Effect of Containment Spray Additives on the Chemical Effect after a Loss of Coolant Accident in Nuclear Power Plants

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1. Introduction

As a part of USNRC GSI-191, evaluation of Kori Unit 1 ECCS recirculation sump performance has been carried out in 2006. The work is derived from the result of first PSR(Periodic Safety Review) of Kori Unit1.
In this work, we have considered the replacement of spray additive in containment building to solve issues of GSI-191 and GL2004-02. We estimated the chemical effect of changing NaOH into TSP(Trisodium Phosphate) based on SRP(Standard Review Plan) 6.5.2. Rev.02. WCAP-16530 methodology is used to compare chemical effects of spray additive(or buffering agents). In the other side, chemical thermodynamic simulation can be utilized. Herein, the results using WCAP-16530 methodology and chemical simulation are presented.[1-3]

2. Methods and Results

Analytical methods to estimate the chemical effects of buffering agents and the results are described here.

2.1 WCAP-16530-NP(Chemical Model)

WCAP-16530-NP have been developed to predict the quantity of precipitates generated under containment sump chemical condition. This chemical model is dependent on release rate of containment material during LOCA condition. Therefore, the determination of the precipitates is started from calculating release rate equation on the containment. The target materials leached from containment include Aluminum, Calcium Silicate, Concrete, E-glass, Min-K, Aluminum Silicate and Mineral Wool. The findings of WCAP16530 is that the predominant precipitates are aluminum oxyhydroxide, sodium aluminum ailicate, and calcium phosphate(for plants using trisodium phosphate for pH control).[3] On this basis, we used this chemical model to predict the amount of precipitation, considering only the release rates of aluminum, calcium, and silicate of Kori1.
Follwings are the model that we calculate the settlement at sump to evaluate the chemical effects on the replacement of buffers on Kori 1. Equation(1) is used to calculate the amount of release(or corrosion) from containment materials.
Release rate equation is below.

$$RR = 10[A + B(pHa) + C(1000/T) + D(pHa)^2 + E(pHa)(T)/1000] \quad (1)$$

Where, A, B, C, D and E are constant from experiments, RR is release rate in mg/(m^2 –min), pHa is initial pH, and T is temperature(Kelvin).

The determination of the quantity of precipitates generated from dissolution condition at containment sump is expressed below. Equation (2), (3) and (4) determine the precipitation considering "the total release of elements from equation(1)".

$$NaAlSi_3O_8(g/L) = [Si\ g/L] \times 3.1 \quad (2)$$
$$AlOOH(g/L) = \{[Al\ g/L] - 0.35 \times [Si\ g/L]\} \times 2.3 \quad (3)$$
$$Ca_3(PO_4)_2\ (g/L) = [Ca\ g/L] \times 2.6 \quad (4)$$

According to the WCAP-16596, the recirculation condition of Kori Unit 1 and the WCAP-16596 condition is similar.
Table 1 shows this similarity below.

Table1. Comparison between Kori Unit 1 and WCAP-16596-NP

parameter	Operation Conditions at PWR (Kori Unit1)[1]	WCAP-16596-NP(Experiments Conditions)[4]
Temp.(^oF)	130 - 215	150
Boron(ppm)	2000 - 2600(RWST)	2500
pH	7.8(NaOH) 7.9(TSP)	8

Because of similarity, we can calculate the amount of settlement by previous equations (1), (2), (3) and (4) of WCAP-16530, based on the containment materials of Kori Unit 1.[1]
We assume that containment sump spray additive is changed from NaOH(at no Cal-Sil) to TSP, at PWR Kori Unit 1. Figure 1 and 2 show that the released Al and the deposition at containment sump is more dominant under NaOH than under TSP without Cal-Sil.
Figure 1 shows that the released Ca is 12 kg(under NaOH) and 11.9kg (under TSP), that the released Si is 58kg (under NaOH) and 58.5kg (under TSP) and that the released Al is 46kg (under NaOH) and 14kg (under TSP). The total precipitations are calculated as 226.6kg under NaOH and 159.73kg under TSP.

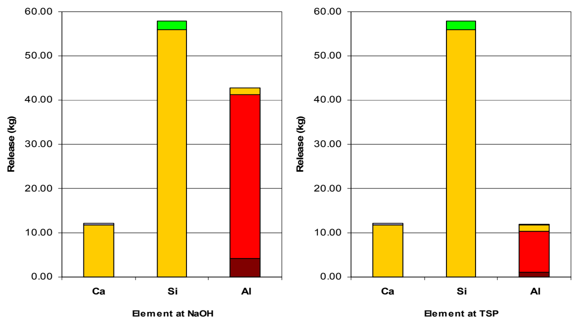

Figure 1. Release from sump using containment spray additive as NaOH(left) and TSP(right) for 24 hours.

