H^+}a_{OH^-}}{a_{H_2O}} = \frac{m_{H^+}m_{OH^-}\gamma_{H^+}\gamma_{OH^-}}{a_{H_2O}} \qquad (9)$$

$$K_1 = \frac{a_{C_2H_7NH^+}a_{OH^-}}{a_{C_2H_7NO}} = \frac{m_{C_2H_7NH^+}m_{OH^-}\gamma_{C_2H_7NH^+}\gamma_{OH^-}}{m_{C_2H_7NO}\gamma_{C_2H_7NO}} \quad (10)$$

$$K_2 = \frac{a_{N_2H_5^+}a_{OH^-}}{a_{N_2H_4}} = \frac{m_{N_2H_5^+}m_{OH^-}\gamma_{N_2H_5^+}\gamma_{OH^-}}{m_{N_2H_4}\gamma_{N_2H_4}} \qquad (11)$$

$$K_3 = \frac{a_{NH_4^+}a_{OH^-}}{a_{NH_3}} = \frac{m_{NH_4^+}m_{OH^-}\gamma_{NH_4^+}\gamma_{OH^-}}{m_{NH_3}\gamma_{NH_3}} \qquad (12)$$

$$Q_1 = \frac{a_{NH_3}a_{C_2H_4O}}{a_{C_2H_7NO}} = \frac{m_{NH_3}m_{C_2H_4O}\gamma_{NH_3}\gamma_{C_2H_4O}}{m_{C_2H_7NO}\gamma_{C_2H_7NO}} \qquad (13)$$

$$Q_2 = \frac{a_{NH_3}}{a_{N_2H_4}} = \frac{m_{NH_3}\gamma_{NH_3}}{m_{N_2H_4}\gamma_{N_2H_4}} \qquad (14)$$

in which m_i and γ_i represent the concentration and activity coefficient of ion i, respectively.

In terms of mass balance, the total concentration of all species after dissociation should be equal to the initial concentrations of the original substances. If $m^0_{C_2H_7NO}$ and $m^0_{N_2H_4}$ are initial concentration, the following mass balance can be derived.

$$m^0_{C_2H_7NO} = m_{C_2H_7NO} + m_{C_2H_7NH^+} + m_{NH_3} + m_{C_2H_4O} \quad (15)$$

$$m^0_{N_2H_4} = m_{N_2H_4} + m_{N_2H_5^+} + m_{NH_3} \qquad (16)$$

Also, to satisfy electroneutrality, the total charge of the solution must be zero after dissociation as Eq. (17).

$$m_{H^+} + m_{NH_4^+} + m_{C_2H_7NH^+} + m_{N_2H_5^+} - m_{OH^-} = 0 \quad (17)$$

There are 9 species with unknown concentrations and 9 corresponding equations to calculate them. The concentration of each species can be determined by using the Newton-Raphson method to solve the non-linear equations. Once the hydrogen ion concentration is calculated, the pH of the liquid can be determined.

2.2 Distribution coefficient

In the secondary system, the fluid does not remain in a single liquid phase. As it goes through the steam cycle and heats up, it separates into liquid and vapor phases, forming a two-phase mixture. During the phase separation, the concentration in the liquid phase differs compared to its single-phase state. This difference can be described using distribution coefficient, which is the ratio of the concentration non-ionized in liquid to its concentration in the vapor phase, as shown in Eq. (18). [5]

$$K_D(T) = \frac{molality_{vapor}}{un - ionized\ molality_{liquid}} \qquad (18)$$

The hydrogen ion concentration was expressed as follows: [4]

$$\frac{K_W}{a_{H^+}} = \frac{K_i\, m_i^o}{(K_D \cdot q + 1 - q)\frac{K_W}{a_{H^+}} + K_i + K_i \cdot q} + a_{H^+} \quad (19)$$

in which q is steam quality, m_i^o and K_i is initial concentration an equilibrium constant of substances i, respectively.

3. SUMMARY

This paper examines the theoretical background and methods for calculating pH in the secondary side of nuclear power plants, particularly in two-phase conditions. To account for volatility, distribution coefficients are used to determine the concentration of substances. By doing so, the developed method and calculation like pH can be used as a plant data for secondary water chemistry of PWR.

ACKNOWLEDGEMENTS

This research was supported by the 'Human Resources Program in Energy Technology' of the Korea Institute of Energy Technology Evaluation and Planning(KETEP), which was funded by the Ministry of Trade, Industry&Energy(MOTIE. Korea) (NO. RS-2024-00398425), and this work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT). (RS-2024-00436693)

REFERENCES

1 I. H. Rhee, 원전 2차계통 Advanced Amine 수화학 적용기술 개발(2011).

2 K. Fruzzetti, Pressurized Water Reactor Secondary Water Chemistry Guidelines, *Rev. 7, EPRI TR-1016555* (2009).

3 E. H. Lee, K. M. Kim, H. P. KIM, Effect of Water Chemistry Factors on Flow Accelerated Corrosion : pH, DO, Hydrazine, *Corrosion Science and Technology, 12(6)* (2013) p.280-287.

4 H. Yun, K. Hwang, S. Moon, Analysis of Pipe Wall-thinning Caused by Water Chemistry Change in Secondary System of Nuclear Power Plant, *Corrosion Science and Technology, 14(6)* (2015) p. 325-330.

5 T. O. Passell, PWR Advanced All-Volatile Treatment Additives, By-Products, and Boric Acid, *EPRI TR-100755* (1992).