

# Computational Thermodynamic Approach to Predict CRUD Formation



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**July, 2016**

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## FY16 L3 Milestone Report

### Computational Thermodynamic Approach to Predict CRUD Formation

**Milestone:**

Generate an open aqueous database with aqueous species and precipitates for CRUD stability and exercise the database in thermochemical calculations to predict the solubility

**Deliverable:**

Thermodynamic database and tables with aqueous species and precipitate phases within the CRUD

**Scope Description:**

The CALPHAD (CALculation of PHase Diagram) approach will be employed to predict the thermochemistry of CRUD at high temperature and pressure in LWR/PWRs. Free energy descriptions of aqueous species using HKF (Helgeson-Kirkham-Flowers) model [1] from the SUPCRT 2007 database [2] will be converted to create an open aqueous thermodynamic database. The aqueous database will be consistent with the existing computational thermodynamic infrastructure, and thus it will facilitate to consider a large number of oxide/hydroxide phases that may form in the coolant. First-principles total energies of precipitates whose thermodynamic descriptions are not readily available in the existing databases, e.g., bonaccordite and porous nickel ferrite clusters from NCSU, will be incorporated into the open database to predict their solubilities. The calculated CRUD thermodynamics will be then used as input for MAMBA simulations to search for bonaccordite formation.

**Constructing Open Aqueous Database:**

Commercial CALPHAD software packages provide aqueous databases (e.g., AQS2 as implemented in Thermo-Calc) that support HKF model and allow calculating thermodynamic properties of aqueous solutions at conditions of temperatures up to 1000°C, pressures up to 5 kbar, and aqueous concentrations up to 6 molality (at room temperature and pressure) or higher (at high temperature and pressure). Within the context of the CALPHAD approach, it is possible to predict the phase stability of complex multicomponent aqueous system by extrapolating parameters of critically evaluated and assessed binary and ternary systems. However, model parameters of individual phases and species within such proprietary databases are often encrypted. Hence, it is not possible to adjust parameters to replicate critical experiments when there is a discrepancy between predicted and observed values.

Due to the fact that most of thermochemical model parameters in the proprietary database have not been critically validated against thorough experiments, there is a possibility that they need to be adjusted in the future. This task focuses on creating a flexible open aqueous database --- whose model parameters can be flexibly adjusted --- that can predict thermochemical properties of complex aqueous solutions including the solubility of CRUD.

Thermo-Calc offers an open aqueous database (PAQS2) that supports the HKF model with a limited number of elements. Although most of aqueous species are missing relevant to CRUD, it can serve as a place holder for an open aqueous database. We used the ASU GEOPIG database<sup>1</sup> and SGTE (Scientific Group Thermodata Europe) substance (SSUB) database to add thermochemical model parameters for missing phases and missing aqueous species (Li, B containing species) along with phases that are relevant with the precipitation of CRUD on top the PAQS2 database. Using this approach, it should be possible to generate a sufficiently complete database to properly predict solubilities of important phases.

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<sup>1</sup> <http://geopig.asu.edu/sites/default/files/slop07.dat>

$$\begin{aligned}
\Delta \bar{G}_{P,T}^o = & \Delta \bar{G}_f^o - \bar{S}_{P_t,T_r}^o (T - T_r) - c_1 \left( T \ln \left( \frac{T}{T_r} \right) - T + T_r \right) \\
& - c_2 \left( \left[ \left( \frac{1}{T - \theta} \right) - \left( \frac{1}{T_r - \theta} \right) \right] \left( \frac{\theta - T}{\theta} \right) - \frac{T}{\theta^2} \ln \left( \frac{T_r (T - \theta)}{T (T_r - \theta)} \right) \right) \\
& + a_1 (P - P_r) + a_2 \ln \left( \frac{\Psi + P}{\Psi + P_r} \right) + \left( \frac{1}{T - \theta} \right) \left[ a_3 (P - P_r) + a_4 \ln \left( \frac{\Psi + P}{\Psi + P_r} \right) \right] \\
& + \omega \left( \frac{1}{\epsilon} - 1 \right) - \omega_{P_t,T_r} \left( \frac{1}{\epsilon_{P_t,T_r} - 1} \right) - \omega_{P_t,T_r} Y_{P_t,T_r} (T - T_r)
\end{aligned} \tag{1}$$

The standard-state thermodynamic property of any aqueous species in water can be represented by a function with seven terms which have specific values for each species as shown in Eq. 1. These seven terms ( $a_{1-4}$ ,  $c_{1-2}$ , and  $\omega$ ) are integration constants for volume (a), heat capacity (c) and temperature and pressure properties of water ( $\omega$ ) [2]. Publically available, all these parameters of individual aqueous species that are relevant with the CRUD precipitation in LWR/PWR have been converted into Thermo-Calc compatible format and included in the construction of open aqueous database.

