

pH Estimation in High Temperature Two-Phase Flow of the PWR Secondary System

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***Keywords** : nuclear plant chemistry, pH, two-phase region, distribution coefficient

1. Introduction

In the secondary system of PWR, the working fluid undergoes continuous changes in pressure, temperature, and steam quality as it circulates through the steam cycle. These variations influence the concentrations of chemical species and the overall water chemistry.

Since the early 1980s, nuclear power plants in Korea have adopted all-volatile treatment (AVT) as a corrosion mitigation strategy. This method involves injecting hydrazine to remove dissolved oxygen and using ammonia to maintain a pH range of 9.0 to 10.0 at ambient temperature. In the early 2000s, ethanolamine (ETA) was introduced as an alternative pH control agent, providing improved protection against flow-accelerated corrosion (FAC). However, ammonia, ETA, and hydrazine are volatile substances. This characteristic causes them to distribute between the liquid and gas phases in the two-phase region of the secondary system, based on their distribution coefficients. As a result, the concentration of each chemical species varies within the two-phase region, leading to pH changes that can influence corrosion behavior. Accurate pH estimation in both the single-phase and two-phase regions is essential for optimizing water chemistry and ensuring long-term system integrity.

Earlier studies have developed several commercial software for calculating pH at high temperatures [1]. Nevertheless, these programs are generally not accessible for public use [2] and have shown limitations in accurately predicting pH under the actual operating conditions of Korean nuclear power plants. Specifically, existing models often fail to account not only for the complex distribution of volatile species in the two-phase region but also for their decomposition into ammonia, leading to discrepancies between predicted and measured pH values. This gap highlights the need for a more accurate and accessible approach to estimating pH in the secondary system, considering the dynamic behavior of ammonia, ETA, and hydrazine in both liquid and vapor phases.

In this study, a theoretical analysis was conducted to examine the factors influencing pH behavior in the secondary system, particularly in the two-phase flow. Based on this, a pH calculation code was developed for a simplified system with a single inlet and outlet, considering variations in flow rate, steam quality and distribution coefficients. A schematic of the two-phase flow and its flow characteristics is presented in Fig. 1.

This work serves as the foundation for the future development of a calculation tool to estimate pH variations in the secondary system, considering the effects of ammonia, ETA, and hydrazine.

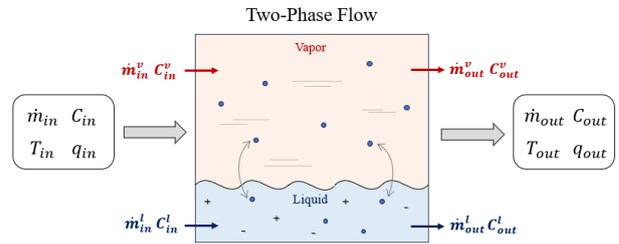
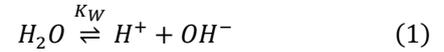


Fig. 1. Schematic of two-phase flow

2. Calculation Methods

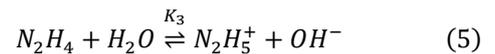
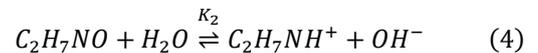
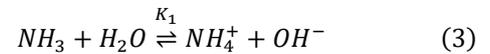
2.1 Chemical reactions

The ionization of water is described by Eq. (1), which serves as the basis for pH calculation:



