Evaluation of pH and Iodine Re-evolution On the Conceptual Design for PCCS

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1. Introduction

In the Passive Containment Cooling System (PCCS) design, if Loss of coolant accident (LOCA) occurs, the iodine isotopes with reactor coolant are spilled out of reactor vessel. The coolant in water phase and condensed water flow to the lower locations in the reactor containment (Containment flooding area [1]). Then, according to NUREG-0800, Standard Review Plan (SRP), it is requested that the pH of the coolant should be above 7.0 to prevent elemental iodine evolution after LOCA [1]. For compliance with this requirement, the tri-sodium phosphate (TSP) with high pH are stored in steel baskets, and they are laid on the lowest floor at containment flooding area to control the pH of the water.

The purpose of this paper is to assess 1) pH value of the containment flooding area and 2) iodine re-evolution from this area in LOCA condition. In order to evaluate the pH value and the iodine re-evolution, two kinds of methodologies, such as, 1) the Equilibrium constant method (ECM) and 2) the Gibbs free energy method (GFM), are applied. According to NUREG/CR-5950, in situations where pH levels fall below ~7, the formation of I_2 will occur in irradiated iodide solutions, so it is recommended to maintain pH values above 7.0. The methodology of NUREG/CR-5950 is used to evaluate the iodine re-evolution as described in subsection of 2.3 of this paper [6].

2. Methodology

In this section the methodologies used to evaluate the pH value and iodine re-evolution are described.

2.1 Equilibrium Constant Method

$$\underbrace{H_3BO_3 + 2H_2O}_{(i)} \rightleftarrows \underbrace{H_3O^+ + B(OH)^{4-}}_{(ii)} \qquad (1)$$

The ionization constants of the forward reaction and the reverse reaction are the same at an equilibrium state. For example, in the equation (1), the constants from (i) to (ii) and (ii) to (i) might be exactly identical. Therefore, the chemical compositions have been changed until a chemical solution reaches the equilibrium states. The evaluation of chemical equilibrium requires all of the equilibrium constants associated with the reaction. Chemical equilibrium states are used in pH calculations. Focusing on H_3BO_3 and TSP which are the most influential materials on the pH when dissolved into water, the equilibrium concentrations are calculated.

2.2 Gibbs Free Energy Method

The pH calculation methodologies using equilibrium constants require all of the equilibrium constants corresponding to each reaction among the basic and acidic materials, so that the equilibrium constant method (ECM) is not proper for complex reactant problems. Instead of ECM, the Gibbs free energy method (GFM) can be used for various acidic and basic materials.

Chemical equilibrium can be explained by the first and second laws of thermodynamics. The Gibbs free energy of a closed system at constant temperature and pressure is defined as function of enthalpy, entropy and temperature as shown in equation (2) [5]. So the thermodynamic definition for Gibbs free energy is given as follows, where ΔH is enthalpy (J/mol), and ΔS is entropy (J/mol-K).

$$\Delta G = \Delta H - T\Delta S \qquad (2)$$

The concept of energy minimization is that a chemical reaction at certain temperature and pressure will be reached at equilibrium states on the condition of minimum Gibbs free energy. So, the final pH can be evaluated by using an activity of hydrogen ion.

As mentioned above, various chemical materials can be considered in the Gibbs free energy method. The chemical materials and generation mechanisms are listed in Table 1.

Table I: Acidic and Basic materials, and generation mechanisms

Acidic Material		Basic Material
Boric Acid	In Coolant	TSP
HI	From nuclear fuels	
HNO_3	Produced in irradiated water and air	
HCl	Produced in irradiated cable insulation	

[1] Containment flooding area is inside of secondary shielding wall in the containment for this paper.

This method was coded using SOLGASMIX program [3]. The SOLGASMIX program is used to evaluate the equilibrium chemical concentrations and the pH for a solution.

2.3 Iodine Re-evolution evaluation Method

In order to evaluate elemental iodine re-evolution, the molecular iodine concentration should be calculated. According to NUREG/CR-5950, the most important parameters which affect molecular iodine generation rate are pH, temperature and iodine concentration.

