

Prediction of Water Chemistry Behavior in the Secondary Side of a PWR Steam Generator

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1. Introduction

In the secondary system of pressurized water reactors (PWRs), variations in pressure, temperature, and steam quality alter the distribution of volatile species between liquid and vapor phases. These changes affect concentrations and pH in wet steam regions such as steam generators, turbines, and condensers, influencing corrosion and long-term system integrity. To control chemistry, ammonia or ethanolamine (ETA) are used as pH agents, and hydrazine as a reducing agent.

Several computational tools have been developed to evaluate such chemistry conditions. However, most of these tools for predicting high-temperature pH are commercially restricted and proprietary, limiting plant-specific applications and model adjustments [1]. As a result, predictions often deviate from measured data in Korean PWRs due to insufficient consideration of species distribution and decomposition.

This study developed a calculation code for the steam generator that integrates mass balance and phase equilibrium to represent flow, temperature, and volatility. It covers major species (N_2H_4 , ETA, NH_3 , Na^+ , Cl^- , SO_4^{2-}) and calculates pH and concentrations along the secondary circuit, providing a practical tool for water chemistry management in nuclear power plants.

2. Calculation Methods

2.1 Mass Balance

In the secondary side of the steam generator, various chemical reactions occur including thermal decomposition, hideout, and liquid-vapor phase partitioning. The mass balance can be established by considering the inlet feedwater (FW), the outlet blowdown (BD) and main steam (MS), as well as internal reactions such as chemical decomposition, hideout, and the generation of chemical species. The blowdown concentration is assumed to be identical to that inside the steam generator. Under steady-state conditions, the mass balance for a given species i can be expressed in terms of the mass flow rates $\dot{m}$ as follows:

$$\dot{m}_{FW}C_{FW,i} - \dot{m}_{BD}C_{SG,i} - \dot{m}_{MS}C_{MS,i} - \dot{m}_{SG}L_iC_{SG,i} + \dot{m}_{SG}G_i = 0 \quad (1)$$

where C_i is the concentration of chemical species i , $\dot{m}_{SG}$ is the total water mass in the steam generator, L_i represents the loss-rate constant associated with its thermal decomposition and hideout, and G_i is the generation-rate constant corresponding to its formation from the decomposition of other species. In this model, hydrazine and ETA are modeled as undergoing losses due to thermal decomposition, Na^+ , Cl^- , and SO_4^{2-} are assumed to experience losses through hideout, and ammonia is generated from the decomposition of hydrazine and ETA. The generation rates can be expressed in terms of the decomposition rates of other substances, as shown in Eq. (2). In particular, the generation rate of ammonia is determined by the decomposition of hydrazine and ETA, as shown in Eq. (3):

$$G_i = \sum_j C_{SG,j}G_{ji} = \sum_j C_{SG,j}L_jk_{ji} \quad (2)$$

$$G_{NH_3} = C_{SG,ETA}L_{ETA}k_{ETANH_3} + C_{SG,hyd}L_{hyd}k_{hydNH_3} \quad (3)$$

where k_{ji} is the mass ratio of thermal decomposition of j to generation of i . In addition, the mass flow rates satisfy the continuity conditions as follows.

$$\dot{m}_{FW} = \dot{m}_{BD} + \dot{m}_{MS} \quad (4)$$

The concentration in the steam generator is given by the sum of the ionized and non-ionized forms of each species. The concentration in the main steam is obtained by multiplying the non-ionized concentration in the steam generator by the distribution coefficient $K_{D,i}$, as expressed in Eq. (5) and (6).

$$C_{SG,i} = C_i + C_{i^+} \quad (5)$$

$$C_{MS,i} = K_{D,i} \times C_i \quad (6)$$

2.2 Equilibrium Constants

The relationship in Eq. (5) is governed by the dissociation equilibrium, which can be expressed in terms of the equilibrium constant K_i as follows:



$$K_i = \frac{a_i + a_{OH^-}}{a_i} = \frac{C_i + C_{OH^-} \gamma_i + \gamma_{OH^-}}{C_i} \quad (8)$$

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

2.3 Charge Conservation

In aqueous solutions, the sum of all ionic charges must remain zero after dissociation, in accordance with the principle of charge conservation as shown in Eq. (9).

$$\sum_i^N |z_i| C_{i+} = \sum_j^M |z_j| C_{j-} \quad (9)$$

where z_i and z_j denote the charge numbers of cations and anions, respectively.

2.4 Computational Approach

The governing equations consist of the mass balance, equilibrium constants, and charge conservation. By combining these relationships, the chemical system is initially formulated as a set of nonlinear equations, which are solved by successive linear approximations. The unknowns are defined as the concentrations of all relevant chemical species and ions in the secondary system water chemistry. Table I summarizes the unknown variables considered in this work.

Table I: Chemical species considered in the calculation

	Unknown Species
Neutral Species	NaOH, NaCl, NaHSO ₄
Volatile Species	N ₂ H ₄ , ETA, NH ₃ , HCl
Cations	N ₂ H ₅ ⁺ , ETAH ⁺ , NH ₄ ⁺ , Na ⁺ , H ⁺
Anions	Cl ⁻ , SO ₄ ²⁻ , NaSO ₄ ⁻ , HSO ₄ ⁻ , OH ⁻

3. Results

The concentrations in the feedwater, blowdown, and main steam of the steam generator were determined by solving the governing equations. In this study, the feedwater values were used as inputs, while those at the main steam and blowdown were obtained from the calculations. The initial input values are listed in Table II, and the model parameters and rate constants are presented in Table III.

