An Equilibrium Calculation on Removal of Sulfate and Metal Ions in a Wastewater Generated From the SP-HyBRID Decontamination Process

H.C. Eun[a,*], J.Y. Jung[a,b], S.Y. Park[a], J.S. Park[a,b], H.J. Won[a], S.B. Kim[a], and B.K. Seo[a]
[a]Korea Atomic Energy Research Institute, 989-111 Daedeok-daero, Yuseong-gu, Daejeon, Republic of Korea
[b]Department of Applied Chemistry and Biological Engineering, Chungnam National University, 99 Daehak-ro Yuseong-gu, Daejeon, Republic of Korea
[*]ehc2004@kaeri.re.kr

1. Introduction

In KAERI, the SP-HyBRID process has been developed to decontaminate the primary coolant system of a nuclear power plant[1]. The SP-HyBRID process consists of a pre-oxidative step and a reductive step, HyBRID. The pre-oxidative step is progressed using H_2SO_4 and $KMnO_4$, and the reductive step is conducted using N_2H_4 (hydrazine), H_2SO_4, and Cu^+. A wastewater is generated from the SP-HyBRID decontamination process of the coolant system. The wastewater contains not only the contamination agents but also the metal ions dissolved during the decontamination process, which typically includes radioactive metal ions such as Co-58, Co-60, Mn-54, and Cr-51, etc.

It is very effective to remove the contaminants from the wastewater for minimizing waste generation. The contaminants can be effectively removed by a precipitation method using $Ba(OH)_2$[2]. In general, when pH in a solution is increased by $Ba(OH)_2$ injection, metal ions in the solution are converted into a hydroxide form, and precipitated to the bottom of the solution[3]. $Ba(OH)_2$ is injected at an equivalent to sulfate ions, and $BaSO_4$ is removed as precipitates as shown in Eq. (1). In this precipitation reaction, the generated OH^- can be consumed to form metal hydroxide for residual metals in the solution, and the amounts of metal ions in a wastewater can be changed with operation conditions of the decontamination process. Therefore, it is necessary to evaluate effects on the removal of metal ions in a wastewater with amounts of them.

$$SO_4^{2-} + Ba(OH)_2 = BaSO_4 + 2OH^- \quad (1)$$

In this study, theoretical equilibrium calculations on removal of sulfate and metal ions in a wastewater surrogate by $Ba(OH)_2$ injection were conducted by using equilibrium calculation software (HSC-Chemistry 9.5). The removal characteristics of metal ions in the surrogate were estimated with changes in the amounts of metal ions.

2. Equilibrium Calculation

Table 1 shows the composition of the wastewater surrogate used in the equilibrium calculation. Except N_2H_4, sulfate forms as input materials were determined for the sulfate and metal ions because sulfate ions in a wastewater from the decontamination process are a main component for dissolving metals. The concentrations of the decontamination reagetns used in the SP-HyBRID process were fixed, and the amounts of dissolved metal ions were changed from 50 to 400 ppm. The concentrations were reduced into mole unit for the equilibrium calculation. The amount of $Ba(OH)_2$ was determined considering the amounts of sulfate ions in the wastewater surrogate. The equilibrium calculation was conducted using HSC-Chemistry 9.5 which is progressed on the base of Gibbs free energies of reactions between input materials[4].

Table 1. Composition of the wastewater surrogate used in the equilibrium calculation

Compounds	Concentration (ppm)
N_2H_4	1604
H_2SO_4	3632
$MnSO_4$	962
K_2SO_4	554
$CuSO_4$	81
Metal (Fe, Cr, Ni, Cu, Zn, Co) ion	50 ~ 400 (respectively)

3. Results

The equilibrium calculation results (metal ion conc.: 50 ppm, respectively) are shown in Fig. 1. According to Fig. 1, sulfate ions in H_2SO_4 is preferentially reacted with $Ba(OH)_2$, and removed into $BaSO_4$. Except for Mn, the metal (M) ions are mostly converted into $M(OH)_2$. Some of them are formed into MO. Mn ions are also mainly converted into $Mn(OH)_2$. However, a considerable amount of Mn ions are formed into liquid phase of $Mn(OH)_2$. Because of that, it is considered that removal of Mn ions in a wastewater from the SP-HyBRID decontamination process will be limited. In this equilibrium calculation, it is predicted that some of K ions are converted into KOH very soluble in water. Thus, removal of K ions by $Ba(OH)_2$ injection will be very few. When the concentrations of metal ions are 400 ppm, respectively, oxide formations of the metal ions are significantly increased. Especially, Ni ions are mainly converted NiO, and a significant amount of Zn ions are also formed an oxide form, ZnO.

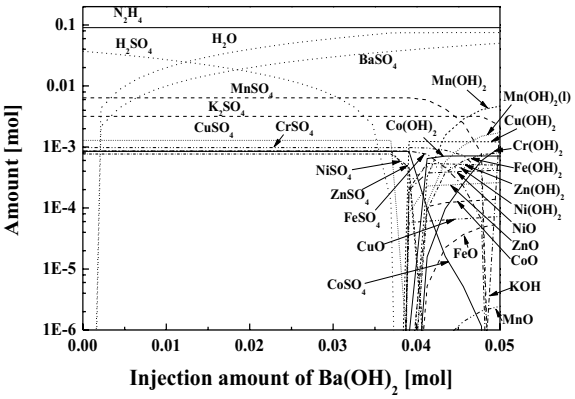

Fig. 1. Equilibrium calculation results (metal ion conc.: 50 ppm, respectively).

4. Conclusion

Through the equilibrium calculation results, it is predicted that the metal ions can be effectively removed into a hydroxide form or an oxide form, except for Mn and K. In case of Mn, it is required to evaluate a residual amount in a wastewater surrogate closely after a wastewater surrogate treatment test. For the removal of K ions, it is necessary to develop a method to separate K ions selectively as an insoluble form in water.

ACKNOWLEDGE

The authors would like to express their appreciation to the National Research Foundation of Korea (NRF) for the award of a grant funded by the Ministry of Science and ICT (MSIT) of the Republic of Korea, in support of the authors' work through the Nuclear Research and Development Program (NRF-2017M2A8A5015144).

REFERENCES

[1] S.B. Kim. H.J. Won, J.K. Moon, W.K. Choi, "Magnetite dissolution using hydrazine-acid solution for chemical decontamination", Transactions of the American Nuclear Society, Vol. 115, Las Vegas, USA (2016).

[2] S.Y. Park, W.K. Choi, S.B. Kim, H.J. Won, M.S. Choi, "Estimation of waste volume for KORI#1 decontamination using SP-HyBRID process, KRS Spring Meeting (2017).

[3] Baijnath, L. Lal, V. Gautam, V. L. Yadav, "A comparative study of the removal efficiency of calcium hydroxide and sodium hydroxide as precipitating agents for chromium (III)", J. Civil Eng. & Environ. Technol., Vol., No. 1 (2014).

[4] A. Ronie, Outokumpu HSC Chemistry for Windows, OutoKumpu Research, Pori, Finland (2002).