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

in which K_W represents the water dissociation constant and a_{H^+} is the activity of hydrogen ions. The ionization reactions of ammonia, ETA, and hydrazine are presented below:



where K_i represents the base strength in terms of an equilibrium constant and is a function of temperature. The equilibrium constant for each ionization reactions is given by:

$$K_W(T) = \frac{a_{H^+} a_{OH^-}}{a_{H_2O}} = \frac{C_H + C_{OH^-} \gamma_{H^+} \gamma_{OH^-}}{a_{H_2O}} \quad (6)$$

$$K_1(T) = \frac{a_{NH_4^+} a_{OH^-}}{a_{NH_3}} = \frac{C_{NH_4^+} C_{OH^-} \gamma_{NH_4^+} \gamma_{OH^-}}{C_{NH_3} \gamma_{NH_3}} \quad (7)$$

$$K_2(T) = \frac{a_{C_2H_7NH^+} a_{OH^-}}{a_{C_2H_7NO}} = \frac{C_{C_2H_7NH^+} C_{OH^-} \gamma_{C_2H_7NH^+} \gamma_{OH^-}}{C_{C_2H_7NO} \gamma_{C_2H_7NO}} \quad (8)$$

$$K_3(T) = \frac{a_{N_2H_5^+} a_{OH^-}}{a_{N_2H_4}} = \frac{C_{N_2H_5^+} C_{OH^-} \gamma_{N_2H_5^+} \gamma_{OH^-}}{C_{N_2H_4} \gamma_{N_2H_4}} \quad (9)$$

where C_i and γ_i correspond to the concentration and activity coefficient of i , respectively.

2.2 Distribution coefficient

As the fluid moves through the steam cycle, it transitions from a single liquid phase to a two-phase mixture of liquid and vapor. During this transition, the concentration of a substance in the liquid phase deviates from its single-phase state. This variation can be quantified using the distribution coefficient, which is defined as the ratio of the non-ionized concentration in the liquid phase to its corresponding concentration in the vapor phase [3], as shown in Eq. (10).

$$K_D(T) = \frac{\text{molality}_{vapor}}{\text{ionized molality}_{liquid}} \quad (10)$$

2.3 Mass balance and charge conservation

There are variations in flow rate, steam quality and temperature throughout the steam cycle in the secondary system. These factors were considered in establishing the mass balance equation. The mass balance equation, incorporating mass flow rate \dot{m} , is expressed as follows:

$$\dot{m}_{in} C_{in}^0 = \dot{m}_{out} C_{out}^0 \quad (11)$$

where C_{in}^0 is the initial concentration added at the inlet. Since the same principle applies to both the inlet and outlet, only the inlet is described in the following equations. When the steam quality (q) is nonzero, the mass flow rates can be expressed as the sum of the flow rates in the vapor and liquid phases.

$$\dot{m}_{in} = \dot{m}_{in}^v + \dot{m}_{in}^l = q\dot{m}_{in} + (1-q)\dot{m}_{in} \quad (12)$$

The mass balance equation in the two-phase region is given by:

$$\dot{m}_{in} C_{in}^0 = \dot{m}_{in}^v \times C_{in}^v + \dot{m}_{in}^l \times C_{in}^l = q\dot{m}_{in} \times C_{in}^v + (1-q)\dot{m}_{in} \times C_{in}^l \quad (13)$$

$$C_{in}^0 = q \times C_{in}^v + (1-q) \times C_{in}^l \quad (14)$$

If the concentration in the liquid phase can be expressed as the sum of the ionized and non-ionized species.

$$C_{in,i}^l = C_{in,i(unionized)}^l + C_{in,i^+}^l \quad (15)$$

The concentration in the vapor phase can be determined by applying the distribution coefficient mentioned in Section 2.2,

$$C_{in,i}^v = K_D \times C_{in,i}^l \quad (16)$$

then Eq. (14) of each chemical species can be rewritten as:

$$C_{in,NH_3}^0 = qK_D C_{in,NH_3}^l + (1-q)(C_{in,NH_3}^l + C_{in,NH_4^+}^l) \quad (17)$$

$$C_{in,ETA}^0 = qK_D C_{in,ETA}^l + (1-q)(C_{in,ETA}^l + C_{in,ETAH^+}^l) \quad (18)$$

$$C_{in,N_2H_4}^0 = qK_D C_{in,N_2H_4}^l + (1-q)(C_{in,N_2H_4}^l + C_{in,N_2H_5^+}^l) \quad (19)$$

