

Equilibrium Calculations for Aqueous Systems of HyBRID Dissolution of Magnetite

Byung-Chul Lee ^{a*}, Seon Byeong Kim ^{b*}, Jei-Kwon Moon ^b

^a Hannam University, 1646 Yuseong-daro, Yuseong-gu, Daejeon, Korea

^b Korea Atomic Energy Research Institute, 111 Daedeok-daro 989 Beon-gil, Yuseong-gu, Daejeon, Korea

*Corresponding authors: bcllee@hnu.kr, sbkim@kaeri.re.kr

1. Introduction

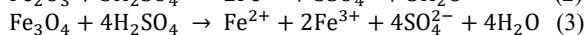
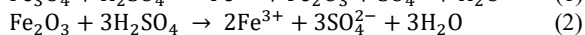
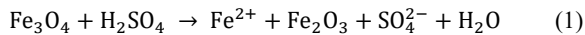
Decontamination is conducted for equipment and systems which have been contaminated by the activity build-up with time evolution for maintenance or decommissioning. The periodic maintenance of a nuclear power plant is mainly focused on reducing the occupational exposure, and additionally on depleting the radioactive waste at the time for decommissioning. The removal of radioisotopes from the primary coolant system of a nuclear power plant takes place with the dissolution of corrosion metal oxide layers deposited with the radioisotopes. Chemical decontamination by oxidative and reductive dissolution is considered to be the most effective method to date. KAERI has developed the HyBRID (Hydrazine-Based Reductive metal Ion Decontamination) process without using any organic acids or organic chelating agents [1]. The solution containing sulfuric acid (H₂SO₄), hydrazine (N₂H₄), and copper sulfate (CuSO₄) provided the acidic and reductive dissolution of transition metal ions from the corrosion metal oxides. In this work we proposed the plausible reaction mechanisms of the acidic and reductive dissolution in the HyBRID process for magnetite and studied the chemical equilibrium of the HyBRID aqueous system for magnetite (Fe₃O₄ - N₂H₄ - CuSO₄ - H₂SO₄ - H₂O). The multicomponent equilibrium compositions were calculated for the heterogeneous aqueous system.

2. Methods and Results

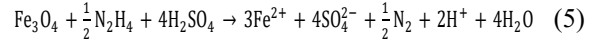
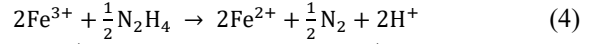
The HyBRID chemical decontamination for the primary coolant system consists of the acidic dissolution by an acid and the reductive dissolution by a reducing agent in order to dissolve transition metal ions from the corrosion metal oxides deposited on the surface of the coolant system. Hydrazine is used as a strong reducing agent and copper ion is used as a catalyst to form copper-hydrazine complexes which transfer electrons from a cuprous ion (Cu⁺) to a ferric ion (Fe³⁺) to be reduced to a ferrous ion (Fe²⁺) [1]. Sulfuric acid is used to control the pH of the solution.

2.1. Reaction Mechanism of HyBRID Dissolution of Magnetite

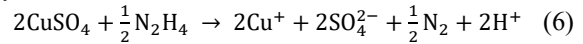
The dissolution reactions of magnetite in aqueous solution of sulfuric acid is:



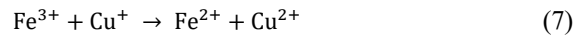
By adding hydrazine into the solution, Fe³⁺ are reduced to Fe²⁺:



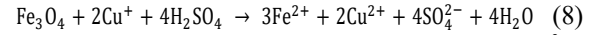
CuSO₄ dissociates in aqueous solution and Cu²⁺ ions are reduced to the Cu⁺ ions by the coordination reaction with hydrazine:



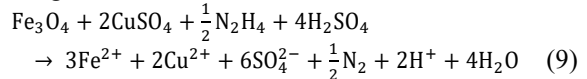
Reduction of Fe³⁺ to Fe²⁺ by oxidative regeneration of Cu⁺ to Cu²⁺ is



Reactions (3) and (7) is combined to yield:



Hydrazine facilitates the transfer of electrons to Fe³⁺ in magnetite via Cu⁺ ions. Finally, the dissolution reaction of magnetite can be summarized as follows:

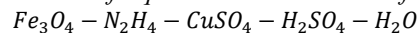


2.2. Calculations of Equilibrium for HyBRID Dissolution of Magnetite

Computation of chemical potential requires the knowledge of thermochemical data. The data of thermodynamic properties for all the species, ions, and elements involved in the HyBRID dissolution reactions were obtained from the database of HSC Chemistry[®] version 9 by Outotec [2]. The enthalpy of formation, the entropy of formation, and the Gibbs energy of formation of species and ions were calculated. Then for individual reactions described above, the enthalpy, entropy, and Gibbs energy change of reaction were calculated at different temperatures from 25 °C to 95 °C.

Calculation of the multicomponent equilibrium compositions in heterogeneous systems like the HyBRID dissolution of magnetite was conducted using the GEM module of the HSC Chemistry[®] 9. The equilibrium composition was calculated using the GIBBS solver, which used the Gibbs energy minimization method. In aqueous solution, the Pitzer model was used to calculate mean activity coefficients of the aqueous species [3,4]. Gas is assumed to behave as ideal mixture. The Pitzer parameters were obtained from the HSC AQUA Pitzer database [4,5]. The AQUA module was used to estimate ion activities, mean activity coefficients, the osmotic coefficient of water, enthalpies, and heat capacities of aqueous solutions.