### Validation of Open Aqueous Database

In order to validate the accuracy of the ORNL open Aqueous database developed in this work, the dissolution reaction of  $\text{LiBO}_2$  in high-temperature water has been calculated and benchmarked against available experimental results [3] and the AQS2 database. The solubility of  $\text{LiBO}_2$  in water can be represented as following isocoulombic reaction:



POLY-3 module as implemented in Thermo-Calc was used to calculate the activity coefficients of individual aqueous species to derive equilibrium constant,  $K$ . The result is plotted with experiments and they are in good agreement as shown in Figure 1. It is encouraging that thermochemical properties of complex aqueous solution can be accurately derived from the current computational approach.

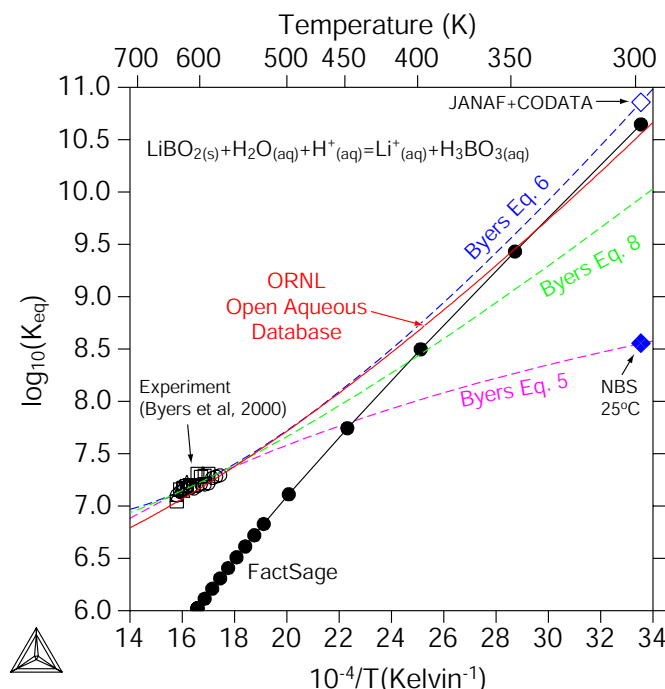


Figure 1 Calculated equilibrium constants for  $\text{LiBO}_2$  dissolution reaction from ORNL Open Aqueous database in comparison with experiments [3]

Next, we wish to benchmark the accuracy of open database against the proprietary AQS2 database from Thermo-Calc. Table 1 shows the calculated activities of aqueous species in Eq. 1 and they are in excellent agreement. This comparison shows that the current open database is as accurate as the commercial database while allowing the adjustment of model parameters when necessary.

Table 1 Calculated activities of aqueous species participating in the  $\text{LiBO}_2$  dissolution reaction from the proprietary AQS2 database as implemented in Thermo-Calc and ORNL database, respectively.

$\log_{10}a$	AQS2 Database	ORNL Open Database
$\text{H}_2\text{O}$	1.176977E-2	1.1756749E-2
$\text{H}^+$	-6.5679188	-6.5679135
$\text{Li}^+$	1.4633286	1.4669439
$\text{H}_3\text{BO}_3$	-0.30784258	-0.3078346

From the created open database, we wish to calculate the solubility of lithium mono- and tetra-borates ( $\text{LiBO}_2$  and  $\text{Li}_2\text{B}_4\text{O}_7$ ) in water under 155 bar as a function of temperature as is presented in Figure 2. Experimentally measured solubility of  $\text{LiBO}_2$  from Byers *et al.* [3] is plotted with the calculated results.

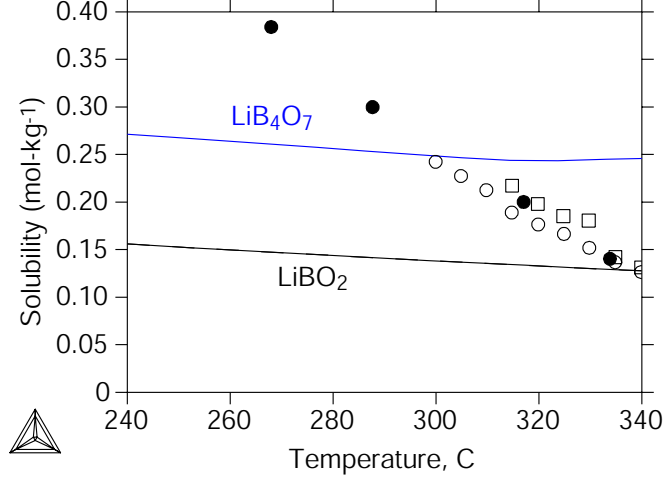


Figure 2 Calculated solubilities of  $\text{LiBO}_2$  and  $\text{Li}_2\text{B}_4\text{O}_7$  in water at the pressure of 155 bar from the open aqueous database created in the present work. Symbols represent the experimentally determined solubility of  $\text{LiBO}_2$  [3].

