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Thermodynamic Assessment of Silica Precipitation in the Primary Coolant of PWR Plants

Dooho Lee[a*], Hyukchul Kwon[a], Kibang Sung[a]
[a]*Korea Hydro & Nuclear Power Co. Ltd., Central Research Institute*
[*]*Corresponding author: dooholee@khnp.co.kr*

1. Introduction

Silica is present in PWR SFP (Spent Fuel Pools) in varying concentration. Increasing silica concentration has been observed in many plants' reactor coolant system (RCS) following a refueling outage as a result of the cross contamination between the refueling cavity and the spent fuel pool.

To have a better understanding of the role of silica on the fuel crud deposition, MULTEQ (MULTiple Equilibrium) calculations were performed in this study to predict high-temperature aqueous and precipitated species such as aluminum, calcium, magnesium, zinc and silica.

2. Methods and Results

2.1 Method of Analysis

MULTEQ database version 7.0 was used for this thermodynamic study to model the precipitates when the silica concentration is at 1 ppm. The code runs were performed for aluminum, calcium, magnesium, zinc individually and collectively at the following conditions:

Table 1. MULTEQ code parameters

	Al (ppb)	Ca (ppb)	Mg (ppb)	Zn (ppb)	pH @310℃
BOC	1	1	1	5	7.1
MOC	1	1	1	5	7.1

These combinations were evaluated both at beginning of cycle (BOC) and mid-cycle (MOC) boron, lithium concentrations. These conditions were as follows:

- BOC : 1400 ppm B and 2.78 ppm Li
- MOC : 700 ppm B and 1.47 ppm Li

A temperature of 330℃ was modeled to represent as high temperature as possible within the constraints of the MULTEQ code.

2.2 Modeling Results

Under all BOC and MOC conditions, the code indicates that aluminum will not precipitate with silica. Instead, aluminum is shown to complex with hydroxide ions to form soluble $Al(OH)_4^-$. Therefore, aluminum in the primary coolant will not deposit on the surfaces of fuel and will be easily removed by CVCS purification system during plant operations. In this regards, aluminum is not expected to create detrimental effects via precipitating on the core and densifying the crud deposit which would aggravate fuel clad corrosion issues.

Calcium is predicted with boron to form CaB_2O_4 when a concentration mechanism exists. At BOC condition, Calcium starts to precipitate at a concentration factor of 48. However, at MOC condition the precipitation occurs at a concentration factor of 78. MULTEQ code suggests that the precipitation of calcium with silica is not likely to occur on the fuel at BOC and MOC conditions.

The existing silica control scheme in the primary water chemistry was based on solubility curves for magnesium silicate precipitation in aqueous solution of silica and magnesium. The code predicts that magnesium will not precipitate with silica at any concentration factors. The equilibrium amount of precipitates of magnesium with boron ($MgOB_2O_3$) is presented in Table 2.

Table 2. The concentration of precipitates (moles) of magnesium and boron

Beginning-of-Cycle			Mid-Cycle	
Conc. Factor	MgOB2O3 (s)	LiBO2 (s)	Conc. Factor	MgOB2O3 (s)
1.00E+00			1.00E+00	
2.30E+00	4.03E-08		2.30E+00	
4.90E+00	1.84E-07		4.90E+00	1.46E-07
9.10E+00	3.66E-07		9.20E+00	3.56E-07
1.00E+01	4.04E-07		1.00E+01	3.91E-07
1.80E+01	7.36E-07		1.80E+01	7.30E-07
2.80E+01	1.15E-06		2.80E+01	1.14E-06
3.80E+01	1.56E-06		3.80E+01	1.56E-06
4.80E+01	1.97E-06		4.80E+01	1.97E-06
5.80E+01	2.38E-06		5.80E+01	2.38E-06
6.80E+01	2.80E-06		6.80E+01	2.79E-06
7.80E+01	3.21E-06		7.80E+01	3.21E-06
8.80E+01	3.62E-06		8.80E+01	3.62E-06
9.80E+01	4.03E-06		9.80E+01	4.03E-06
1.00E+02	4.11E-06		1.00E+02	4.11E-06
1.80E+02	7.41E-06		1.80E+02	7.41E-06
2.80E+02	1.15E-05		2.30E+02	9.46E-06
3.80E+02	1.56E-05	3.92E-02		
4.80E+02	1.98E-05	7.95E-02		
5.80E+02	2.39E-05	1.20E-01		
6.80E+02	2.80E-05	1.60E-01		
7.80E+02	3.21E-05	2.00E-01		
8.80E+02	3.62E-05	2.41E-01		
9.80E+02	4.03E-05	2.81E-01		
1.00E+03	4.12E-05	2.89E-01		