Also, to satisfy charge conservation, the total charge of the solution must be zero after dissociation as Eq. (20)

$$C_{H^+}^l + C_{NH_4^+}^l + C_{C_2H_7NH^+}^l + C_{N_2H_5^+}^l - C_{OH^-}^l = 0 \quad (20)$$

Equilibrium constant equations (Eq. (6)-(9)), mass balance (Eq. (17)-(19)), and charge conservation (Eq. (20)) are used to establish the non-linear equation. To solve the non-linear equations, the Newton-Raphson method is applied. As a result, the concentrations of each chemical species in the liquid and vapor phases can be determined. After determining the hydrogen ion concentration in the liquid phase, pH is calculated using Eq. (2).

3. Results and Discussions

By solving the non-linear equations, it is possible to obtain the concentration of both ions and chemical species distributed between the vapor and liquid phases. To calculate the pH at the inlet and outlet of a two-phase flow system, it is necessary to know the temperature, flow rate, and steam quality at each location. Additionally, the initial concentration at the inlet must be known to compute the pH at the outlet.

The example calculated in this study models the inlet as saturated liquid, which transitions into wet steam at the outlet. However, due to the limitations in available data, the calculations were performed separately for ammonia and ETA rather than for a system where all species are present simultaneously. The inlet conditions used for the calculations are summarized in Table I. In this study, there is a single inlet and outlet, meaning the mass flow rate remains the same at both points. Therefore, the concentration at the inlet and outlet is identical according to Eq. (11). Table II and III present individual results for cases where either ammonia or ETA was added.

Table I: Flow and thermodynamic conditions [4]

	Inlet	Outlet
NH ₃ Initial conc. (ppb)	1364	-
ETA Initial conc. (ppb)	2500	-
Mass flow rate (kg/s)	1605.84	-
Temperature (°C)	232.22	289.39
Steam quality	0	0.9975

Table II: Calculation results for inlet and outlet (NH₃)

	Inlet	Outlet
Conc. in liquid (ppb)	1364	1.02
Conc. in vapor (ppb)	0	1362.98
Estimated pHr	6.18	5.82

Table III: Calculation results for inlet and outlet (ETA)

	Inlet	Outlet
Conc. in liquid (ppb)	2500	10.48
Conc. in vapor (ppb)	0	2489.52
Estimated pHr	6.18	6.13

The steam quality is 0 at the inlet, indicating a single-phase flow. Consequently, no chemical species are present in the vapor phase. In contrast, the steam quality is 0.9975 at the outlet, meaning the fluid contains almost no moisture. Both ammonia and ETA have migrated to the vapor phase, with distribution coefficients of 3.62 for ammonia and 0.65 for ETA. This difference in volatility directly affects the pH at the outlet, as a higher distribution coefficient leads to more species migrating to the vapor phase, thereby lowering the pH in the liquid phase. ETA has been used as a substitute for ammonia due to its lower volatility. It maintains a higher pH in the liquid phase, reducing the risk of FAC. For this reason, the estimated pH values of 5.82 for NH₃ and 6.13 for ETA closely match expected trends. This suggests that the calculations in this study provide an accurate description of the actual system chemistry.

4. Conclusions

In this study, a general equation was formulated to calculate the pH in the two-phase region of the secondary system, incorporating mass flow rate, steam quality, and distribution coefficients to account for the effects of phase separation on pH distribution. A simplified calculation was performed to demonstrate its applicability. While this study provides a theoretical framework, further experimental validation is necessary to improve its predictive capability. To build upon this work, future pH research will focus on developing an advanced pH calculation model that incorporates localized chemical reactions and phase distributions in the secondary system, including the steam generator, turbine, and moisture separator. Additionally, the model

will account for the thermal decomposition of ETA and hydrazine, which generate ammonia [5].

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)

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