A Study of Waste Treatment in SP-HyBRID Decontamination Process Using On-Line Monitoring

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1. Introduction

In general, decontamination of nuclear power plants usually generates highly radioactive wastewater. Current radioactive waste should be stored in a safe radioactive waste disposal facility, since complete removal in a short period of time is not possible. The amount of radioactive waste product can be a very sensitive issue because it must be stored in a limited processing facility. Therefore, it is one of the most important factors to minimize the amount of waste product in the wastewater treatment after decontamination. SP-HyBRID [1], decontamination process developed by KAERI, was developed to solve the problem of material damage [2] and wastewater treatment of commercial decontamination agent using organic acids. In the SP-HyBRID process, a wastewater containing sulfate, hydrazine and various metals including radioactive cobalt is formed after decontamination. Sulfate ion and metal ion are removed by precipitation by adding barium hydroxide, and hydrazine is removed by adding hydrogen peroxide. In this study, when the wastes produced after the SP-HyBRID process were removed by the above described method, the research for effective removal method of ions in wastewater and the determine the amount of additive to minimize waste were conducted. Real time process monitoring was used to minimize waste generation.

2. Experimental Methods

The wastewater produced by the SP-HyBRID process was prepared for the experiment. It was assumed that iron, chromium and nickel, the main components of the oxide film of the PWR primary system which is subject to decontamination, was dissolved. This assumption was applied to make a simulated wastewater similar to the real decontamination wastewater.

Table 1. Condition of Simulated Wastewater

SP-HyBRID	6.33 mM $KMnO_4$, 37.02 mM H_2SO_4, 57.91 mM N_2H_4, 0.5 mM $CuSO_4$
Dissolved metal ions	Fe 50 ppm, Cr 50 ppm , Ni 25 ppm

In this study, the process of precipitation of wastewater ions was divided into two steps. The first step was addition of barium hydroxide for metal and sulfate ion removal. Barium hydroxide was dissolved in water and added to the solution. The second step was to remove the hydrazine by adding hydrogen peroxide. During the addition of the barium hydroxide solution and the hydrogen peroxide, the pH, ORP and conductivity of the wastewater were monitored in real time. A small amount of barium hydroxide solution and hydrogen peroxide were added periodically. The solution was sampled at each interval. The concentrations of various metal ions, sulfate ions and hydrazine in the sample solution were analyzed using ICP and UV.

3. Results

The results of monitoring recorded during decontamination waste treatment are shown in Fig. 1. As the process progressed, a change in each value was observed. Results of analyzing the components of each solution are shown in Fig. 2 and Table 2. Since the concentration difference of each ion was large, most of ions is represented by the removal rate, and barium ion is expressed by concentration unit in Fig. 2. Table 2 shows the concentration of hydrazine in the solution before and after the addition of hydrogen peroxide. Monitoring data was interpreted by each step through Fig. 2 and Table 2.

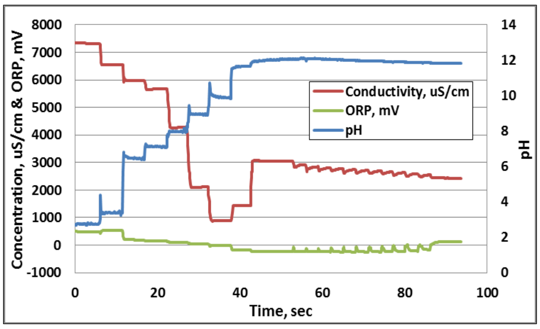

Fig. 1. Monitoring Data on pH, ORP and Conductivity during Wastewater Treatment Process.

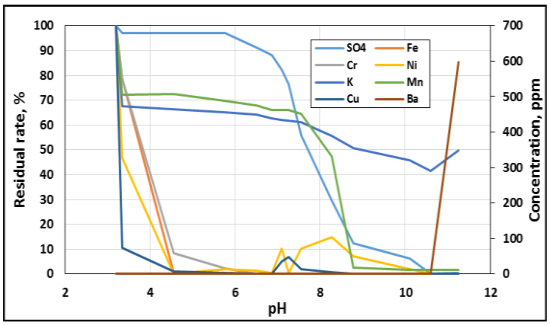

Fig. 2. Behavior of Ions in Wastewater by Addition of Barium Hydroxide.

Table 2. Concentration of Hydrazine before and after Addition of Hydrogen peroxide

Condition	Concentration, ppm	Remove efficiency, %
Before addition of hydrazine	1442	0
After addition of hydrazine	0.1	99.99

In the barium hydroxide addition step to remove metal and sulfate ions, the pH was increased by barium hydroxide. As the pH increased, most of the dissolved metal ions precipitated. pH range of the precipitated metal ions was different. It can be seen that the precipitation of metal ions depends on the solubility in each pH range[3]. But potassium was not removed in wastewater. It was assumed that potassium was not removed due to the absence of precipitation by the formation of hydroxides at high pH. To remove potassium, an ion exchange resin process should be added. And it was also confirmed that sulfate ions were precipitated to barium sulfate. Barium ions were detected in the treated solution because of excessive addition of barium hydroxide after the removal of the sulfate ions. This phenomenon is the same as the result of conductivity monitoring. In the addition step of hydrogen peroxide for hydrazine removal, the addition of hydrogen peroxide increased the ORP. In the addition step of hydrogen peroxide for hydrazine removal, graph shows that ORP increases and decreases with each addition of hydrogen peroxide. This phenomenon appears to be due to the presence of hydrazine in solution. When hydrazine was removed by more than 99%, it was confirmed that the ORP did not decrease any more.

4. Conclusion

As a result of monitoring and analyzing solutions at each step of wastewater treatment, it can be seen the removal state of the ions dissolved from the conductivity monitor. And, since the precipitation of metal ions was dependent on the pH, it was confirmed that the metal removal interval can be predicted using pH monitoring. The residual amount of hydrazine can be deduced through ORP monitoring. In this way, it is possible to judge the optimum amount of the additives necessary for treatment of wastewater in process in real time. This is a very effective method in minimizing the amount of final waste. Therefore, it is expected that it will help to perform efficient and accurate wastewater treatment at low cost.

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