There is a notable discrepancy between the calculated and experimental solubility of  $\text{LiBO}_2$  in water; the current model underestimates the solubility at low temperatures. Although thermodynamic descriptions of individual phases and aqueous species are accurate within the experimental error range, further adjusting of model parameters is usually required to self-consistently reproduce phase equilibrium data. However, such an effort requires much more comprehensive experimental exploration of large compositional space at a given temperature, which is beyond the scope of current work package. *Nevertheless, the present task provides a groundwork to develop a high-fidelity aqueous thermochemistry model to predict conditions to form CRUD in LWR/PWR when critical experimental dataset is available.*

### Evaluating Gibbs Free Energy of Bonaccordite Phase

Next, we evaluate finite-temperature thermodynamic description of bonaccordite ( $\text{Ni}_2\text{FeBO}_5$ ) to be included in the aqueous calculations.

$$G(\text{Ni}_2\text{FeBO}_5) = 2G^{\text{fcc}}(\text{Ni}) + G^{\text{bcc}}(\text{Fe}) + G^{\text{rhomb}}(\text{B}) + \frac{5}{2}G^{\text{Gas}}(\text{O}_2) + \Delta H_f(-T\Delta S_f) \quad (3)$$

An initial parameter, particularly formation enthalpy at room temperature ( $\Delta H_f$ ), has been obtained from the first-principles total energy calculations based on density functional theory (DFT) provided by NCSU [4]. Formation entropy has not been introduced for the sake of simplicity. However, it was found that entropy at room temperature ( $S_{298\text{K}}$ ) of bonaccordite was too high in comparison with similar other oxide phases. Hence, we evaluated  $\Delta S_f(\text{Ni}_2\text{FeBO}_5)$  from the estimated  $S_{298\text{K}}(\text{Ni}_2\text{FeBO}_5)$  based on the ‘Latimer’ approximation approach [5], which separately takes into account ionic contribution to the entropy of solid states. As shown in Table 2, estimated  $S_{298\text{K}}$  of select oxides are in good agreement with the same values evaluated from the SSUB database.

Table 2 Estimated  $S_{298\text{K}}$  values of select oxide phases from the ‘Latimer’ approach [5] in comparison with the values from the SSUB database. The averaged values of the ‘Latimer’ estimation have been used to take into account error bar associated with the cations.

Oxide phase	$S_{298\text{K}}$ (J/mol-K)	
	‘Latimer’ approach	SSUB
$\text{SrTiO}_3$	95.2	109.0

$\text{Fe}_2\text{NiO}_4$	117.9	125.9
$\text{Al}_2\text{Sr}_3\text{O}_6$	269.1	255.4
$\text{Cr}_2\text{NiO}_4$	113.7	119.2
$\text{MgTi}_2\text{O}_5$	137.5	125.2
$\text{Ni}_2\text{FeBO}_5$	164.2	

In addition to evaluating  $\Delta S_f(\text{Ni}_2\text{FeBO}_5)$ , binary oxides (i.e., NiO,  $\text{Fe}_2\text{O}_3$ , and  $\text{B}_2\text{O}_3$ ) instead of pure elements have been used as reference states to better describe heat capacity based on the Nuemann-Kopp additivity rule of bonaccordite as well. Thermodynamic properties of bonaccordite from the evaluated model parameters are presented in Figure 3.

