

Advanced treatment process of secondary waste solution of HyBRID decontamination agent

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1. Introduction

Decontamination for nuclear power plants(NPPs) is defined as the removal of contamination from surface of facilities or equipment by washing, chemical or mechanical cleaning, or other techniques. It is also used to reduce the dose rate of radioactive materials that worker may receive where it is not wanted. Another importance of decontamination is to minimize the magnitude of the secondary waste after decontamination for public health and safety reasons.

Recently, Korea Atomic Energy Research Institute(KAERI) has developed a new chemical decontamination agent HyBRID(Hydrazine based reductive metal ion decontamination, HyBRID) for primary coolant system of NPPs, which is based on chelating reagent-free with hydrazine(N_2H_4), sulfuric acid(H_2SO_4), and metal ions of copper. In line with reducing the secondary decontamination waste, the HyBRID decontamination agents is specialized for waste volume of decontamination solution compared to the chemical oxidation reduction decontamination system which is commercialized as decontamination technology.

Although the HyBRID is able to reduce the secondary waste of decontamination, it also requires the waste treatment process. Because of radioactive materials and related components in HyBRID, it is essential to treat to reduce their contents such an extent that can be either released to the environment or recycled.

To date, ion exchange resins and chemical precipitation are widely used to remove the decontamination chemicals, radioactive materials, metal ions, anion ions, and etc. The main advantages of ion-exchange resins are selectivity and less sludge volume. However, the use of ion-exchange resin leads to generation of resin waste, which requires additional procedures for their treatment or storage. If the metal and anion ions in the waste solution can be removed by precipitation, the waste sludge would be significantly decreased.

The aim of this study was to establish the treatment process of decontamination waste solution by using chemical precipitation method. Chemical precipitation that solute dissolved in a solution precipitates out on a carrier that forces it to bind together is proven technology for the removal of metals, other inorganic compounds, and suspended solids[1]. Because of high concentration of sulfates in HyBRID decontamination agent, removal of sulfate ions is more important factor

than that of other metal ions for whole treatment process. So, we developed the treatment process by using a chemical precipitation method as a sulfate removal process, which could reduce the volume of the secondary waste through the addition of barium hydroxide($Ba(OH)_2$). In this case, system for separation or appropriate disposal of solid is necessary. So, we also designed and fabricated the equipment for separation of precipitates of barium sulfate($BaSO_4$). Details of each process such as $BaSO_4$ precipitation phenomenon, its increase of particle size, and separation efficiency will be discussed in this study.

2. Experimental

For investigation of $BaSO_4$ precipitation phenomenon and separation efficiency, we prepared simulated HyBRID decontamination waste solution through the continuous decontamination process.

Briefly, the 0.63 mM potassium permanganate ($KMnO_4$) solution with desired H_2SO_4 (4000 ppm) for oxidation process was prepared. And then, hydrazine (N_2H_4) was added above solution to decompose $KMnO_4$ followed by addition of HyBRID decontamination agent (N_2H_4 , H_2SO_4 , and copper sulfate ($CuSO_4$)). Some metal ions such as Fe, Cr, Ni, also dissolved in waste solution.

Sulfate removal was carried out by adding $Ba(OH)_2$ to HyBRID decontamination waste solution. The solution was stirred at 400 rpm using magnetic stirrers for 1 h. The effective parameters of the $BaSO_4$ precipitation was varied according to the concentration of $Ba(OH)_2$, reaction time and temperature, stirring speed.

Separation of $BaSO_4$ precipitate was demonstrated by the equipment, which can continuously produce $BaSO_4$ and separate solution and $BaSO_4$. The HyBRID decontamination and $Ba(OH)_2$ solution were feed in mixing tank for $BaSO_4$ foaming and the precipitates were separated by filtration system.

