

# *Development of a Chemical Equilibrium Model for a Molten Core-Concrete Interaction Analysis Module*

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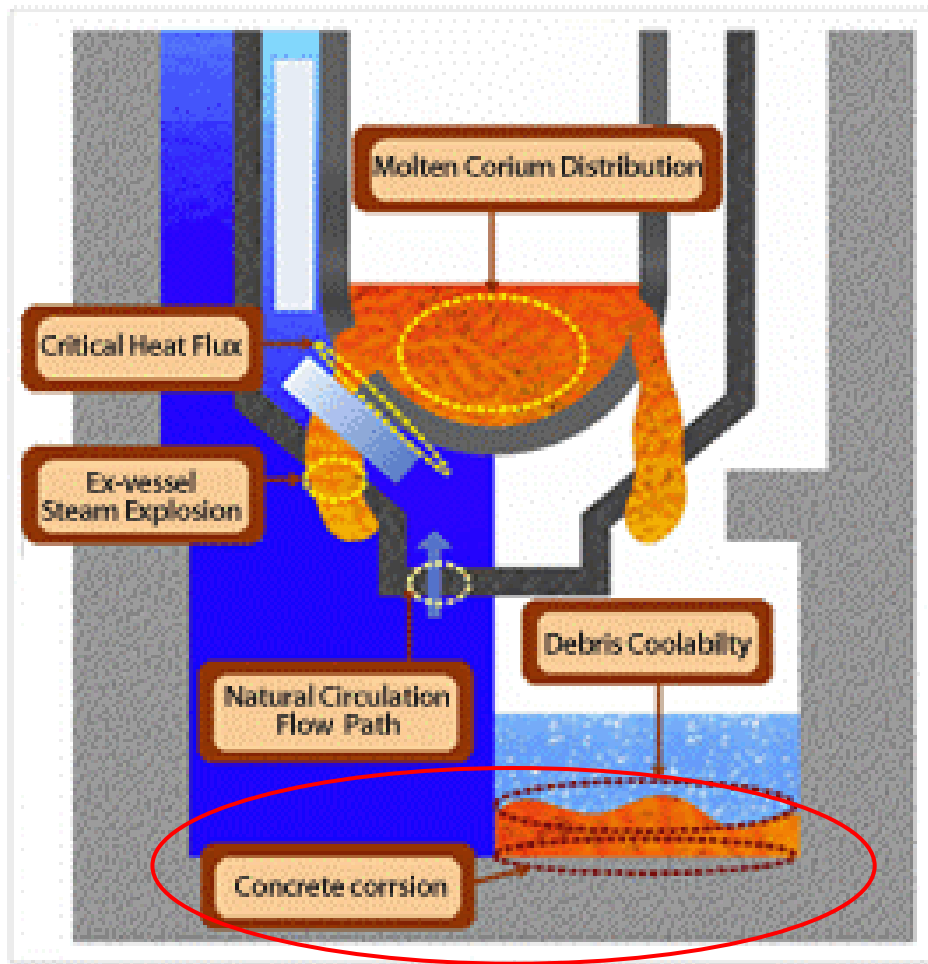
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# 1. Introduction



During a severe accident, there is a possibility of leak out of molten core from the reactor vessel. This molten core could interact with the reactor cavity region which consists of concrete. In this process, components of molten core react with components of concrete through a lot of chemical reactions. As a result, many kinds of gas species are generated and those move up forming rising bubbles into the reactor containment atmosphere.

These rising bubbles are the carrier of the many kinds of the aerosols coming from the MCCI (Molten Core Concrete Interaction) layers. To evaluate the amount of the aerosols released from the MCCI layers, the amount of the gas species generated from those layers should be calculated.

# 1. Introduction

## ■ Marginal Conditions

- ▶ The chemical equilibrium state originally implies the final state of the multiple chemical reactions; therefore, investigating the equilibrium composition of molten core can be applicable to predict the gas generation status.

## ■ Strategy

- ▶ The most common way for finding the chemical equilibrium state is a minimization of total Gibbs free energy of the system.
- ▶ To minimize it, a steepest descent method was applied and an initial guess of the solution was derived.
- ▶ In this paper, the method to make good guess of initial state is suggested and chemical reaction results are compared with results of CSSI report No 164 [4].

