

A Study on the Proper Amount of Ba(OH)₂ for the Wastewater Treatment From the SP-HyBRID Decontamination Process

J.Y. Jung^{a,b}, H.C. Eun^a, S.Y. Park^{a,*}, H.J. Won^a, J.S. Park^a, S.B. Kim^a, B.K. Seo^a, and S.J. Park^b

^aKorea Atomic Energy Research Institute, 989-111 Daedeok-daero, Yuseong-gu, Daejeon, Republic of Korea

^bDepartment of Applied Chemistry and Biological Engineering, Chungnam National University, 99 Daehak-ro Yuseong-gu, Daejeon, Republic of Korea

*nsypark@kaeri.re.kr

1. Introduction

SP-HyBRID, which has been developed in KAERI, is a new decontamination process for the primary coolant system of PWR. This SP-HyBRID process does not contain any organic chemicals in the decontamination solution[1]. Therefore a wastewater generated from the SP-HyBRID process only contains inorganic chemical included in the decontamination solution and dissolved from oxide at the inner surface of RCS. Among those, various metal ions as well as sulfate ions are removed by precipitation method using Ba(OH)₂ instead of ion-exchange method to reduce the secondary waste volume[1]. Sulfate ions react with barium ions, and then are precipitated as a form of barium sulfate. pH in the wastewater increases by the added Ba(OH)₂, and metal ions are precipitated as a form of metal hydroxide[2,3]. Most of the metal ions in the wastewater can be separated, and the use of ion exchange resins for purifying the wastewater can be minimized. However, if an excess amount of Ba(OH)₂ is used to remove sulfate ions completely in the wastewater, a certain amount of barium ions can be residual in a purified wastewater, and cause a problem to need an additional treatment process. It is necessary to determine a proper amount of Ba(OH)₂ for purifying the wastewater.

In this study, precipitation tests of sulfate and metal ions in a wastewater surrogate were conducted to derive a required amount of Ba(OH)₂. A proper amount of Ba(OH)₂ was determined by removal tests of sulfate ions in a solution without metal ions changing a Ba(OH)₂ injection amount. And a removal performance of sulfate and metal ions in a wastewater surrogate was evaluated at the determined use of Ba(OH)₂. The drinking water quality standards expressed in Table 1 were utilized to evaluate these test results.

Table 1. Drinking water quality standards

Species of ions	Concentration [ppm]
SO ₄ ²⁻	< 200
Ba	< 0.7
Cu	< 1
Fe	< 0.3
Cr	< 0.05
Ni	< 0.01
Mn	< 0.05
Zn	< 3

2. Experimental Methods

2.1 Determination of a proper use of Ba(OH)₂

A solution containing only sulfuric acid and hydrazine without metal ions was prepared to determine a proper use of Ba(OH)₂. Theoretical mole ratio of the reaction between sulfate and barium ion is 1:1 as shown in the Eq. (1). The molar ratio was determined at 0.8 ~ 1.05 of barium ion over sulfate ion. Test solutions were mixed at 200rpm under room temperature in a 500ml solution. After the mixing for 1 h, a sample was taken from the solution, and then filtered to analyze concentrations of sulfate and barium. The concentrations of sulfate and barium were analyzed using UV-vis spectroscopy and ICP-OES, respectively.



2.2 Removal of sulfate and metal ions

A wastewater surrogate was prepared to conduct removal tests of sulfate and metal ions as shown in the Table 2. The composition of metal ions in the wastewater surrogate used in this study were chosen to be as close to those values expected in a real primary coolant decontamination wastewater as

possible. The amount of added $\text{Ba}(\text{OH})_2$ was determined by the results obtained through section 2.1. The removal tests of sulfate and metal ions in the wastewater surrogate were performed in 1L solution. The test conditions and analyzing methods were same with tests described in section 2.1

Table 2. Composition of wastewater surrogate used in this study

Concentration of compositions [ppm]	
SP-HyBRID	KMnO_4 1000, H_2SO_4 3630, N_2H_4 1856, CuSO_4 80
Dissolved metal ions	Fe, Cr, Ni, Cu, Zn, Co (50, 75, 100 respectively)

3. Results

In the determination test of a proper $\text{Ba}(\text{OH})_2$ use, when $\text{Ba}(\text{OH})_2$ was injected at a higher molar ratio than 1, barium ions in the tested solution were greatly increased as shown in Table 3. When $\text{Ba}(\text{OH})_2$ was injected in the range of 0.95 to 1, the concentrations met the drinking water quality standards. Since the standard of barium ion is very low comparing with sulfate ion, in determining the amount of $\text{Ba}(\text{OH})_2$, emphasis was on low barium ion concentrations. Considering the results in Table 3 and the drinking water quality standards, 0.975 was determined as a proper molar ratio. In the precipitation test of sulfate and metal ions in the wastewater surrogate using this molar ratio of $\text{Ba}(\text{OH})_2$ injection, it was confirmed that concentrations of sulfate and metal ions in the purified wastewater surrogate also meet the standards. Concentration of sulfate ion in solution was below 0.5ppm. Barium ion remain below 0.4ppm. The dissolved metal ions in Table 2 were not detected on ICP-OES. (Limit detection : 0.01ppm)

Table 3. Concentration of residual sulfate and barium ions in the tested solution after the determination test of a proper $\text{Ba}(\text{OH})_2$ use

Molar ratio	SO_4^{2-} [ppm]	Ba^{2+} [ppm]
0.8	531	0.3
0.9	256	0.4
0.925	225	0.48
0.95	79	0.22
0.975	39	0.18
1	2	0.32
1.05	0	87.32

4. Conclusion

To meet the drinking water quality standards about the concentrations of sulfate and metal ions in a purified wastewater after purifying a wastewater from the SP-HyBRID decontamination process, an proper use of $\text{Ba}(\text{OH})_2$ was at 0.975, and it was confirmed that the removal of sulfate and metal ions was effective. This result can be utilized to reduce an overdose of $\text{Ba}(\text{OH})_2$ during the purification of the wastewater treatment process, and contribute to the reduction of final waste.

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.Y. Park, H.J. Won, M.S. Choi, S.B. Kim, W.K. Choi, and J.K. Moon, Waste Minimization of HyBRID Decontamination Process, WM2017 Conference, March 5-9, Phoenix, Arizona, USA (2017).
- [2] M. M. Pourbaix, "Atlas of electrochemical equilibria in aqueous solutions", National Association of Corrosion Engineers (1974).
- [3] Tomasz Suponik "ENSURING PERMEABLE REACTIVE BARRIER EFFICACY AND LONGEVITY", Environmental Engineering of the Polish Academy of Sciences (2010).