Effect of Chemical Additives in Sump on Boric Acid Solubility

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1. Introduction

Boric acid precipitation, which happens in the pressurized water reactor core during post-LOCA long-term cooling period, could adhere to fuel rod surfaces and, as a result, block the fuel assembly cooling channels. Deposition of boric acid and other impurities on the fuel rods will increase thermal resistance, and then induce fuel temperature to exceed its safety limit, finally causes reactor core damage or meltdown. Therefore, recently, the boric acid precipitation issue was raised by NRC when nuclear power plants in USA, for example, Waterford EPU, applied for power uprate licenses. NRC highlighted boric acid precipitation as a generic issue due to non-conservatism in vendor's model in 2005. Also the Westinghouse Owners Group held meetings to discuss the methodology to avoid boric acid precipitation in the current PWR nuclear power plants.

Until now there is no database for evaluating the properties of a boric acid-water mixture, together with chemical additives, such as Sodium Hydroxide (NaOH), Tri-sodium Phosphate (Na_3PO_4) and fiberglass, being added from the containment sump, when the concentration is close to the solubility limit. Therefore, this study investigated boric acid solubility when boric acid is mixed with NaOH, Na_3PO_4 and other chemical additives. Another purpose of this study is to determine the relationship between boric acid solubility and the effects of chemical additives, boric acid volatility, boiling phenomenon, etc. The empirical equation of boric acid solubility in the mixture solution is deduced from experiment results and chemical dynamics theories.

2. Description of KAIST Low-Pressure Boric Acid Experiment

The KAIST low-pressure boric acid test facility was designed and experiments were performed to investigate boric acid solubility when boric acid solution was mixed with chemical additives. In this paper we only concern NaOH and Trisodium phosphate.

2.1 Experiments with Sodium Hydroxide (NaOH)

Preliminary experiments, which only considered NaOH, were performed with temperature range from 20℃ to 100℃ and pressure at 1 bar. At first 1 g NaOH was added into 100 g distilled water, which was maintained at 20℃. Then, high purified boric acid powder was slowly added into the solution, until boric acid cannot dissolve anymore in the well stirred solution. Then, maintaining the NaOH content, we increased its temperature by 10℃ and added more boric acid into the solution until new equilibrium was achieved to find the boric acid solubility at this condition. We performed experimental tests using 2 g, 3 g, 4 g, and 5 g of NaOH with the temperature range from 20℃ to 100℃ and took the same procedure as described above. The final results are shown in Figure. 1.

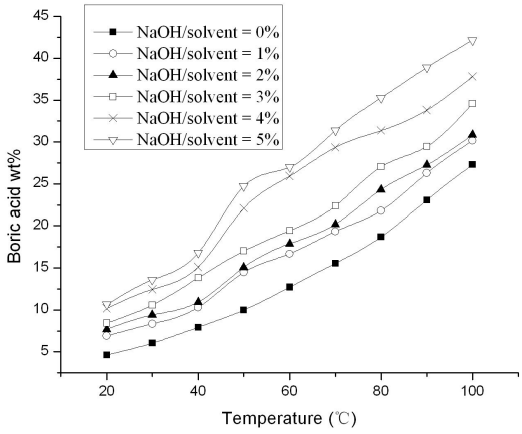

Figure 1. Boric acid solubility in wt% when mixed with NaOH.

2.2 Experiments with Trisodium Phosphate (TSP)

Trisodium phosphate (TSP) is the main chemical additive that added into the sump tank when LOCA happens in most PWR type nuclear power plants, such as Korean Standard Nuclear Power Plant (KSNP). The purpose of using TSP is to maintain the pH value of safety injection coolant, which dissolves much larger amount of boric acid than normal operation. The coolant in the reactor primary side during post-LOCA long-term cooling period is a mixture solution of boric acid, NaOH, TSP and other chemical additives or impurities from the sump tank. Therefore, it is an essential preceding step to get the database on solubility of mixture solution with boric acid and TSP for studying solubility for more complicated mixture solution.

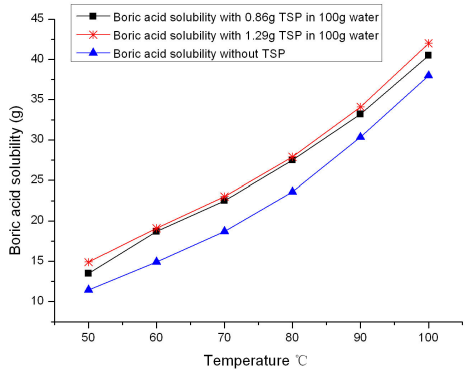

Figure 2. Boric acid solubility when mixed with TSP.

The above figure shows that TSP obviously increases boric acid solubility at given temperature and pressure range. And boric acid solubility increment increases as the amount of TSP increases. The reason why TSP induces an increase in boric acid solubility can attribute to TSP which is a weak alkaline salt when it dissolves in water. Therefore it can neutralize boric acid solution and change chemical dissolution equilibrium toward the direction in which more boric acid dissolves. The related chemical reactions are as follows:

$$Na_3PO_4 + 2\,H_2O \leftrightarrow 3\,Na^+ + H_2PO_4^- + 2\,OH^- \quad (1)$$

$$H_3BO_3 + H_2O \leftrightarrow H_2B0_3^- + H^+ \quad (2)$$

3. Analytical Model for Boric Acid Solubility

According to solubility theories in physical chemistry, the analytical model for boric acid solubility is given as follows:

$$x_2 = (\frac{1}{\gamma_2}) \cdot \exp(\frac{\Delta h_{fusion}}{R} \times \frac{1}{T_{melting}} - \frac{\Delta h_{fusion}}{R} \times \frac{1}{T}) \quad (3)$$

where x_2 and γ_2 stand for boric acid solubility in mole fraction and for the activity coefficient of boric acid, respectively.

By coupling the analytical model with experiment data, the following empirical equation of boric acid solubility for boric acid and NaOH mixture solution was obtained:

$$S = a \cdot \exp(-\frac{2628.2228}{273.15 + T} + 6.0404) \quad (4)$$

where a is an empirical parameter related to the chemical activity coefficient. Table I shows a and γ for various ratios of NaOH/Solvent.

TABLE I. a and γ for various ratios of NaOH/Solvent

N/S	0%	1%	2%	3%	4%	5%
a	115.4	139.9	150.5	175.4	219.6	261.5
γ	2.97	2.45	2.27	1.95	1.56	1.31

4. Conclusions

Boric acid solubility for mixture of boric acid and many kinds of chemical additives and impurities in sump, such TSP, glass fiber, calcium silicate, aluminum and mineral wool, is one of the most significant factors to determine precipitation. This study provides more realistic solubility database and analytical method considering the complicated situation during post-LOCA long-term cooling period in the PWR type nuclear power plants. As further experimental results come out, it will provide reliable and realistic solubility database on boron precipitation.

REFERENCES

[1] J.M.Prausnitz. Molecular Thermodynamics of Fluid-Phase Equilibria, chapter 6, Prentice-Hall Inc., N.J., 1969
[2] J.Tuunanen et al. "Experimental and analytical studies of boric acid concentrations in a VVER-440 reactor during the long-term cooling period of loss-of-coolant accidents", Nucl. Eng. & Des.**148** pp.217-231, 1994