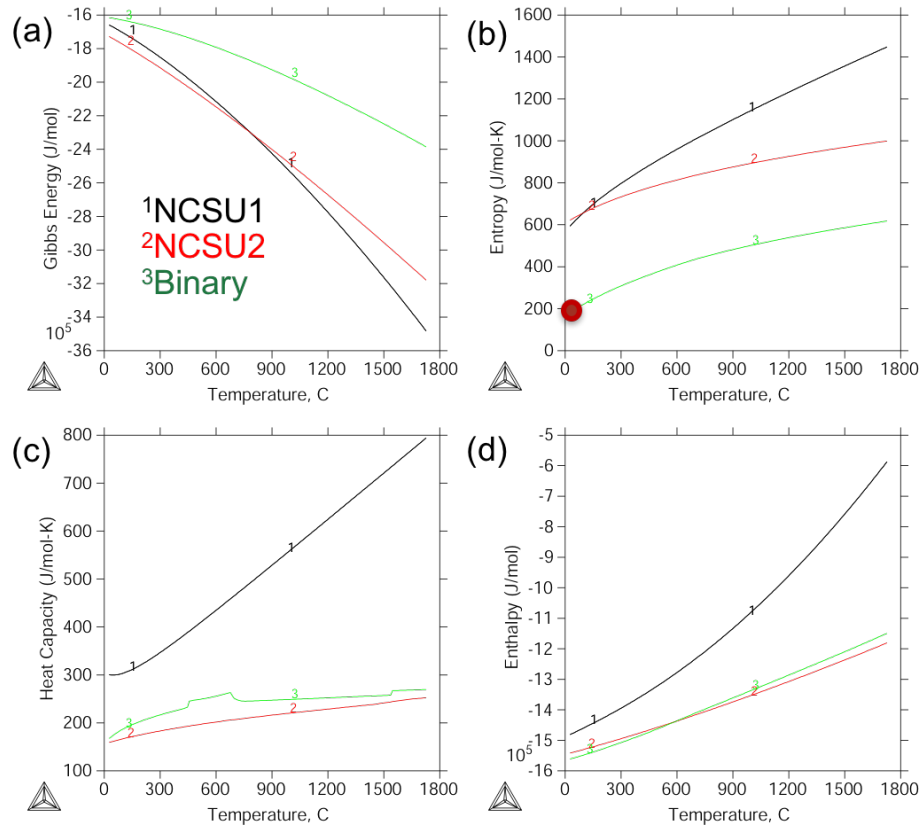


Figure 3 Calculated finite-temperature thermodynamic properties of bonaccordite: (a) Gibbs free energy, (b) entropy, (c) heat capacity and (d) enthalpy. DFT total energy and estimated  $S_{298\text{K}}$  from the ‘Latimer’ approach of have been used to evaluate enthalpy and entropy of formation, respectively.

### Solubility Calculations for PWR Coolant Containing Fe, Ni, Li and B:

A series of preliminary equilibrium calculations performed using POLY-3 Gibbs energy minimizer module as implemented in Thermo-Calc to investigate the formation of CRUD in water. We wish to construct a comprehensive aqueous phase diagram as a function of metal concentration and temperature by fully exploiting the predictive capability of the computational thermodynamic approach based on an extrapolation scheme. However, an attempt to map the phase stabilities as a function of two-dimensional elemental compositions was not successful due to a numerical convergence issue. On the other hand, we could manage to run a series of step calculations as a function of temperature at given elemental concentration. We considered 1kg of water at 155 bar pressure with arbitrary composition of Fe, Ni, Li and B.