The addition of zinc to the primary coolant can be beneficial by dose rate reduction and PWSCC (Primary Water Stress Corrosion Cracking) mitigation. However, these benefits of zinc injection could be negated by detrimental effects if zinc were to deposit on fuel surfaces. Most prominent species is willemite, which is zinc orthosilicate (Zn_2SiO_4) with formal composition $2ZnO \cdot SiO_2$.[1]

MULTEQ code shows that when no concentrating mechanism is present, zinc during plant operation is expected to remain in the ionic form. In comparison, the precipitation of zinc with silica occurs at a concentration factor of 28 at any conditions (BOC and MOC). At present, an acceptable silica concentration is administered by KNF(KEPCO Nuclear Fuel Company) as less than 2.0 ppm for low duty plants and less than 1.0 ppm for high duty plants.

Impurities are not expected to be present in the primary coolant only one at a time, therefore it is needed to assess the formation of precipitates when all four cations are present at the same time. MULTEQ code suggests that five kinds of precipitates are formed during plant operations. The concentrations of precipitates in equilibrium are shown in Table 3 (BOC) and 4 (MOC).

Table 3. The concentration of precipitates (moles) at BOC condition

Conc. Factor	Zn2SiO4 (s)	CaB2O4 (s)	MgOB2O3 (s)	CaMg(SiO3)2 (s)	LiBO2 (s)
1.00E+00					
2.30E+00			4.03E-08		
4.90E+00			1.84E-07		
9.10E+00			3.66E-07		
1.00E+01			4.04E-07		
1.80E+01			7.36E-07		
2.80E+01	4.61E-07		1.15E-06		
3.80E+01	8.81E-07		1.56E-06		
4.80E+01	1.28E-06	9.87E-08	1.97E-06		
5.80E+01	1.67E-06	4.69E-07	2.38E-06		
6.80E+01	2.05E-06	8.06E-07	2.80E-06		
7.80E+01	2.43E-06	1.12E-06	3.21E-06		
8.80E+01	2.80E-06	1.42E-06	3.62E-06		
9.80E+01	3.18E-06	1.71E-06	4.03E-06		
1.00E+02	3.25E-06	1.77E-06	4.11E-06		
1.80E+02	6.19E-06		3.47E-06	3.94E-06	
2.80E+02	9.83E-06		4.99E-06	6.53E-06	
2.90E+02	1.02E-05		5.15E-06	6.78E-06	3.00E-03

Table 4. The concentration of precipitates (moles) at MOC condition

Conc. Factor	Zn2SiO4(s)	MgOB2O3(s)	CaMg(SiO3)2(s)
1.00E+00			
2.30E+00			
4.90E+00		1.46E-07	
9.20E+00		3.56E-07	
1.00E+01		3.91E-07	
1.80E+01		7.30E-07	
2.80E+01	4.34E-07	1.14E-06	
3.80E+01	8.49E-07	1.17E-06	3.84E-07
4.80E+01	1.24E-06	1.14E-06	8.32E-07
5.80E+01	1.63E-06	1.20E-06	1.18E-06
6.80E+01	2.01E-06	1.30E-06	1.49E-06
7.80E+01	2.38E-06	1.43E-06	1.78E-06
8.80E+01	2.75E-06	1.57E-06	2.05E-06
9.80E+01	3.12E-06	1.71E-06	2.32E-06
1.00E+02	3.19E-06	1.74E-06	2.37E-06
1.20E+02	3.92E-06	2.04E-06	2.89E-06

3. Conclusions

This thermodynamic study implies that all hardness cations such as aluminum, calcium and magnesium already have precipitates with boron under current normal plant operating conditions. However, In-core boiling can increase the amount of precipitates with silica, such as CaB_2O_4 and $CaMg(SiO_3)_2$. For all cases modeled, a 1 ppm silica concentration will not result in precipitation of SiO_2.

REFERENCES

[1] Status Report on Estimation of Solubility for Zinc Silicates in PWR Primary Coolant. EPRI, Palo Alto, CA: 1999. TE-114135.