

Speciation and Removal Properties of Cobalt in the SP-HyBRID™ Waste Solution

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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. This process called to SP-HyBRID process. 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.

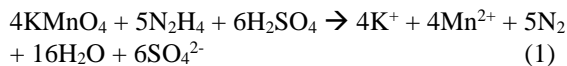
There are several sorts of radioactive material such as Co-60, Co-58, Mn-54, Cr-51 and so on in the SP-HyBRID decontamination solution. These radioactive materials are co-precipitated with the $BaSO_4$ precipitates. Therefore, the precipitation characteristics of these materials play an important role in the purification of the liquid decontamination wastes.

In this paper, to review purifying limit and to evaluate the precipitation behavior of the cobalt ion, the chemical equilibrium of various ions in the waste solution was calculated. Especially, the speciation and removal limiting value of Co^{2+} and Co^{3+} ion was reviewed.

2. Methods and Results

2.1 Waste Treatment Process of SP-HyBRID Process

After pre-oxidative decontamination step, remaining MnO_4^- ion must be decomposed. As a reagent for decomposing MnO_4^- ions, N_2H_4 is used, and the reaction formula is as follows;



After the decomposition of oxidative reagent is completed, further 0.05M N_2H_4 is added to apply the reductive decontamination step and sulfuric acid is added to adjust the pH of the solution. Metallic ions and radioactive materials such as, Fe^{2+} , Ni^{2+} , Cr^{3+} , Co-60, Co-58, Mn-54, Cr-51 and so on, dissolve into the decontamination solution.

Barium hydroxide added into the solution to precipitate of sulfate ion during the waste treatment

process. Metallic ion and radioactive materials are co-precipitated with a $BaSO_4$ precipitate as follows:



The speciation behavior of the cobalt component in the precipitation process is very important because the cobalt component is the most abundant among the radioactive materials. Table 1 shows the solution conditions for calculating the speciation and removal behavior of cobalt components in the precipitation process.

Table 1: Chemical Composition and Concentration of Calculation System

Composition	Concentration, M
K^+	0.007
Mn^{2+}	0.007
Co^{2+}	0.0001
N_2H_4	0.05
SO_4^{2-}	0.04
Ba^{2+}	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]
$H_2O + Co^{2+} = CoOH^+ + H^+$	-9.697[2]
$2H_2O + Co^{2+} = Co(OH)_2 + 2H^+$	-18.794[2]
$3H_2O + Co^{2+} = Co(OH)_3^- + 3H^+$	-31.491[2]
$4H_2O + Co^{2+} = Co(OH)_4^{2-} + 4H^+$	-46.288[2]
$4H_2O + Mn^{2+} = Mn(OH)_4^{2-} + 4H^+$	-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]
$Co^{2+} + SO_4^{2-} = CoSO_4$	2.300[2]
$K^+ + SO_4^{2-} = KSO_4^-$	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
$10\text{H}_2\text{O} + \text{Ba}^{2+} = \text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O} + 2\text{H}^+$	-24.394[2]
$\text{H}_2\text{O} + \text{Co}^{2+} = \text{CoO} + 2\text{H}^+$	-13.586[6]
$2\text{H}_2\text{O} + \text{Co}^{2+} = \text{Co}(\text{OH})_2 + 2\text{H}^+$	-13.094[2]
$2\text{H}_2\text{O} + \text{Mn}^{2+} = \text{Mn}(\text{OH})_2 + 2\text{H}^+$	-15.194[2]
$6\text{H}_2\text{O} + \text{Co}^{2+} + \text{SO}_4^{2-} = \text{CoS}$	2.474[6]
$\text{Ba}^{2+} + \text{SO}_4^{2-} = \text{BaSO}_4$	9.980[2]
$\text{Mn}^{2+} + \text{SO}_4^{2-} = \text{MnSO}_4$	-2.583[6]