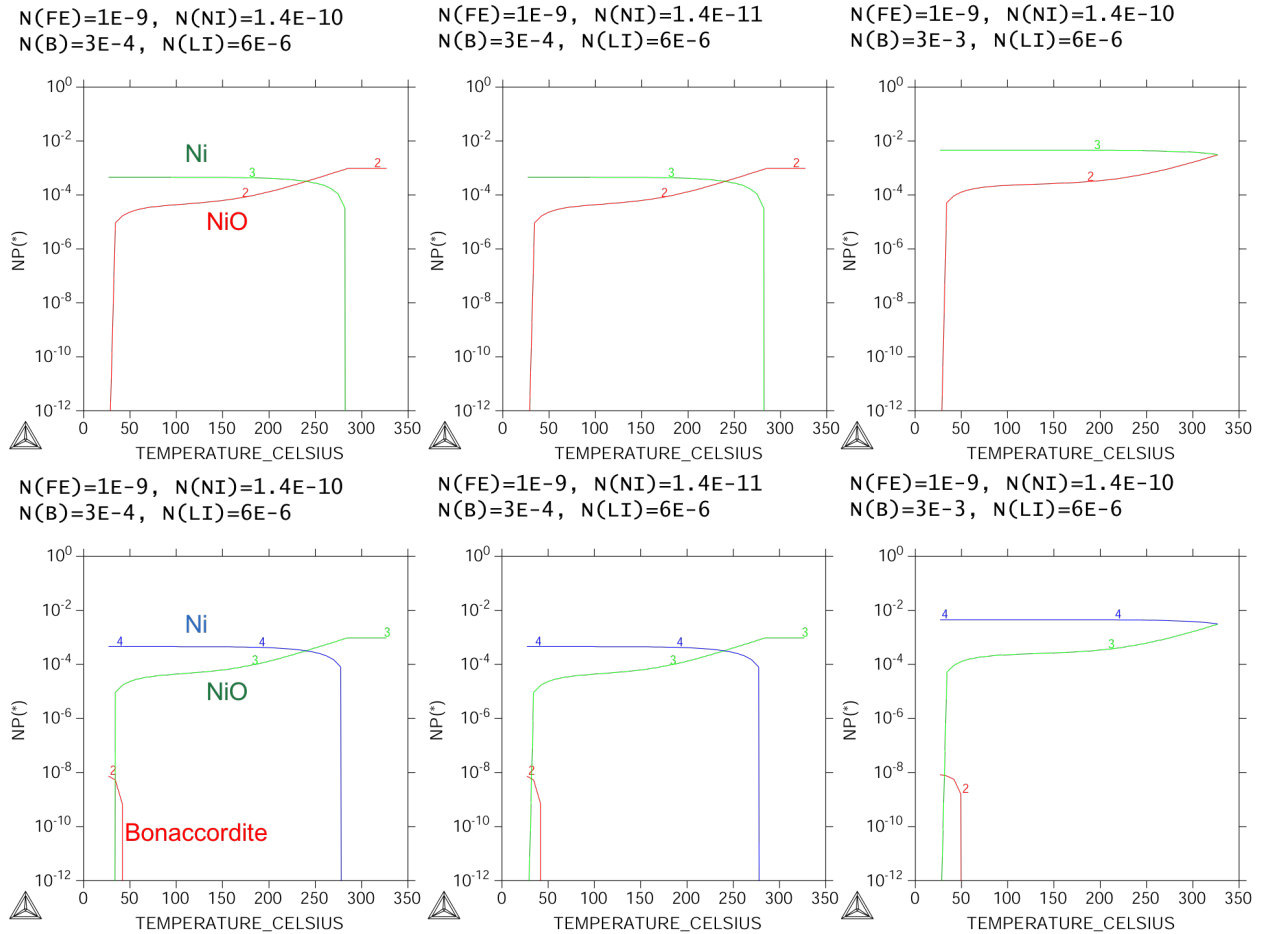


Figure 4 Calculated phase fraction of precipitate phases at arbitrary concentrations of Fe, Ni, Li and B with (top) adjusted and (bottom) unadjusted Gibbs free energy of bonaccordite.

We started with a series of point equilibrium calculations with different elemental compositions. The major precipitate phases predicted with dilute elemental composition were Ni metal and NiO as shown in Figure 4. The calculated diagram shows that the precipitation of bonaccordite is highly sensitive to the Gibbs energy model parameters used within the equilibrium calculations.

Temperature 300.00 K ( 26.85 C), Pressure 1.55000E+07  
 Number of moles of components 5.55111E+01, Mass in grams 1.00004E+03  
 Total Gibbs energy -1.70181E+07, Enthalpy -1.58471E+07, volume 9.96673E-04



Component	Moles	W-Fraction	Activity	Potential	Ref.stat
H2O	5.5510E+01	9.9996E-01	1.1177E+00	2.7750E+02	AQUEOUS
H+1	-1.0009E-03	-1.0088E-06	1.0992E-09	-5.1455E+04	SER
ZE	1.0009E-03	1.0008E-16	1.4388E-07	-3.9297E+04	REF_ELEC
B	1.0000E-04	1.0811E-06	3.7100E-58	-3.2985E+05	SER
FE	1.0000E-04	5.5845E-06	2.5798E-13	-7.2301E+04	SER
NI	5.0044E-04	2.9370E-05	2.7773E-02	-8.9389E+03	SER
LI	6.0000E-06	4.1644E-08	1.1266E-51	-2.9262E+05	SER

AQUEOUS		Status	ENTERED	Driving force	0.0000E+00
Moles	5.5510E+01, Mass	1.0000E+03,	Volume fraction	1.0000E+00	Mass fractions:
H2O	1.00000E+00	LI	4.16460E-08	FE	1.69995E-10
NI	1.66960E-07	B	3.86690E-08	ZE	2.23624E-18

Constitution:	SiteFraction	Molality	Activity	log10Act
H2O	1.00000E+00	5.55084E+01	1.00000E+00	-0.0000
OH-1	1.84662E-07	1.02503E-05	9.30346E-06	-5.0314
LI+1	1.08086E-07	5.99969E-06	5.43686E-06	-5.2647
NI+2	5.02264E-08	2.78799E-06	2.50612E-06	-5.6010
BO3H3	3.94473E-08	2.18966E-06	1.98872E-06	-5.7014
BO2-1	2.49884E-08	1.38707E-06	1.25900E-06	-5.9000
NIOH+1	1.01389E-09	5.62794E-08	5.10218E-08	-7.2922
H2	5.74507E-10	3.18900E-08	2.89632E-08	-7.5382
FE+2	3.35077E-11	1.85996E-09	1.67177E-09	-8.7768
H+1	1.98641E-11	1.10262E-09	9.98566E-10	-9.0006
FEOH+1	1.93760E-11	1.07553E-09	9.74901E-10	-9.0110
HNIO2-1	7.70302E-12	4.27583E-10	3.88305E-10	-9.4108
LIOH	2.80398E-12	1.55645E-10	1.41392E-10	-9.8496
HFE02	1.17333E-12	6.51300E-11	5.91660E-11	-10.2279
FE02-1	3.51533E-13	1.95130E-11	1.77047E-11	-10.7519
HFE02-1	2.69574E-13	1.49636E-11	1.35837E-11	-10.8670
FE0	1.57763E-13	8.75716E-12	7.95526E-12	-11.0993
NI02-2	5.80938E-16	3.22470E-14	2.90718E-14	-13.5365
FE0+1	1.50972E-18	8.38021E-17	7.59633E-17	-16.1194
H2O2	1.00000E-20	0.00000E+00	1.33184E-55	-54.8755
HO2-1	1.00000E-20	0.00000E+00	2.82037E-58	-57.5497
FE2O2H2+4	1.00000E-20	0.00000E+00	1.58091E-44	-43.8011
FE+3	1.00000E-20	0.00000E+00	3.17292E-29	-28.4985
FEOH+2	1.00000E-20	0.00000E+00	2.34690E-22	-21.6295
O2	1.00000E-20	0.00000E+00	2.56907E-77	-76.5902