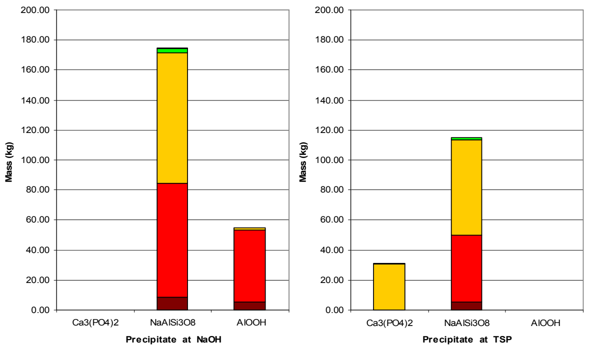

Figure 2. The amount of precipitation using containment spray additive as NaOH(left) and TSP(right) for 24 hours.

2.2 Chemical Thermodynamic Simulation (PHREEQC)

PHREEQC has been known as "common freeware" developed by USGS(United State Geological Survey) laboratory group. That is designed to calculate the chemical reaction under various conditions. Generally PHREEQC consists of data input file, chemical species definition file, simulation date file, condition file, selected output file, and dat file. Specially "dat file" can cover all the range of simulation. Sometimes "dat file" can carry out the chemical simulation without other files, because of that file having simulation part, condition part and chemical reaction part.[5]

"Aqueous model" of PHREEQC is largely dependent on the equilibrium constant of chemical reaction and temperature. It is shown that all possible solutions react within water condition. Therefore, we change default data file as named "llnl.dat" from USGS(United State Geological Survay) laboratory group to calculate the precipitation at NaOH and TSP. We change temperature and chemical equilibrium constant according to chemical index from NIST database.[6]

Because main parameter is equilibrium constant , the equilibrium constants of the chemical precipitations derived from equation (1), (2), (3) and (4) were inserted into "llnl.dat". We use mol concentration in the condition of Kori Unit 1(37,917 ft^3 [1,074,000 Liter] at sump volume , 200 $^oF \sim 110\,^oF$ at temperature, and 7.9 at pH).

Mol concentration of elements were consisted of Al (1.6 m mol under NaOH, 0.5 m mol under TSP), Ca (0.3 m mol under NaOH and TSP), and Si (1.8 m mol under NaOH, 1.9 m mol under TSP) based on volume unit $Liter^{-1}$. Figure 3 is the trend of precipitation under TSP(without Cal-Sil) from simulation.

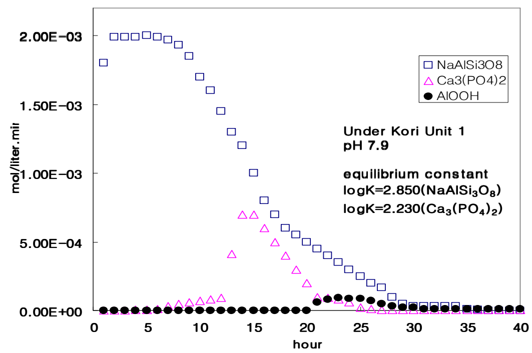

Figure 3. The trend of settling rate under TSP(without Cal-Sil) based on Kori Unit 1.

Simulation results show that total settling amount is 5 m mol/ Liter under NaOH and 2.2 m mol/Liter under TSP. These results are relative values. Because of the usage of the modified llnl.dat considering only equilibrium constant and temperaure without other conditions, the results could be used as a reference.

3. Conclusion

Methods of analysis for chemical effects of changing NaOH to TSP in Kori Unit 1 and results are described.

TSP spray additive is very effective to reduce precipitation in Kori 1. The reduced precipitation is about 40% by WCAP-16530 methodology and about 50% by PHREEQC simulation.

We conclude that in surrogating the containment spray additive at PWR, TSP(without Cal-Sil) is more excellent than NaOH in both aspect of chemical precipitation and corrosion rate. That means loss of NPSH(Net Positive Suction Head) during containment sump recirculation is largely decreased. The advantage of TSP resolve the GSI-191 chemical effect issues.

REFERENCES

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[6]http://webbook.nist.gov/chemistry.