

# Thermodynamic Analysis of Dissolution Reaction Mechanism of Magnetite in HyBRID Chemical Decontamination

Byung-Chul Lee<sup>1),\*</sup>, Eun-Ju Lee<sup>1)</sup>, Seon-Byeong Kim<sup>2)</sup>, Jei-Kwon Moon<sup>2)</sup>, and Hui-Jun Won<sup>2)</sup>

<sup>1)</sup> Hannam University, 1646, Yuseong-daero, Yuseong-gu, Daejeon, Republic of Korea

<sup>2)</sup> Korea Atomic Energy Research Institute, 111, Daedeok-daero 989beon-gil, Yuseong-gu, Daejeon, Republic of Korea

\*bclee@hnu.kr

## 1. Introduction

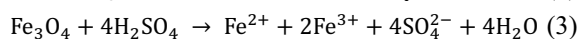
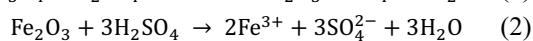
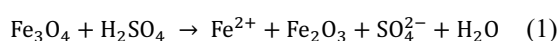
The removal of radioactive isotopes from the primary coolant system takes place with the dissolution of corrosion metal oxide layers in which radioisotopes are deposited. Chemical decontamination by oxidative and reductive dissolution is considered to be the most effective method to date. KAERI has developed the HyBRID process without using any organic acids or organic chelating agents [1, 2]. In this work we proposed the plausible reaction mechanisms of the acidic and reductive dissolution involved in the HyBRID process and studied the thermodynamic analysis of the dissolution reaction mechanisms of magnetite.

## 2. Mechanism of Magnetite Dissolution Reactions

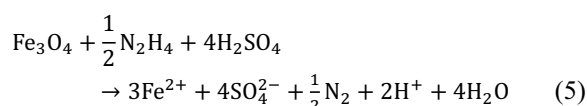
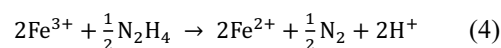
The HyBRID process uses hydrazine as a strong reducing agent and copper ion as a catalyst to form copper-hydrazine complexes which transfer electrons from  $\text{Cu}^+$  to  $\text{Fe}^{3+}$  to be reduced to  $\text{Fe}^{2+}$  [2]. Sulfuric acid is used to control the pH of the solution.  $\text{Cu}^{2+}$  are reduced by hydrazine to produce  $\text{Cu}^+$ . The resulting  $\text{Cu}^+$  are oxidized to  $\text{Cu}^{2+}$  after reducing the  $\text{Fe}_3\text{O}_4$  layer, and the  $\text{Cu}^{2+}$  are rapidly reduced to  $\text{Cu}^+$  by hydrazine, thereby completing redox cycling. Hydrazine participates in the reaction pathway of reducing  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  and simultaneously regenerating oxidized  $\text{Cu}^{2+}$  into  $\text{Cu}^+$ . [3]

### 2.1 Dissolution of Magnetite Using $\text{N}_2\text{H}_4/\text{H}_2\text{SO}_4$

The dissolution reactions of magnetite in aqueous solution of sulfuric acid are:

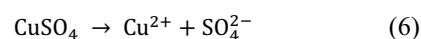


By adding hydrazine into the solution,  $\text{Fe}^{3+}$  are reduced to  $\text{Fe}^{2+}$ :

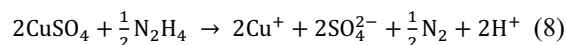
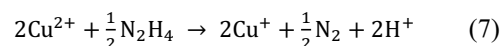


### 2.2 Dissolution of Magnetite Using $\text{N}_2\text{H}_4/\text{H}_2\text{SO}_4/\text{CuSO}_4$

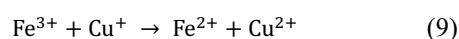
$\text{CuSO}_4$  dissociates in aqueous solution:



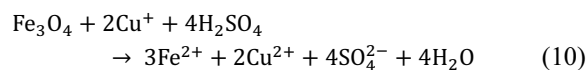
The  $\text{Cu}^{2+}$  ions are reduced to the  $\text{Cu}^+$  ions by the coordination reaction with hydrazine:



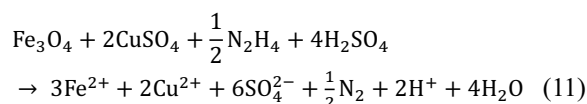
Reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  by oxidative regeneration of  $\text{Cu}^+$  to  $\text{Cu}^{2+}$  is