The first step is the evaluation of the concentration of molecular iodine (I_2) in a solution as a function of the pH of the solution. Next, the partition coefficient of iodine between the aqueous and gas phases at the gas-liquid interface is calculated as a function of temperature. And then, the mass transfer of I_2 from the bulk of the solution to the bulk of the gas space can be calculated using two-film model for liquid-gas interfacial transfer. Finally, the integrated amount of I_2 re-evolved to gas space is the equation (3) which is the integration of the re-evolution rate with respect to time. The required physical properties are mass transfer coefficient, K_g in the gas (m/s), and the surface area, A (m^2) of pool where iodine re-evolution is occurred.

$$I_{2,total\ re-evolved} = \int K_g [I_2]_{gas,i} A dt \qquad (3)$$

A graphical representation of the equation (3) is provided in Fig.1 for curves of three initial concentrations of I^-: 10^{-4} g-atoms/L, 10^{-5} g-atoms/L, and 10^{-6} g-atoms/L. Figure 1 is a replica of the same figure provided in NUREG/CR-5950.

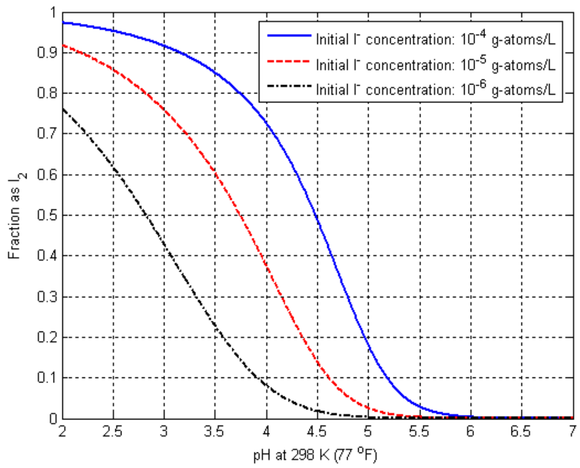

Figure1. Fraction of iodide conversion to iodine as a function of pH

3. Evaluation

3.1 pH evaluation

First of all, the pH value of containment flooding area was calculated using the ECM to calculate pH value on the onset of a LOCA and to estimate the minimum TSP quantity. Also, the equilibrium constants of TSP and boron were only considered to simplify the calculation. So, the pH value evaluated by ECM method is 7.118 and the minimum TSP quantity which is required to maintain pH value above 7.0 is 31,488,398 gram.

Next, the pH value was evaluated using the GFM to determine a long term pH value. All of the chemical materials which impact on pH value are considered including boric acid, cesium compounds, hydriodic acid, nitric acid and TSP. Finally, the pH value evaluated by GFM method is 7.273. The both results were compared to demonstrate from the two methods, so that the pH value of containment flooding area is maintained above 7.0. Both results using the two methods indicate the pH value of the containment flooding area will be maintained above 7.0 from the onset of a LOCA to 30 days [2].

3.2 Iodine re-evolution evaluation

For the reason that the pH value of the containment flooding area will be maintained above 7.0 during LOCA is going on. The iodine re-evolution in the containment flooding area was not considered.

However, it was assumed that the TSP does not contribute to control the pH in the IRWST in this paper. In this case as mentioned in section 3.1, the iodine re-evolution should be considered, and the methodology described in section 2.3 was applied in this method.

In case that TSP cannot affect pH control, the pH value based on the GFM was estimated to be about 4.3. And, the estimated pH value and the design parameters including temperature, pressure, and surface area and so on were applied to equation (3). According to Regulatory Guide 1.183, the release fractions for LOCA event are applied [2]. So, the total released iodine amounts by a LOCA are 138 moles, and the re-evolved iodine amounts after 72 hours from onset of a LOCA is 117 moles. The 117 moles are about 84% of the total released iodine in the containment flooding area. The results are clear that 84% of released iodine will be re-evolved to containment gas space after 72 hours from onset of a LOCA. ,

4. Conclusion

The pH value of the containment flooding area was evaluated using both methods of the ECM and GFM, and then the results were compared each other. The results for both methods meet the criteria that a pH value should be above 7.0, so iodine re-evolution will not be happened.

The GFM results are about 1% larger than the ECM results. Although the evaluation using GFM considered TSP, Boron and other acidic materials, the results are relatively higher than the ECM results. It means that ECM is the more conservative method than the GFM.

Also, according to the results, the pH evaluation was appropriately evaluated.

However, to confirm the importance of pH control measurement, the pH value of the containment flooding area without TSP was calculated in this paper. The results cannot be above 7.0 from the onset of a LOCA to 72 hours, the value is about 4.3. In terms of iodine re-evolution, the collected water in the containment flooding area has high temperature and pressure conditions which can considerably affect to pH value, so 84% of iodine in flooded water will be re-evolved to the containment gas space before 72 hours from onset of a LOCA.

Finally, it is verified that pH control is completely important for preventing iodine re-evolution and radiological consequence analysis.

ACKNOWLEDGEMENTS

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