# 2. Method

## ■ Total Gibbs Free Energy

$$G(\mathbf{n}) = \sum_{i=1}^N n_i \left[ \left( \frac{G_i^\circ}{RT} \right) + \ln P + \ln \left( \frac{n_i}{n} \right) \right] \quad (1)$$

where

$G_i^\circ$  : standard Gibbs free energy of a species  $i$

$G$  : Gibbs free energy of a mixture

$n_i$  : mole of species  $i$

$$n = \sum_{i=1}^N n_i.$$

$N$  : total number of species

$$\sum_{i=1}^N a_{ji} n_i = b_j \quad (2)$$

where

$a_{ji}$  : the number of atoms of element  $j$   
in a molecule of species  $i$

$b_j$  : the total number of atoms of element  $j$ .

**The chemical equilibrium state is pursued by seeking the positive set of  $n_i$  which minimizes Eq. (1). While finding this state, total number of atoms of each element should be conserved as shown in Eq. (2).**

# 2. Method

## ■ Steepest Descent Method

Let  $\mathbf{n}_0$  be set as initial mole of species and the quadratic approximation of a Taylor's expansion  $G(\mathbf{n})$  of about  $\mathbf{n}_0$  is given as follows.

$$G(\mathbf{n}) = G(\mathbf{n}_0) + \sum_{i=1}^N \frac{\partial G(\mathbf{n}_0)}{\partial n_i} \Delta_i \quad \frac{\partial G(\mathbf{n})}{\partial n_i} = \left( \frac{G_i^\circ}{RT} \right) + \ln P + \ln \left( \frac{n_i}{n} \right), \quad (4)$$

$$+ \frac{1}{2} \sum_{i=1}^N \sum_{k=1}^N \frac{\partial^2 G(\mathbf{n}_0)}{\partial n_i \partial n_k} \Delta_i \Delta_k \quad (3) \quad \frac{\partial^2 G(\mathbf{n})}{\partial n_i^2} = \frac{1}{n_i} - \frac{1}{n}, \quad (5)$$

where

$$\Delta_i = n_i - n_{i0}.$$

$$\frac{\partial^2 G(\mathbf{n})}{\partial n_i \partial n_k} = -\frac{1}{n}. \quad (6)$$

Eq. (4) ~ (6) are partial differential equations of  $G(\mathbf{n})$ .

# 2. Method

## ■ Steepest Descent Method

From Eq. (3) ~ (6), Eq. (7) can be derived.

$$G(\mathbf{n}) = G(\mathbf{n}_0) + \sum_{i=1}^N \left( \left( \frac{G_i^\circ}{RT} \right) + \ln P + \ln \left( \frac{n_{i0}}{n_0} \right) \right) \Delta_i + \frac{1}{2} \sum_{i=1}^N n_{i0} \left( \frac{\Delta_i}{n_{i0}} - \frac{\Delta}{n_0} \right)^2. \quad (7)$$

# 2. Method

## ■ Method of Lagrange Multipliers

The method of Lagrange multipliers is a strategy for finding the local maxima and minima of a function subject to equality constraints such as Eq. (2).

After shifting the term in the left side of Eq. (2) to the right side, a new variable  $\lambda_j$  is introduced to prior terms. And then the summation of  $\lambda_j$  multiplied terms and Eq. (7) are united. Finally, Eq. (8) is derived.

$$\tilde{G}(\mathbf{n}) = G(\mathbf{n}) + \sum_{j=1}^M \lambda_j \left( -\sum_{i=1}^N a_{ji} x_i + b_j \right). \quad (8)$$

$M$  : total number of elements

$\lambda_j$  : Lagrange Multiplier

$$\left. \frac{\partial \tilde{G}(\mathbf{n})}{\partial n_i} \right|_{n_{i0}} = \left[ \left( \frac{G_i^\circ}{RT} \right) + \ln P + \ln \left( \frac{n_{i0}}{n_0} \right) \right] + \left[ \frac{n_i}{n_{i0}} - \frac{n}{n_0} \right] - \sum_{j=1}^M \lambda_j a_{ji} = 0. \quad (9)$$

To minimize  $\tilde{G}(\mathbf{n})$ ,  $\left. \frac{\partial \tilde{G}(\mathbf{n})}{\partial n_i} \right|_{n_{i0}}$  should be zero.