3. Results and discussion

Prior to investigation of $BaSO_4$ precipitation, sulfuric acid and barium hydroxide solution were prepared. According to Eq. (1), white $BaSO_4$ solids were obtained and its reaction follows as:

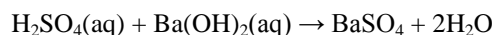


Fig. 1 shows the sulfate concentration and pH of the top solution after formation of BaSO₄ according to the reaction time, temperature, stirring speed, and amount of Ba(OH)₂. As can be seen Fig. 1, the sulfate concentration was significantly decreased after Ba(OH)₂ solution. Especially, sulfate can be removed when the volume ratio of SO₄²⁻ and Ba²⁺ was more than 1.1. In addition, the sulfate concentration was increased according to the reaction temperature. So, the reaction temperature is critical factor for sulfate removal. Because of increase solubility at high temperature, some barium sulfate concentration may remain in the solution.

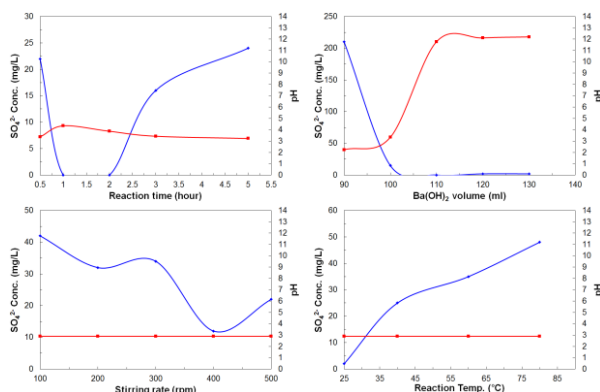


Fig. 1. Sulfate concentration as a function of effective parameters.

We also measured the metal ion concentration in the solution after BaSO₄ precipitation by using inductively coupled plasma atomic emission spectroscopy(ICP-AES). If metal ions can be simultaneously removed when the BaSO₄ is foamed, it could be beneficial for the treatment process system. Table 1 indicates the concentration of metal ions after BaSO₄ precipitation.

Table 1. Concentration of metal ions after BaSO₄ precipitation.(ppm)

Ba(OH) ₂	0 ml	100 ml	103 ml	105 ml	110 ml
pH	-	10.91	11.13	11.24	11.37
SO ₄ ²⁻	4000	96	64	36	
Fe	19.35	0.1	0.1	0.1	0.1
Ni	13.13	0.1	0.1	0.1	0.1
Cr	12.86	0.6	0.4	0.1	0.1
Cu	3.54	0.1	0.1	0.1	0.1
K	9.72	125.2	121.9	111.5	111.2
Mn	434.35	0.1	0.1	0.1	0.1

As can be seen in Table 1, the sulfate ions are dominant factor of HyBRID decontamination waste solution. After adding Ba(OH)₂, the sulfate ions were significantly decreased according to the amount of Ba(OH)₂. Simultaneously, other metal ions also removed or precipitated with sulfate ions as metal hydroxides at pH 11 except for potassium ion. This result indicates that metal and sulfate ions are co-

precipitated without any additives. Our BaSO₄ precipitation method is beneficial for removal of sulfate and metal ions in HyBRID decontamination waste solution. Also, we designed and fabricated the separation equipment which separates BaSO₄ and solution by using filtration system.

3. Conclusions

The waste solution treatment of HyBRID decontamination agents was developed by adding Ba(OH)₂ as BaSO₄ precipitation process. We observed the high sulfate removal efficiency with metal ions except for potassium ions. For the BaSO₄ separation, we have optimized the separation process condition according to effective parameters. Our waste treatment strategy would be beneficial for lower waste volume and cost.

REFERENCES

- [1] R. Ostman, M. Beggas, H. Saibi, Study of coprecipitation of strontium(Sr²⁺) with barium sulphate(BaSO₄) in aqueous solution, J. Mat. Sci. Eng. A, Vol 5, P. 305, 2015.

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