

Removal and Speciation Behavior of Cations in the Waste Solution of SP-HyBRID Process

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1. Introduction

KAERI has been developing a new decontamination process that minimize the primary, secondary waste and ion exchange resin usages in the solution purifying step [1]. The process is hydrazine base reductive metal ion decontamination for decommissioning (HyBRID) and consists of N_2H_4 , H_2SO_4 and Cu^{2+} ions. A sulfuric acid permanganate process ($H_2SO_4 + KMnO_4$) is used in HyBRID as a pre-oxidative decontamination step. To minimize the waste volume, residual hydrazine is decomposed with hydrogen peroxide and the sulfate ions are precipitated by the addition of $Ba(OH)_2$ followed by filtration with a filter press.

In the decontamination waste, Fe(II), Cr(III) and Ni(II) exist as primary wastes and K(I), Mn(II), Ba (II), Cu (II) and sulfate ions as secondary wastes. There are also trace amounts of radioactive materials such as Co-60, Co-58, Mn-54 and Cr-51 and so on. They should be cleaned as much as possible to reuse or release the solution. Traditionally, they have been removed using ion exchange resins, but in the SP-HyBRID decontamination process most of the anions and cations are removed by precipitation.

In this paper, to review purifying limit and to evaluate the precipitation behavior of the ions, the chemical equilibrium of various ions in the waste solution was calculated. Especially, the purification of cations such as K(I), Mn(II), Ba(II), Fe(II) and sulfate ions were concentrated, and the speciation and removal limiting value of them was reviewed.

2. Methods and Results

2.1 Calculation of Chemical Equilibrium

A mixture of $KMnO_4$ and sulfuric acid is used as a decontaminating agent in the oxidative step and these reagents are not consumed during decontamination thoroughly, and these reagents remain in the solution even after the decontamination is completed. Therefore, in order to apply reductive decontamination after oxidizing agent, MnO_4^- ions, which is a strong oxidizing agent, must be decomposed. As a reagent for decomposing MnO_4^- ions, N_2H_4 which is a reducing agent is used, and the reaction formula is as follows;



After the decomposition of MnO_4^- ions is completed, N_2H_4 , a reducing agent, is added to apply the reductive decontamination step and sulfuric acid is added to adjust the pH of the solution. Assuming that the concentration of Fe (II) ions dissolved in the solution and released into the solution is 1 mM, the system can be set up as shown in Table 1.

Table 1: Chemical Composition and Concentration of Calculation System

Composition	Concentration, M
K(I)	0.007
Mn(II)	0.007
Fe(II)	0.001
N_2H_4	0.05
SO_4^{2-}	0.04
Ba(II)	0 – 0.04

2.2 Calculation of Chemical Equilibrium

To calculate of chemical equilibrium of the liquid waste system, MINEQL+ (ver. 5.0) program was used. Tables 2 and 3 show the reactions and equilibrium constants that can be achieved by the species shown in Table 1 and the speciation of each species was calculated using the MINEQL+ program. Since 0.04 M sulfate is present in the system, it was titrated by Ba (II) ion up to 0.04M.

Table 2: The Reaction of Aqueous Species and Equilibrium Constants

Reaction	Log K
$H_2O = OH^- + H^+$	-13.997[2]
$H_2O + Ba^{2+} = BaOH^+ + H^+$	-13.357[3]
$H_2O + Fe^{2+} = FeOH^+ + H^+$	-9.397[3]
$2H_2O + Fe^{2+} = Fe(OH)_2 + 2H^+$	-20.494[3]
$3H_2O + Fe^{2+} = Fe(OH)_3^- + 3H^+$	-28.991[3]
$4H_2O + Mn^{2+} = Mn(OH)_4^{2-} + 4H^+$	-48.288[2]
$H_2O + Mn^{2+} = MnOH^+ + H^+$	-10.597[3]
$3H_2O + Mn^{2+} = Mn(OH)_3^- + 3H^+$	-34.800[4]
$H^+ + SO_4^{2-} = HSO_4^-$	1.990[3]
$Fe^{2+} + SO_4^{2-} = FeSO_4$	2.390[3]
$K^+ + SO_4^{2-} = KSO_4^-$	0.850[3]
$Mn^{2+} + SO_4^{2-} = MnSO_4$	2.250[3]
$H^+ + N_2H_4 = HN_2H_4^+$	8.100
$2H^+ + N_2H_4 = H_2N_2H_4^{2+}$	7.000

Table 3: The Reaction of Potential Precipitates and Equilibrium Constants

Reaction	Log K
$10\text{H}_2\text{O} + \text{Ba}^{2+} = \text{Ba}(\text{OH})_2 + 8\text{H}_2\text{O} + 2\text{H}^+$	-24.394[2]
$\text{H}_2\text{O} + 0.95\text{Fe}^{2+} = \text{Fe}_{0.95}\text{O} + 2\text{H}^+$	-11.688[5]
$2\text{H}_2\text{O} + \text{Fe}^{2+} = \text{Fe}(\text{OH})_2 + 2\text{H}^+$	-13.564[2]
$2\text{H}_2\text{O} + \text{Mn}^{2+} = \text{Mn}(\text{OH})_2 + 2\text{H}^+$	-15.194[2]
$7\text{H}_2\text{O} + \text{Fe}^{2+} + \text{SO}_4^{2-} = \text{FeS}$	2.209[7]
$\text{Ba}^{2+} + \text{SO}_4^{2-} = \text{BaSO}_4$	9.980[2]
$\text{Mn}^{2+} + \text{SO}_4^{2-} = \text{MnSO}_4$	-2.583[6]