2.3 Results of Equilibrium Calculations for System of



The equilibrium calculations were conducted at the experimental conditions given in Table 1. The system

pressure was 1 bar and the temperature was varied from 25 °C to 95 °C at 5 °C intervals. The amounts of species at equilibrium were observed at different raw amounts of N_2H_4 and $CuSO_4$.

Table 1. Recipe of experiments for the HyBRID dissolution of magnetite

Reagent	Phase	Raw amount [mol]
Fe_3O_4	solid	2.16×10^{-4} (0.05 gram)
H_2SO_4	aqueous	0.03377
N_2H_4	aqueous	0.05791
$CuSO_4$	solid	5×10^{-4}
H_2O	aqueous	55.5 (1 liter)

In the acidic dissolution of magnetite using H_2SO_4 only, Fig. 1 shows the effect of the raw amount of sulfuric acid in feed on the equilibrium amounts of $Fe_2O_3(s)$ undissolved, Fe^{2+} ion, and Fe^{3+} ion as a function of temperature. It should be noted that the operating temperature of the KAERI HyBRID process is 95 °C. When the raw amount of H_2SO_4 increased threefold, the amount of $Fe_2O_3(s)$ undissolved was greatly reduced and detected only at temperatures higher than about 80 °C. As a result, the amount of Fe^{3+} greatly increased because $Fe_2O_3(s)$ was decomposed by the added sulfuric acid according to the reaction (2).

Fig. 2 illustrates the effect of the addition of N_2H_4 on the dissolution of magnetite. Compared at the same raw amount of H_2SO_4 , the dissolution capability was greatly enhanced with the addition of a small amount of N_2H_4 , N_2H_4 was regarded to act as a strong reducing agent that reduced Fe^{3+} to Fe^{2+} by the reaction scheme (4).

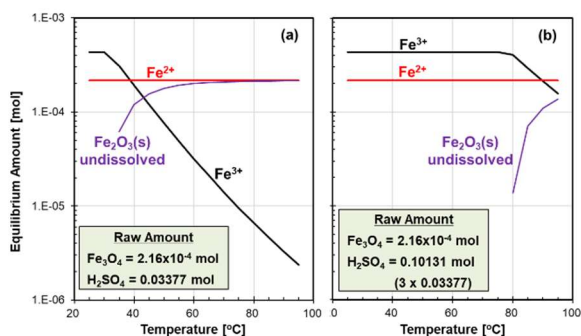


Fig. 1. Effect of the raw amount of H_2SO_4 on the equilibrium amounts of species in acidic dissolution of magnetite.

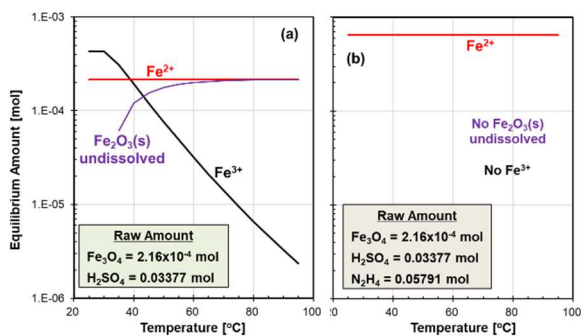


Fig. 2. Effect of the addition of N_2H_4 on the dissolution of magnetite.

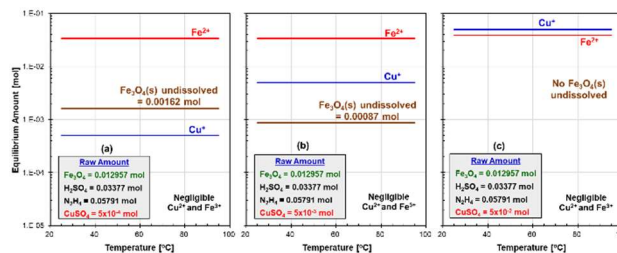


Fig. 3. Effect of the addition of $CuSO_4$ on the dissolution of magnetite.

Fig. 3 shows the effect of the addition of $CuSO_4$ on the dissolution capability of magnetite as a function of temperature. Equilibrium calculations were performed at the same raw amounts of H_2SO_4 and N_2H_4 . Increasing the raw amount of $CuSO_4$ resulted in the decrease of the amount of $Fe_3O_4(s)$ undissolved and the increase of the amount of Cu^+ . At the highest amount of $CuSO_4$ (5×10^{-2} mol), the $Fe_3O_4(s)$ undissolved was no more detected. This observation is attributed to the reduction of Cu^{2+} to Cu^+ by the coordination reaction with N_2H_4 , shown in the reaction (6).

3. Conclusions

The chemical equilibrium of the HyBRID aqueous system for magnetite ($Fe_3O_4 - N_2H_4 - CuSO_4 - H_2SO_4 - H_2O$) was calculated at different amounts of raw reagents at various temperatures from 25 °C to 95 °C and at 1 bar. The equilibrium composition was calculated using the Gibbs energy minimization method and the Pitzer model was used for the aqueous solution. The equilibrium calculations showed that the capability of dissolution of magnetite was greatly enhanced with the addition of N_2H_4 and $CuSO_4$ due to the facilitated reduction by them. In case of using H_2SO_4 only, the dissolution capability decreased with increasing the temperature. However, when N_2H_4 was added, the decrease of dissolution capability was overcome since N_2H_4 was used to reduce to Fe^{2+} ions.

Acknowledgement

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