# 2. Method

## ■ Method of Lagrange Multipliers

We solve for  $n_i$  in Eq. (9) obtaining Eq. (10)

$$n_i = -n_{i0} \left[ \left( \frac{G_i^\circ}{RT} \right) + \ln P + \ln \left( \frac{n_{i0}}{n_0} \right) \right] + n_{i0} \frac{n}{n_0} + n_{i0} \sum_{j=1}^M \lambda_j a_{ji}. \quad (10)$$

We can derive Eq.(11) by summing over i in Eq. (10).

$$\sum_{i=1}^N n_{i0} \left[ \left( \frac{G_i^\circ}{RT} \right) + \ln P + \ln \left( \frac{n_{i0}}{n_0} \right) \right] = \sum_{j=1}^M \lambda_j b_j \quad (11)$$

# 2. Method

## Method of Lagrange Multipliers

Substitution of Eq. (10) into Eq. (2) gives Eq. (12)

$$\sum_{i=1}^N a_{ji} n_i = b_j \quad (2) \quad n_i = -n_{i0} \left[ \left( \frac{G_i^\circ}{RT} \right) + \ln P + \ln \left( \frac{n_{i0}}{n_0} \right) \right] + n_{i0} \frac{n}{n_0} + n_{i0} \sum_{j=1}^M \lambda_j a_{ji}. \quad (10)$$

$$b_j \left( \frac{n}{n_0} - 1 \right) + \lambda_1 \sum_{i=1}^N a_{ji} n_{i0} a_{1i} + \dots + \lambda_M \sum_{i=1}^N a_{ji} n_{i0} a_{Mi} = \sum_{i=1}^N a_{ji} n_{i0} \left[ \left( \frac{G_i^\circ}{RT} \right) + \ln P + \ln \left( \frac{n_{i0}}{n_0} \right) \right] \quad (12)$$

From Eq. (12), M linear equations can be obtained and one linear equation from Eq. (11).

$$\sum_{i=1}^N n_{i0} \left[ \left( \frac{G_i^\circ}{RT} \right) + \ln P + \ln \left( \frac{n_{i0}}{n_0} \right) \right] = \sum_{j=1}^M \lambda_j b_j \quad (11) \quad \sum_{i=1}^N a_{ji} n_{i0} \left[ \left( \frac{G_i^\circ}{RT} \right) + \ln P + \ln \left( \frac{n_{i0}}{n_0} \right) \right] \quad (12)$$

## 2. Method

### ■ Guess of Initial Equilibrium State

$$G(\mathbf{n}) = \sum_{i=1}^N n_i \left[ \left( \frac{G_i^\circ}{RT} \right) + \ln P + \ln \left( \frac{n_i}{n} \right) \right] \quad (1)$$

- ▶ In Eq. (1), there are two natural logarithm terms. That implies that molar amount of each species considered in the chemical equilibrium calculation should be larger than zero value.
- ▶ For this reason, before the search of equilibrium state, we have to set a suitable initial state.
- ▶ The restriction is that the number of atoms of each element should not be changed. Under this condition, each element is assigned evenly to a species which has this kind of element.