2.3 Calculation Results

The figures from Fig.1 to Fig.3 show the speciation of each component with increasing precipitation of Ba (II), sulfate, N_2H_4 , and Mn(II) ions. Fig. 1 shows that the concentration of sulfate decreases steadily with the addition of Ba(II). In the log scale graph, the purifying limit of barium ions is about $7.1\text{E}-8\text{M}$. However, as the ratio of Ba(II): SO_4^{2-} ratio became closer to 1:1, the threshold increased sharply.

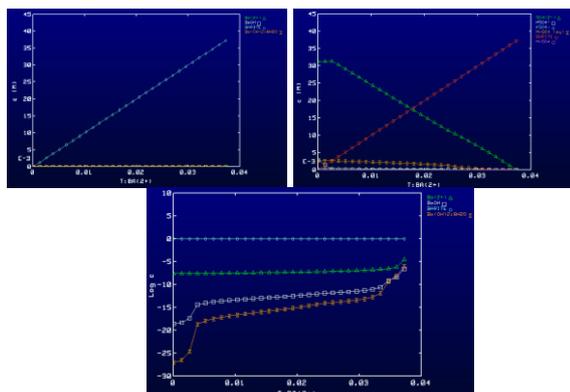


Fig.1 Speciation of Ba(II) (upper, left, lower(log scale)) and sulfate(upper, right) ions with increase of total Ba(II) concentration.

Fig.2 shows the speciation of N_2H_4 . It is initially present in the $\text{H}-\text{N}_2\text{H}_4^+$ phase but later in the N_2H_4 phase, which is thought to be influenced by pH.

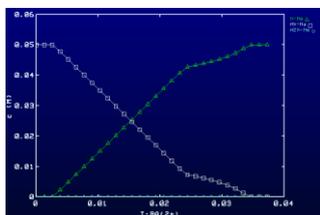


Fig.2 Speciation of N_2H_4 with increase of total Ba(II) concentration.

Fig. 3 shows the speciation of the Mn(II) component. Mn(II) and $\text{MnSO}_4(\text{aq})$ were predominant in the early stage, but $\text{Mn}(\text{OH})_2$ precipitated in the latter stage. The ionic components in the solution mainly existed as ions such as Mn(II), $\text{MnSO}_4(\text{aq})$ and MnOH^+ . The concentration of these ions was significantly decreased

as the ratio of Ba(II): SO_4^{2-} ratio approached 1. The final limit value was $1.25\text{E}10^{-7}\text{M}$.

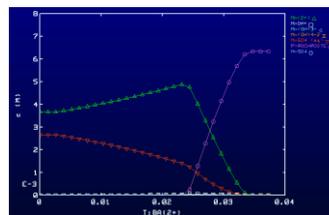


Fig.3 Speciation of Mn(II) ion with increase of total Ba(II) concentration.

For the Fe(II) component, ionic Fe species did not decrease before the addition of Ba(II) was about $6.5\text{E}-3\text{M}$, but decreased rapidly thereafter. Most of Fe(II) ions were precipitated within 50% of Ba (II) and the final removal limit was $5.0\text{E}-7$.

3. Conclusions

Balance calculation of several cations present in the SP-HyBRID decontamination solution was performed by BaSO_4 precipitation. The speciation of cations such as Mn (II), Fe (II) and Ba (II) in BaSO_4 titration was calculated and their removal thresholds were derived. In the future, the properties of other elements such as Cr(III), Ni(II) and Co(II) will be evaluated.

REFERENCES

- [1] 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)
- [2] NIST Standard Reference Database 46, ver. 4.0, National Institute of Standards and Technology, Critical Stability Constants of Metal Complexes Database (1997)
- [3] NIST Standard Reference Database 46, ver. 3.0, National Institute of Standards and Technology, Critical Stability Constants of Metal Complexes Database (1997)
- [4] J.D. Allison, D.S. Brown and K.J. Novo-Gradac, A Geochemical Assessment Model for Environmental Systems: USEPA, Office of Research and Development, Washington, DC, EPA/600/3-91/021
- [5] NIST Standard Reference Database 13, ver. 1.0, National Institute of Standards and Technology, NIST JANAF Thermochemical Tables(1985).
- [6] NIST Standard Reference Database 2, ver. 1.1, National Institute of Standards and Technology, NIST Chemical Thermodynamics Database (1992).
- [7] D.K. Nordstrom, L.N. Plummer, D. Langmuir, E. Busenberg, H. May, B.L. Jones, and D.L. Parkhurst, Revised chemical equilibrium data for major water-mineral reactions and their limitation. In: D.C. Melchior and R.L. Bassett, (eds), Chemical Modeling in Aqueous Systems II, American Chemical Society Symposium Series 416, 398 (1990).