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Development of a new chemical process for radioactive waste treatment

Bo-Bae Cho [a,] So-Yun Jeong [a], Hyun-Young Shin [a], Chan-Hee Park[a], Sung-Ryul Kim [a], Jung-Min Oh [a], Ba-Ro Lee [a], Hye-Jin Kim [a], Ji-Ung Kim [a], Wook-Jae Yoo [a], Kyu-Tae Park [a*]
[a]Orbitech Co., Ltd., Corporate R&D Center, 1130, Beoman-ro, Geumcheon-gu, Seoul
[*]Corresponding author: paradoxno1@orbitech.co.kr

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1. Introduction

The current treatment methods for liquid waste, including laundry and decontamination wastewater generated in nuclear power plants, are not yet well established, and the need for effective solutions continues to grow. The liquid waste consists of radioactive metal ions (Cu^{2+}, Ni^{2+}, Co^{2+}, etc.) and organic materials such as surfactants and oxalic acid. One of the most widely applied technologies is CORD-UV(chemical oxidizing reducing decontamination with UV) process. In these processes, significant amounts of sludge and secondary waste are inevitably produced. And these conventional methods face challenges in terms of long processing times, high cost, and generation of large volumes of secondary waste.

An effective management strategy for liquid organic radioactive waste is necessary to ensure proper processing, safe handling, storage, and disposal with low cost, small volume of secondary waste. [1]

Metal-oxalates precipitate through a reaction with oxalic acid and various metal ions such as Cu^{2+}, Ni^{2+}, Ca^{2+}, Mg^{2+}. [2,3,4] Additionally, metal ions such as Cu^{2+} and Ni^{2+} precipitate as $Cu(OH)_2$ and $Ni(OH)_2$ in a hydroxide solvent. Using this reaction, oxalic acid and radioactive metal ions from organic radioactive waste can be removed simultaneously.

This study proposes a multi-step chemical precipitation process as a pre-treatment method for liquid organic radioactive waste, aiming to improve overall decontamination efficiency and enable recycling or final solidification of treated effluent. The chemical reaction is controlled by the concentration of Ca^{2+} ions and pH adjustment of the solvent.

The treated water, which is the effluent of the chemical process, could be reused or safely released in an eco-friendly manner. Furthermore, the amount of sludge and secondary waste was significantly reduced compared to conventional methods.

Representative results of the chemical process are presented.

2. Methods and Results

The simulated liquid organic radioactive waste (SLORW) was prepared using stable metal ions (Cu^{2+}(2 mM), Ni^{2+}(2 mM)) instead of radioactive metal ions dissolved in oxalic acid (20 mM). The solvent color is clear cyan due to the mixing of Cu^{2+} ions(blue) and Ni^{2+} ions(green).

Although the SLORW contains both oxalic acid and metal ions (Cu^{2+}, Ni^{2+}), the metal ions concentration is low, and more suitable reaction conditions, such as pH control and coagulant, are needed to effectively remove both materials.

2.1 Oxalate precipitation

Ca^{2+} ions react with oxalic acid within the pH range of 0.5 to 2, while Mg^{2+} ions react above pH 2. [4]

To compare the results at different pH levels, calcium hydroxide (v/v 0.27, 0.36, 0.50, 0.80) was first added to the SLORW at pH < 2, and then magnesium hydroxide was used to adjust the pH to 5-6, 7, and 8-9. Calcium hydroxide was used as a 35% aqueous solution (Samcheon), and 0.1 M magnesium hydroxide was prepared by dissolving solid magnesium hydroxide in distilled water (D.W.).

The clear cyan color of SLORW changed to a cloudy blue due to the formation of white precipitates, namely CaC_2O_4 and MgC_2O_4. The more calcium and magnesium hydroxide added, the cloudier the blue became. In the Next step, to compare the results based on presence or absence of the white precipitation, the SLORW was used both before and after filtration.

2.2 Metal ions precipitation

Many metal ions react with ferrocyanide, especially potassium Ferrocyanide, to form insoluble precipitates or complexes. [5] To remove the metal ions (Cu^{2+}, Ni^{2+}) in SLORW, 0.1 M potassium ferrocyanide was added, and the color turned to purple with precipitation. Before filtration, SLORW was cloudier purple, and after filtration, SLORW was a clean purple. Then, to remove residual ferrocyanide as Prussian blue ($Fe_2[Fe(CN)_6]$), 0.1 M iron chloride was added.

2.3 Results

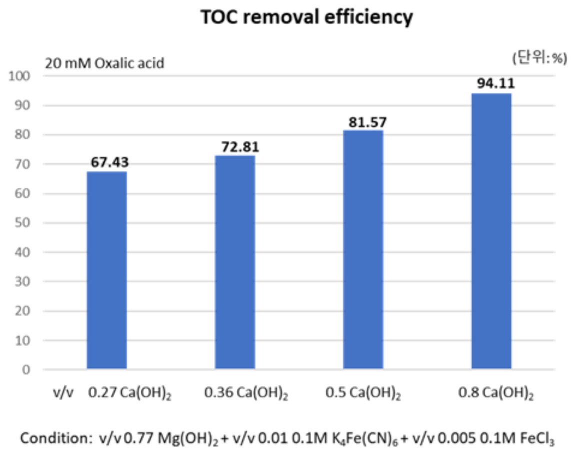
The removal efficiency of oxalic acid and metal ions (Cu^{2+}, Ni^{2+}) in the SLORW was confirmed through TOC analysis and ICP measurement of the effluent from the chemical process. At each chemical process step, TOC and ICP were measured, and the reaction trends were identified. The final sludge was dried at 60 ℃ and analyzed using XRD patterns.