# 3. Numerical Procedure

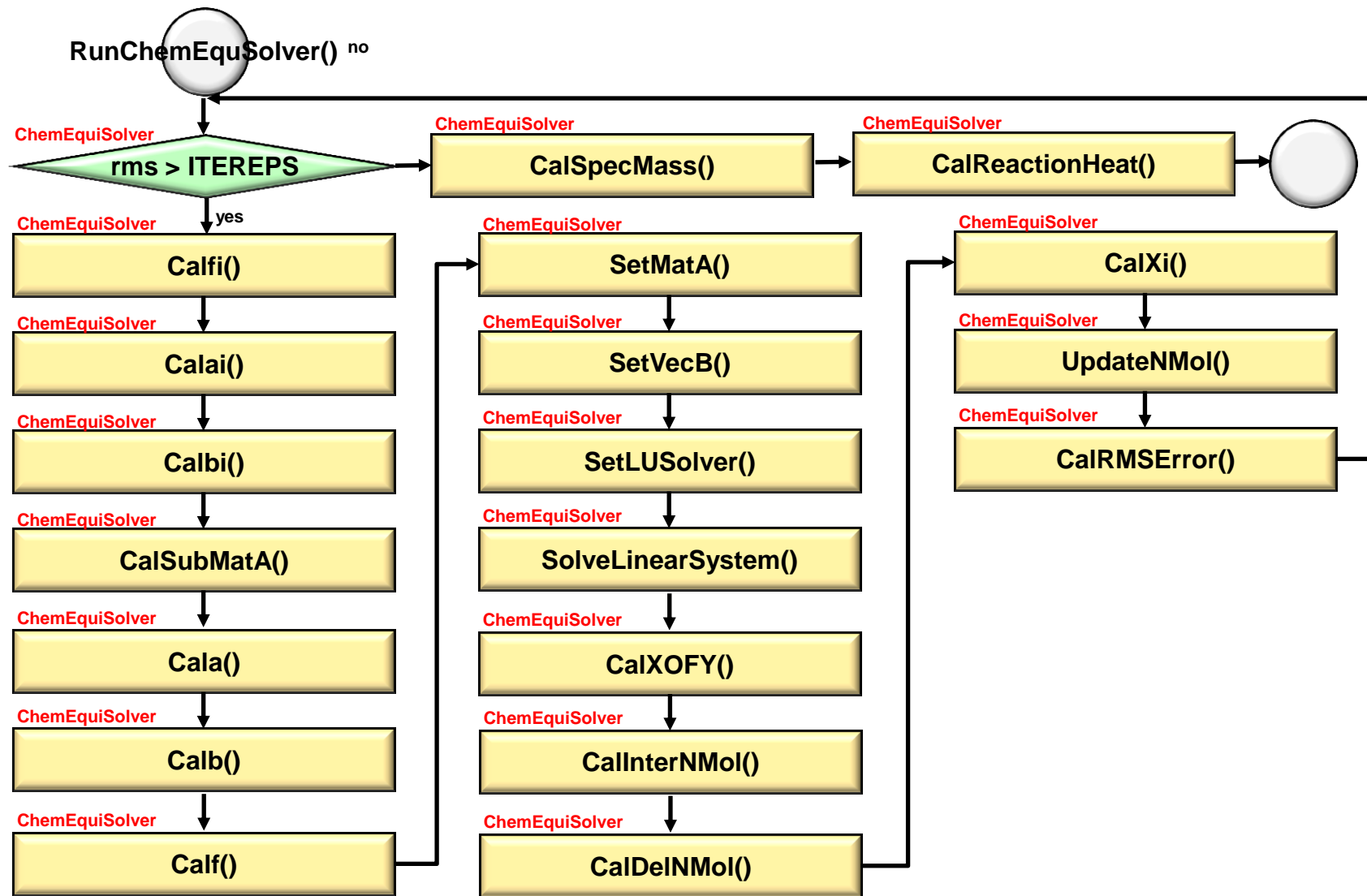
## ■ Numerical Procedure

- ▶ If the assumed initial state is applied, the coefficients of the Eq. (11) and (12) can be determined. Then  $M+1$  dimensional linear system is established.
- ▶ If this linear system is solved, we can get  $M$  Lagrange Multipliers and  $n/n_0$ .
- ▶ we can calculate mole changes  $\Delta_i = n_i - n_{i0}$  which is direction numbers indicating the relevant direction of descent. The changed distance will be limited by the fractional amount  $\xi \Delta_i$ .
- ▶  $\xi$  is the largest value satisfying following conditions.
  - all mole numbers are positive.
  - Eq. (13) should be negative.

$$\frac{dG(\mathbf{n})}{d\xi} = \sum_{i=1}^N \Delta_i \left[ \left( \frac{G_i^\circ}{RT} \right) + \ln P + \ln \frac{n_{0i} + \xi \Delta_i}{n_0 + \xi \Delta} \right] \quad (13)$$

# 3. Numerical Procedure

- Flow Chart:



# 4. Gibbs Free Energy Library

## ■ Gibbs Free Energy Library

- ▶ The Gibbs free energy value according to the temperature can be calculated from the free energy function given as follows.

$$\begin{aligned} f(T) &= -\frac{G^\circ(T) - H^\circ(298.15K)}{T} \\ &= a_0 + a_1x + a_2x^2 + a_3x^3 \\ &\quad + a_4 \ln(x) + a_5 / x + a_6x \ln(x) \end{aligned} \quad (14)$$

where  $x = T / 10000$

**Coefficients of the species are gotten from VANESA Code Manuel [5] and JANAF Database [6].**

# 5. Verification

## ■ Verification

- ▶ The developed chemical equilibrium module was examined by using data given in CSNI Report No. 164[4]. Input conditions are given Table 1 and Table 2.

**Table 1. Input Conditionis2 [4]**

Temperature	Pressure
2000 K	1 atm

**Table 2. Input Conditionis2 [4]**

Species	Mole	Species	Mole
UO <sub>2</sub>	10 <sup>5</sup>	Zr	10 <sup>4</sup>
SiO <sub>2</sub>	10 <sup>5</sup>	Fe	10 <sup>5</sup>
SrO	10 <sup>2</sup>	CaO	10 <sup>5</sup>
La <sub>2</sub> O <sub>3</sub>	10 <sup>2</sup>	CeO <sub>2</sub>	10 <sup>3</sup>
Mo	10 <sup>2</sup>	H <sub>2</sub> O	10 <sup>2</sup>
CO <sub>2</sub>	10 <sup>2</sup>		