2.3 Results of Calculation

Fig.1 show the speciation of Co^{2+} components with increasing of BaSO_4 precipitation. Co^{2+} and CoSO_4 (aq) were predominant in the early stage, but $\text{Co}(\text{OH})_2$ precipitated in the latter stage. Fig. 2 is a graph showing the logarithm of the x-axis in order to observe the characteristics of the trace components. The ionic components in the solution mainly existed as ions such as Co^{2+} , CoSO_4 (aq), CoOH^+ , $\text{Co}(\text{OH})_3^-$, CoOOH^- and so on. When the content of Barium hydroxide is increased to 0.035M or more, most cobalt components are co-precipitated with $\text{Co}(\text{OH})_2$ and the limit value of total ionic cobalt component is $3.5\text{E}-6\text{M}$ in the waste solution.

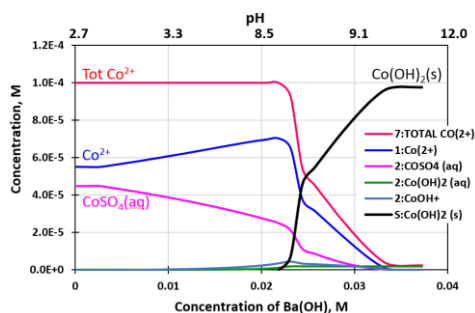


Fig. 1 Speciation behavior of Co^{2+} components (linear scale) during the titration with barium hydroxide.

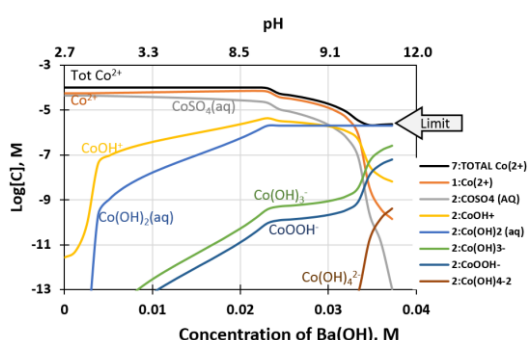


Fig. 2 Speciation behavior of aqueous Co^{2+} components (log scale) during the titration with barium hydroxide.

Fig. 3 is a graph showing the calculation results of Co^{2+} ions and Co^{3+} ions simultaneously to compare the co-precipitation characteristics of Co^{2+} ions to that of Co^{3+} ions. In the case of the Co^{3+} ion, the limit of the total ionic Co^{3+} component in the solution is lowered to

$3.8\text{E}-22\text{M}$. This value is about 1/1000 lower than that of Co^{2+} ions. This is because the co-precipitation rate of $\text{Co}(\text{OH})_3$ is 100%, but that of $\text{Co}(\text{OH})_2$ is 97.7%.

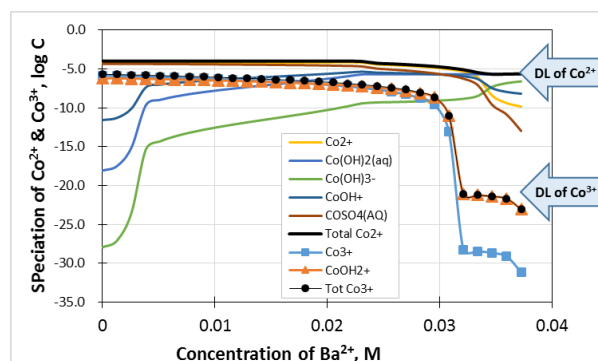


Fig.3 Speciation of Co^{2+} and Co^{3+} ion with increasing of total $\text{Ba}(\text{OH})_2$ concentration.

3. Conclusions

In order to observe the removal characteristics of Co-60 and Co-58 during the BaSO_4 precipitation step of the SP-HyBRID decontamination process, equilibrium calculations were performed, and the removal and speciation characteristics of cobalt ions in the solution were observed. It is found that the precipitation of Co^{3+} ions rather than that of Co^{2+} ions is 1000 times more effective.

ACKNOWLEDGEMENTS

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