Solution Properties:		pH =	9.0006	Eh =	-0.4073 V	I =	0.0000
		pe =	-6.8420	Ah =	-39.2968 kJ	m* =	0.0000
		Aw =	1.0000	os =	0.9987	pKw =	14.0320
		At1=	1.0000E-20	At2=	1.0250E-05	(equiv_mol/kg_H2O)	

BONACCORDITE		Status	ENTERED	Driving force	0.0000E+00
Moles	8.6781E-04, Mass	2.5459E-02,	Volume fraction	0.0000E+00	Mass fractions:
NI	4.44566E-01	FE	2.11515E-01	ZE	3.78741E-12
H2O	3.41147E-01	B	4.09456E-02	LI	0.00000E+00

NI_S		Status	ENTERED	Driving force	0.0000E+00
Moles	3.0297E-04, Mass	1.7781E-02,	Volume fraction	0.0000E+00	Mass fractions:
NI	1.00000E+00	LI	0.00000E+00	B	0.00000E+00
H2O	0.00000E+00	FE	0.00000E+00	ZE	0.00000E+00

FE2NI104_S		Status	ENTERED	Driving force	0.0000E+00
Moles	1.2508E-05, Mass	4.1881E-04,	Volume fraction	0.0000E+00	Mass fractions:
FE	4.76551E-01	NI	2.50405E-01	LI	0.00000E+00
H2O	3.07446E-01	ZE	3.41326E-12	B	0.00000E+00

It was found that the formation of nickel ferrite was not predicted unless the concentration of Fe and Ni is relatively high ( $10^{-4}$ ) at low temperatures. The point equilibrium calculations at low temperatures and high Fe/Ni concentration predicted the co-precipitation of nickel ferrite and bonaccordite when unadjusted Gibbs free energy of bonaccordite was used. Even with the erroneous energetics of bonaccordite, its precipitation was only predicted at low temperatures as shown in Figure 4.

Temperature 400.00 K ( 126.85 C), Pressure 1.550000E+07  
 Number of moles of components 5.55108E+01, Mass in grams 1.00003E+03  
 Total Gibbs energy -1.74711E+07, Enthalpy -1.54302E+07, volume 1.05803E-03

Component	Moles	W-Fraction	Activity	Potential	Ref.stat
H2O	5.5510E+01	9.9997E-01	2.6381E+00	3.2262E+03	AQUEOUS
H+1	-7.0377E-04	-7.0931E-07	1.4428E-07	-5.2386E+04	SER
ZE	7.0377E-04	7.0375E-17	2.1493E-06	-4.3403E+04	REF_ELEC
B	1.0000E-04	1.0811E-06	7.3202E-44	-3.3033E+05	SER
FE	1.0000E-04	5.5845E-06	1.2311E-10	-7.5888E+04	SER
NI	3.5189E-04	2.0652E-05	2.4526E-02	-1.2332E+04	SER
LI	6.0000E-06	4.1645E-08	7.5511E-41	-3.0725E+05	SER

AQUEOUS Status ENTERED Driving force 0.0000E+00  
 Moles 5.5510E+01, Mass 1.0000E+03, Volume fraction 1.0000E+00 Mass fractions:  
 H2O 9.99999E-01 NI 1.28684E-07 FE 2.16251E-09 H+1 -3.06328E-07  
 B 1.08110E-06 LI 4.16458E-08 ZE 3.03927E-17