# 5. Verification

## ■ Verification

**Table 3. Chemical Equilibrium Calculation Results**

Species	Code	CSNI	Species	Code	CSNI	Species	Code	CSNI	Species	Code	CSNI
H2	99.9913	99.9941	MoO3(g)	5.97E-15	4.75E-19	Si2(g)	0.000102	4.19E-07	SrOH(g)	7.05E-10	4.90E-08
H2O(l)	8.52E-06	0.00025771	MoOH(g)	5.55E-13	8.24E-15	UO2(l)	99490.3	99989.38	Sr(OH)2(l)	4.39E-13	4.58E-07
H2O(g)	0.006527	0.00532128	Mo(OH)2(g)	6.23E-17	3.59E-17	U(l)	509.147	10.7413	Sr(OH)2(g)	1.37E-14	8.61E-12
O2	1.39E-10	2.06E-14	(MoO3)2	7.06E-32	3.03E-36	U(g)	9.84E-05	1.05E-09	SrSiO3	8.57E-03	4.48656
C(m)	62.253	99.9586	CaO(l)	10383.8	10580.1	UO(g)	0.064076	1.05E-06	SrZrO3	99.9912	95.3612
CO	37.7464	0.0414293	Ca(l)	30.2746	23.6922	UO2(g)	0.480503	2.46E-06	La2O3(l)	99.9822	99.9312
CO2	0.000556	4.09E-07	Ca(g)	85.0747	0.067974	UO3(g)	0.00246	1.18E-08	La(g)	5.22E-06	1.21E-09
Fe(l)	99949.7	99979.3	CaO(g)	5.63E-05	2.81E-08	UOH(g)	6.46E-08	2.42E-11	LaO(g)	3.56E-02	7.43E-06
FeO(l)	15.4298	20.6424	CaOH(g)	0.004351	0.000567	U(OH)2(g)	9.62E-12	1.41E-13	LaOH(g)	4.19E-08	4.42E-10
Fe(g)	34.8714	0.03430098	Ca(OH)2(g)	1.39E-07	2.46E-08	ZrO2(l)	9819.17	9766.83	La(OH)2(g)	1.45E-08	6.19E-09
FeO(g)	5.28E-05	3.36E-08	Ca2(g)	3.01E-05	3.20E-08	Zr(l)	10.8583	10.4068	La2O(g)	1.75E-10	4.32E-14
FeOH(g)	9.41E-07	9.51E-08	CaSiO3(s)	29867.3		Zr(g)	1.28E-08	2.48E-11	La2O2(g)	1.27E-07	8.41E-12
Fe(OH)2(g)	1.46E-10	1.33E-08	CaSiO3_cw	31777.2	89396.1	ZrO(g)	6.42E-05	4.70E-08	CeO2(l)	1.55E+01	19.8189
Fe2O3(s)	3.86E-11	8.58E-11	CaSiO3_w	27856.4		ZrO2(g)	1.51E-06	7.29E-10	Ce(g)	2.90E-06	1.26E-09
Fe3O4(s)	1.94E-15	3.47E-14	SiO2(l)	925.249	889.645	ZrOH(g)	4.27E-12	1.04E-11	CeO(g)	2.17E-02	6.19E-06
Mo(l)	100	100	Si(l)	8601.22	9581.71	Zr(OH)2(g)	1.02E-11	1.39E-11	CeOH(g)	1.92E-08	3.85E-10
Mo(g)	6.18E-08	2.73E-11	Si(g)	0.359455	0.000405	ZrSiO4	69.9787	127.406	Ce(OH)2(g)	2.58E-11	2.01E-11
MoO(g)	4.42E-11	2.71E-12	SiO(g)	902.302	0.661123	SrO(l)	0.000225	0.150694	CeO2(g)	8.50E-04	6.09E-07
MoO2(l)	1.69E-07	1.00E-07	SiO2(g)	0.000233	1.12E-07	Sr(l)	3.04E-06	0.001566	Ce2O3	492.263	490.006
MoO2(g)	1.52E-11	2.17E-15	SiOH(g)	7.51E-06	4.04E-07	Sr(g)	1.36E-05	6.54E-06			
MoO3(l)	3.05E-13	8.07E-14	Si(OH)2(g)	2.17E-09	4.80E-09	SrO(g)	1.26E-10	4.11E-11			

Absence of Gibbs energy data of the species such as Fe<sub>2</sub>SiO<sub>4</sub>, CaFe<sub>2</sub>O<sub>4</sub>, U(OH)<sub>3</sub>, UO(OH), UO<sub>2</sub>(OH), U<sub>3</sub>O<sub>7</sub>, La, Ce. 15/ 8



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