Table II: Initial input values [2]

	Location	Value
T (°C)	FW	232
	MS	290
	BD	290
$\dot{m}$ (kg/sec)	FW	1605.8
	BD	16.058*
q	FW	0
	MS	1
	BD	0
m_{SG} (kg)	-	68,000
C_{FW} (ppb) [3]	N ₂ H ₄	92.41
	ETA	1600
	NH ₃	800
	Na ⁺	0.036
	Cl ⁻	0.33
	SO ₄ ²⁻	0.006

* set to 1% of the feedwater flow rate

Table III: Model parameters for decomposition, hideout, and generation

	Species	Value
L_d (/sec)	N ₂ H ₄	0.015266
	ETA	1.15×10^{-5}
L_h (/sec)	Na ⁺	0.0014
	Cl ⁻	0.006
	SO ₄ ²⁻	0.00027
k_{ji} (kg)	N ₂ H ₄ → NH ₃	0.467
	ETA → NH ₃	0.333

The decomposition rates L_d , as well as the hideout rates L_h , were adjusted to match the plant data. For the parameter k_{ji} , the coefficient for hydrazine decomposition into ammonia was adopted from earlier experimental data [3]. In contrast, the coefficient for ETA was derived from the stoichiometric ratio of ammonia formed during its decomposition [4]. Table IV shows the calculated pH_T at each location. The concentrations of each chemical species are shown in Fig. 1, where they are compared with plant data and the predictions from the EPRI PCS code [3].

Table IV: Calculated results

	SG Blowdown	Main Steam	Feedwater
T (°C)	290	290	232
Steam quality	0	1	0
pH _T	6.08	-	6.23
N ₂ H ₄ Conc. (ppb)	103.28	24.86	92.41
ETA Conc. (ppb)	2693.07	1587.36	1600
NH ₃ Conc. (ppb)	239.15	822.55	800
Na ⁺ Conc. (ppb)	0.52	0	0.036
Cl ⁻ Conc. (ppb)	1.24	0	0.33
SO ₄ ²⁻ Conc. (ppb)	0.28	0	0.006

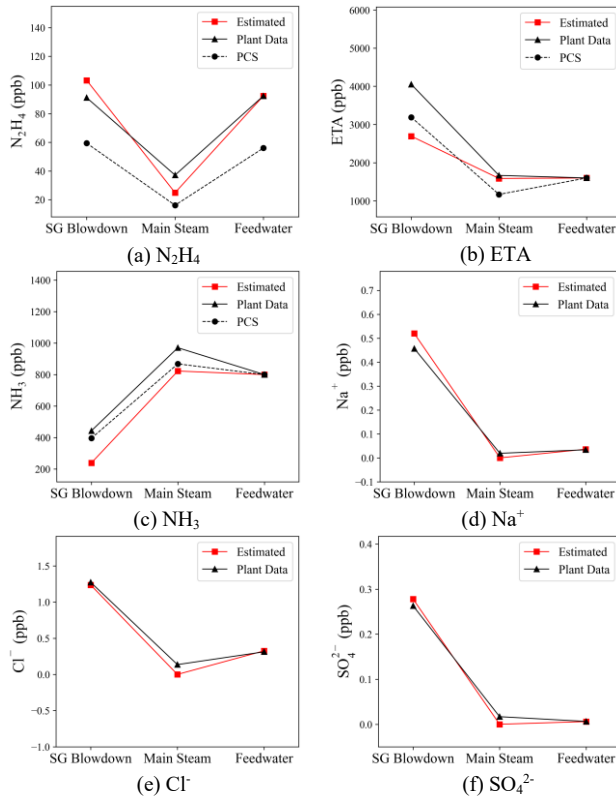


Fig 1. Predicted species concentrations at FW, BD and MS

Hydrazine shows reasonable concordance with the plant data, exhibiting higher concentrations in the blowdown and lower values in the main steam. For ETA, the predictions correspond more closely with the plant data in the main steam, whereas discrepancies remain in the blowdown. Ammonia exhibits a greater concentration in the main steam relative to the feedwater than hydrazine and ETA, which clearly indicates its stronger volatility. Nevertheless, as with ETA, noticeable differences in the absolute values remain when compared with the plant data. The predicted concentrations of ionic species are broadly consistent with the plant data at both the main steam and blowdown. In particular, the fact that the predicted and measured values are of a similar scale indicates that the model captures both the hideout behavior and the distribution into the main steam well.

4. Conclusions and Future Work

In this study, a computational model was developed to predict species concentrations and pH in the secondary system of PWR, focusing on the secondary side of steam generators. The model integrates mass balance, phase equilibrium, and charge conservation to represent thermal decomposition, hideout, and liquid-vapor partitioning. Under steady-state conditions, feedwater inputs were used to calculate concentrations in the blowdown and main steam. The results showed good agreement with plant data for hydrazine, while

discrepancies remained for ETA in the blowdown. For ammonia, deviations were observed in the blowdown but its higher concentration in the main steam relative to the feedwater was well reproduced, reflecting its strong volatility. Ionic species predictions were consistent in scale with plant measurements, confirming that the model captures both hideout and steam partitioning behaviors. While the model has been implemented and applied in practice, further validation with additional plant data is required to improve its predictive accuracy. Future work will extend the model to include the turbine, moisture separator/reheater, and condenser, enabling more comprehensive predictions across the secondary system.

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