Combining reactions (3) and (8) gives



Hydrazine facilitates the transfer of electrons to  $\text{Fe}^{3+}$  in magnetite via  $\text{Cu}^+$  ions. From reactions (8) and (10), the dissolution reaction can be summarized:



## 3. Results and Discussion

The data of thermodynamic properties for all the species involved in the dissolution reactions of magnetite were obtained from the database of HSC Chemistry<sup>®</sup> version 9 by Outotec [4]. The

temperature dependence of heat capacity is given by:

$$C_{p,i}^0(T) = A_i + 10^{-3}B_iT + 10^5C_iT^{-2} + 10^{-6}D_iT^2 \quad (12)$$

Fig. 1 shows the standard heat of reaction ( $\Delta H_{r,T}^0$ ) for individual reactions of the HyBRID dissolution of magnetite. The values of  $\Delta H_{r,T}^0$  for all the reactions are negative, giving that the reactions are all exothermic. Fig. 2 shows the effect of temperature on the equilibrium constants ( $K$ ) for the reactions. The  $K$  values were much greater than 1 for all the reactions and decreased with the increase of the temperature.  $\ln K$  showed a nearly linear relationship to the inverse of the temperature for all the reactions.

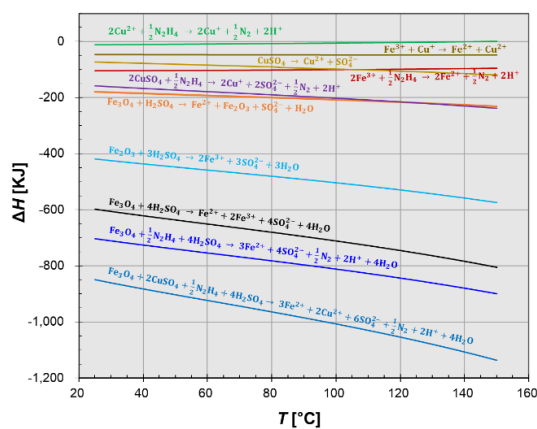


Fig. 1. Standard heat of reaction for dissolution reactions of magnetite.

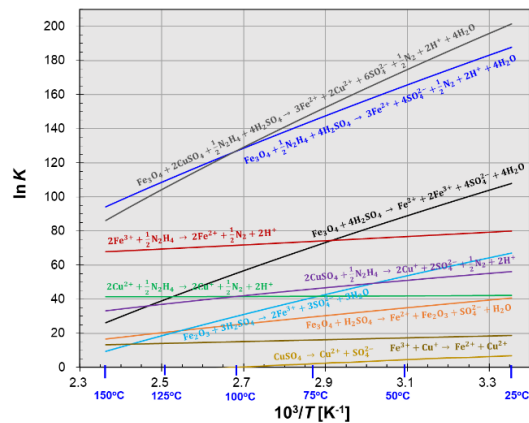


Fig. 2. Equilibrium constant for dissolution reactions of magnetite.

Table 1. Comparison of equilibrium constant ( $K$ ) for three main reactions of the dissolution of oxides

Reaction No.	$\ln K$		
	25°C	60°C	95°C
(3)	107.8	81.3	58.1
(5)	187.7	156.9	130.2
(11)	201.5	164.0	131.1

The spontaneity of the main dissolution reactions for magnetite was evaluated by comparing the equilibrium constant ( $K$ ), as shown in Table 1. Compared to the acidic dissolution using  $H_2SO_4$  only, the equilibrium constant greatly increased by adding hydrazine, indicating that the reaction spontaneity improved significantly by hydrazine. The reaction spontaneity slightly increased by further addition of copper sulfate.

#### 4. Conclusion

The chemical equilibrium of the dissolution reactions for magnetite using the HyBRID method for the decontamination of the coolant system of NPPs was investigated. Complete sets of the dissolution reaction mechanisms of magnetite were presented. For individual reactions, the standard heat of reaction, the standard entropy change of reaction, the standard Gibbs energy change of reaction, and the equilibrium constant were calculated in the temperature range of 25°C to 150°C. All the reactions were exothermic. The reaction spontaneity improved significantly by adding hydrazine and slightly increased by further addition of copper sulfate.

#### ACKNOWLEDGEMENT

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