Pilot Scale Waste Treatment Test for SP-HyBRID Decontamination Process

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1. Introduction

There are many chemical decontamination techniques that use organic acids, such as oxalic acid, citric acid, nitrilo triacetic acid (NTA), and ethylenediamine-tetraacetc acid (EDTA) [1-3]. However, such organic acids and chelating ligands are often problematic for the safety of radioactive wastes. KAERI has been developing a new decontamination process that does not contain any organic chemicals in the decontamination solution and minimizes the use of ion exchange resin in the solution purifying step [4]. 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 or candle filter. In small scale beaker test, it was shown that the total volume of solid waste for SP-HyBRID process can be reduced 1/10 less than that of a commercial process and spent ion exchange resigns can be reduced to 1% of that of a commercial process.

Our study was concerned with the large scale waste treatment performance of SP-HyBRID process. The precipitation property and solid-liquid separation property of liquid waste for SP-HyBRID process were evaluated with large scale filter press system.

2. Experimental Methods

2.1 Precipitation of Liquid Waste

The chemical composition in liquid waste of SP-HyBRID process was composed of sulfate ion and various cations as shown in table 1. Measured chemical compositions in the solution after precipitation were showed in the table also. $Ba(OH)_2$ solution was added in the simulated waste solution to precipitate with $BaSO_4$ particles. Before and after precipitation of the liquid was sampled and analyzed with atomic absorption spectroscopy.

2.2 Solid-Liquid Separation

The most important step in the liquid waste treatment of SP-HyBRID process is Solid-Liquid Separation (SLS) step. In this work, filter press was selected in SLS step. Fig. I. is showed a filter press system used in this study. Two types of additive were added in the liquid waste to improve the filtration properties.

Table I. Chemical composition of simulated liquid waste before and after precipitation

Treatment	Chemical composition, ppm							
	SO_4^{2-}	Fe	Cr	Ni	K	Mn	Cu	Ba
Before	4,100	57.9	60.2	30.4	238	341	40.1	0
After	0	0	0	0	171	0	0	0.4

Fig. 1. Photo of Bench-Scale of Filter Press

3. Test Results and Considerations

3.1 Properties of $BaSO_4$ Precipitation

As shown in Table 1, the major composition of liquid waste is sulfate ion. The precipitation reaction of sulfate with a barium hydroxide is as follows;

$$H_2SO_4 + Ba(OH)_2 \rightarrow BaSO_4 + 2H_2O \quad (1)$$

Because of the very low value of the solubility product for $BaSO_4$ (i.e., 1.084 x 10^{-10} at 25°C), sulfate ions can be removed from the solution with the addition of the same concentration of barium ions, which is then followed by solid-liquid separation of the precipitated particles. The necessary concentration of barium hydroxide to precipitate of 28.25 mM sulfate is about 30 mM. After precipitation, the liquid was sampled and analyzed with AA.

Fig. 2 shows an on-line-monitoring result (pH and conductivity) during the precipitation of sulfate ion with adding of $Ba(OH)_2$ solution. With step by step addition of $Ba(OH)_2$ solution, conductivity of the solution decreased in steps and pH of the solution increased in steps. The value of final conductivity is about 1,000 μS/cm which is contributed by remained potassium ions.

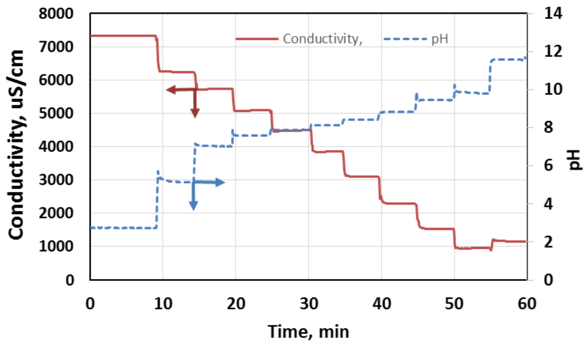

Fig. 2. Conductivity and pH Change during a Precipitation of $BaSO_4$ Sludge

Fig. 3 shows the cation removal behaviors during a precipitation of $BaSO_4$. The primary waste (Fe, Cr, Ni) and Cu ion were removed in the initial step (pH<6), however, Mn ion was removed at higher pH (pH <9) and K ion removed only about 50% at the final step.

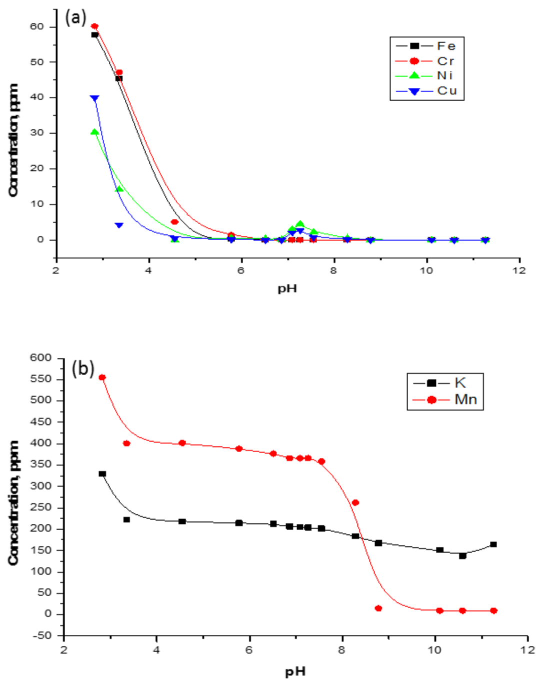

Fig. 3. Removal Behaviors of Cations during a Precipitation of $BaSO_4$; (a) Primary Waste, (b) Secondary Waste

Fig.4 shows the morphology of cake made by filter press with 60 L of simulated liquid waste (Table 1). With the bench-scale filter press (Fig.1), the waste solution was filtered twice with 30 L. Total weight of the cake was 1,630 g, water content was 37.45%, pure cake weight was 1,020 g which from sludge of 570 g and from additive of 450 g. This values agree well with theoretical value within the experimental error range.

Fig. 4. Photo of Cake made by Filter Press

4. Conclusions

Pilot scale waste treatment test for SP-HyBRID decontamination process has been performed with filter press system. Purification behavior was evaluated with on-line monitoring of conductivity and solution pH, as well as cation removal behaviors. The waste reduction mechanism of SP-HyBRID decontamination process was well validated and the advantages of this process were verified on a pilot scale instrument.

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