Constitution:	SiteFraction	Molality	Activity	log10Act
H2O	9.99998E-01	5.55084E+01	9.99998E-01	-0.0000
BO3H3	1.77677E-06	9.86261E-05	1.08274E-04	-3.9655
OH-1	1.63551E-07	9.07847E-06	5.93884E-05	-4.2263
LI+1	1.08085E-07	5.99966E-06	1.24170E-05	-4.9060
H2	5.89355E-08	3.27143E-06	3.56153E-06	-5.4484
NI+2	3.72376E-08	2.06700E-06	1.09231E-05	-4.9617
BO2-1	2.47075E-08	1.37148E-06	9.26748E-06	-5.0330
H+1	2.60876E-09	1.44809E-07	1.90749E-07	-6.7195
NIOH+1	2.26076E-09	1.25491E-07	3.54901E-07	-6.4499
FE+2	3.09326E-10	1.71703E-08	8.51403E-08	-7.0699
FEOH+1	2.32466E-10	1.29039E-08	3.25850E-08	-7.4870
HFE02	1.27529E-10	7.07898E-09	9.10147E-09	-8.0409
FE02-1	2.07884E-11	1.15393E-09	5.93722E-09	-8.2264
FEO	6.63440E-12	3.68266E-10	4.73481E-10	-9.3247
LIOH	3.58194E-12	1.98828E-10	2.55634E-10	-9.5924
HNIO2-1	1.16713E-12	6.47859E-11	6.38958E-10	-9.1945
HFE02-1	8.27251E-13	4.59195E-11	3.39530E-10	-9.4691
FEO+1	9.93537E-16	5.51498E-14	1.41719E-13	-12.8486
NI02-2	2.96979E-16	1.64849E-14	7.33341E-13	-12.1347
FE0H+2	1.72054E-20	9.55045E-19	4.73568E-18	-17.3246
H2O2	1.00000E-20	0.00000E+00	4.73952E-41	-40.3243
FE2O2H2+4	1.00000E-20	0.00000E+00	2.70482E-39	-38.5679
FE+3	1.00000E-20	0.00000E+00	4.11229E-24	-23.3859
HO2-1	1.00000E-20	0.00000E+00	3.80674E-44	-43.4194
O2	1.00000E-20	0.00000E+00	1.21203E-56	-55.9165

Solution Properties: pH = 6.7195 Eh = -0.4498 V I = 0.0000  
 pe = -5.6677 Ah = -43.4030 kJ m\* = 0.0001  
 Aw = 1.0000 Os = 0.9997 pKw = 10.9458  
 At1= 1.0000E-20 At2= 9.0785E-06 (equiv\_mol/kg\_H2O)

NI\_S Status ENTERED Driving force 0.0000E+00  
 Moles 2.9971E-04, Mass 1.7590E-02, Volume fraction 0.0000E+00 Mass fractions:  
 NI 1.00000E+00 LI 0.00000E+00 B 0.00000E+00 H+1 0.00000E+00  
 H2O 0.00000E+00 FE 0.00000E+00 ZE 0.00000E+00

FE2NI104\_S Status ENTERED Driving force 0.0000E+00  
 Moles 3.4986E-04, Mass 1.1714E-02, Volume fraction 0.0000E+00 Mass fractions:  
 FE 4.76551E-01 NI 2.50405E-01 LI 0.00000E+00 H+1 -3.44023E-02  
 H2O 3.07446E-01 ZE 3.41326E-12 B 0.00000E+00

As temperature increases, the precipitation of nickel ferrite was predicted even with a smaller amount of Ni and Fe concentration ( $\sim 10^{-7}$ ). This is consistent with experimental observation that the formation of CRUD occurs near the boiling temperature. However, the formation of bonaccordite at elevated temperatures was not predicted.

Temperature 600.00 K ( 326.85 C), Pressure 1.550000E+07  
 Number of moles of components 5.55100E+01, Mass in grams 1.00000E+03  
 Total Gibbs energy -1.86838E+07, Enthalpy -1.44780E+07, volume 1.51185E-03

Component	Moles	W-Fraction	Activity	Potential	Ref.stat
H2O	5.5510E+01	1.0000E+00	9.3115E+01	2.2618E+04	AQUEOUS
H+1	-2.2356E-16	-2.2532E-19	2.9930E-07	-7.4939E+04	SER
ZE	3.4405E-16	3.4415E-29	2.2127E-06	-6.4959E+04	REF_ELEC
B	1.0000E-04	1.0811E-06	3.7668E-32	-3.6097E+05	SER
FE	1.0000E-07	5.5847E-09	1.5740E-09	-1.0112E+05	SER
NI	1.0000E-07	5.8690E-09	1.5835E-03	-3.2168E+04	SER
LI	6.0000E-06	4.1646E-08	6.0587E-29	-3.2413E+05	SER

AQUEOUS Status ENTERED Driving force 0.0000E+00

```

Moles 5.5510E+01, Mass 1.0000E+03, Volume fraction 1.0000E+00 Mass fractions:
H2O 9.99999E-01 LI 4.16460E-08 H+1 3.79363E-10 ZE -3.76390E-20
B 1.08110E-06 FE 2.18817E-09 NI 1.77984E-10
Constitution:
SiteFraction Molality Activity log10Act
H2O 9.99995E-01 5.55084E+01 9.99995E-01 -0.0000
H2 2.76073E-06 1.53245E-04 4.04172E-04 -3.3934
BO3H3 1.80059E-06 9.99487E-05 2.72763E-04 -3.5642
OH-1 1.12167E-07 6.22625E-06 2.50381E-02 -1.6014
LI+1 1.07943E-07 5.99178E-06 2.19592E-04 -3.6584
H+1 5.42295E-09 3.01021E-07 1.74430E-06 -5.7584
BO2-1 8.86423E-10 4.92042E-08 2.25879E-04 -3.6461
FEO2-1 3.71488E-10 2.06208E-08 3.11140E-05 -4.5070
HFEO2 2.59215E-10 1.43887E-08 7.48364E-08 -7.1259
LIOH 1.45780E-10 8.09203E-09 4.20871E-08 -7.3759
FEO 6.61220E-11 3.67035E-09 1.90897E-08 -7.7192
NIOH+1 5.28830E-11 2.93547E-09 3.84867E-07 -6.4147
FEOH+1 6.81046E-12 3.78040E-10 3.12130E-08 -7.5057
HFEO2-1 2.16272E-12 1.20050E-10 7.95943E-07 -6.0991
NI+2 1.01402E-12 5.62868E-11 9.73434E-08 -7.0117
HNIO2-1 7.34552E-13 4.07740E-11 8.76278E-07 -6.0574
FE+2 4.91358E-14 2.72746E-12 3.63749E-09 -8.4392
FEO+1 5.73606E-16 3.18401E-14 2.82324E-12 -11.5493
NIO2-2 3.21733E-16 1.78590E-14 1.84818E-07 -6.7333
HO2-1 1.00000E-20 0.00000E+00 1.50080E-27 -26.8237
H2O2 1.00000E-20 0.00000E+00 1.94424E-25 -24.7113
FE2O2H2+4 1.00000E-20 0.00000E+00 3.99928E-38 -37.3980
FE+3 1.00000E-20 0.00000E+00 3.77485E-23 -22.4231
FEOH+2 1.00000E-20 0.00000E+00 1.13967E-16 -15.9432
O2 1.00000E-20 0.00000E+00 6.71029E-33 -32.1733
Solution Properties: pH = 5.7584 Eh = -0.6733 V I = 0.0000
pe = -5.6551 Ah = -64.9595 kJ m* = 0.0003
Aw = 1.0000 Os = 0.9999 pKw = 7.3598
At1= 1.0000E-20 At2= 6.2262E-06 (equiv_mol/kg_H2O)

```

```

FE2NI104_S Status ENTERED Driving force 0.0000E+00
Moles 2.1286E-07, Mass 7.1273E-06, Volume fraction 0.0000E+00 Mass fractions:
FE 4.76551E-01 NI 2.50405E-01 LI 0.00000E+00 H+1 -3.44023E-02
H2O 3.07446E-01 ZE 3.41326E-12 B 0.00000E+00

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```

NI101_S Status ENTERED Driving force 0.0000E+00
Moles 1.3312E-07, Mass 4.9712E-06, Volume fraction 0.0000E+00 Mass fractions:
NI 7.85792E-01 ZE 2.67777E-12 B 0.00000E+00 H+1 -2.69892E-02
H2O 2.41197E-01 LI 0.00000E+00 FE 0.00000E+00

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## Summary

The current project exploited computational thermodynamic modeling approach to predict the solubility of CRUD in high-temperature water pertinent to LWR/PWR conditions. An ORNL open aqueous database that support the HKF model has been successfully created from the ASU GEOPIG database containing Fe, Ni, Zn, Li and B. All the phases and aqueous species that are relevant to precipitation of CRUD in LWR/PWR have been included in the database including nickel ferrite and bonaccordite. The computation results from the aqueous database using Thermo-Calc showed that formation of major CRUD constituent, nickel ferrite, is only favored when the concentration of Ni and Fe is sufficiently high enough at low temperatures. Near the boiling temperature, critical amount for metals for oxide precipitation was lower than that of lower temperatures. The precipitation of bonaccordite has been predicted only when the temperature range is relatively low. It has been also shown that that phase stabilities of oxide precipitates and aqueous species are quite sensitive to model parameters used within and further experimental validation maybe needed. This project established a ground work to incorporate critical experiments in the future to reevaluate thermodynamic model parameters of CRUD phases and aqueous species to accurately predict aqueous thermochemistry relevant to LWR/PWR coolant system.

## References

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