The TOC removal efficiency was higher with the mixed use of $Ca(OH)_2$ and $Mg(OH)_2$ than with the exclusive use of $Mg(OH)_2$ for the SLORW. Also, no significant difference in TOC removal efficiency was observed at each chemical step (hydroxide, ferrocyanide, and iron chloride) across all pH ranges when $Mg(OH)_2$ was used exclusively. However, in the mixed use of $Ca(OH)_2$ and $Mg(OH)_2$, the TOC removal rate increased as pH rose, and it further increased after adding potassium ferrocyanide. (Table 1.) Thus, TOC removal efficiency is more effective when Ca^{2+} ions are added and the process is conducted at pH 8-9

Table 1. TOC removal efficiency of mixed use of $Ca(OH)_2$-$Mg(OH)_2$ and exclusive used of $Mg(OH)_2$

Step (mixed use of $Ca(OH)_2$ and $Mg(OH)_2$)	pH 5-6	pH 7	pH 8-9
Ca-$Mg(OH)_2$	33.60	38.96	44.43
[BF] $K_4Fe(CN)_6$-$FeCl_3$	48.87	52.51	64.25
[AF] $K_4Fe(CN)_6$-$FeCl_3$	48.56	52.37	64.19
Step (exclusive use of $Mg(OH)_2$)	pH 5-6	pH 7	pH 8-9
$Mg(OH)_2$	20.82	27.57	29.80
[BF] $K_4Fe(CN)_6$-$FeCl_3$	29.55	23.59	25.77
[AF] $K_4Fe(CN)_6$-$FeCl_3$	20.35	22.22	18.64

*addition volume of $Ca(OH)_2$ (v/v) 0.27



Condition: v/v 0.77 $Mg(OH)_2$ + v/v 0.01 0.1M $K_4Fe(CN)_6$ + v/v 0.005 0.1M $FeCl_3$

Figure 1. TOC removal efficiency of mixed use of $Ca(OH)_2$-$Mg(OH)_2$ (v/v 0.27, 0.36, 0.50, 0.80)

In addition, the TOC removal efficiency increases as the volume of $Ca(OH)_2$ is raised.

Additionally, the removal efficiency of metal ions (Cu^{2+}, Ni^{2+}) was higher with the mixed use of $Ca(OH)_2$ and $Mg(OH)_2$ than with the exclusive use of $Mg(OH)_2$ for the SLORW. With mixed use of $Ca(OH)_2$-$Mg(OH)_2$, at > pH 7, the removal efficiency of Cu^{2+} is > 98% and that of Ni^{2+} is >93%. With exclusive use of $Mg(OH)_2$, at > pH 7, the removal efficiency of Cu^{2+} is > 76% and that of Ni^{2+} is >53%. By ion, the Cu^{2+} removal efficiency was higher than that of Ni^{2+} under both conditions (mixed and exclusive use). It was expected that Cu^{2+} would be removed prior to Ni^{2+}removal due to its higher affinity for precipitation. (Table 2, 3)

Table 2. The metal ions (Cu^{2+}, Ni^{2+}) removal efficiency for mixed use of $Ca(OH)_2$ and $Mg(OH)_2$;

Cu^{2+}	pH 5-6	pH 7	pH 8-9
[BF] $K_4Fe(CN)_6$-$FeCl_3$	89.45	99.42	99.96
[AF] $K_4Fe(CN)_6$-$FeCl_3$	98.53	98.53	99.99
Ni^{2+}	pH 5-6	pH 7	pH 8-9
[BF] $K_4Fe(CN)_6$-$FeCl_3$	70.10	94.97	99.69
[AF] $K_4Fe(CN)_6$-$FeCl_3$	93.26	93.26	99.97

Table 3. The metal ions (Cu^{2+}, Ni^{2+}) removal efficiency with exclusive used of $Mg(OH)_2$.

Cu^{2+}	pH 5-6	pH 7	pH 8-9
[BF] $K_4Fe(CN)_6$-$FeCl_3$	77.09	83.02	89.45
[AF] $K_4Fe(CN)_6$-$FeCl_3$	73.98	76.68	82.56
Ni^{2+}	pH 5-6	pH 7	pH 8-9
[BF] $K_4Fe(CN)_6$-$FeCl_3$	67.16	66.05	87.19
[AF] $K_4Fe(CN)_6$-$FeCl_3$	55.35	52.56	57.16

3. Conclusions

In this study, oxalic acid and metal ions (Cu^{2+}, Ni^{2+}) from SLORW were removed through a chemical precipitation process. With the addition of calcium and magnesium hydroxide, oxalic acid precipitated as CaC_2O_4 and MgC_2O_4. Additionally, metal ions reacted with potassium ferrocyanide to form insoluble precipitates. TOC removal increased with higher $Ca(OH)_2$ dosage (v/v 0.27-0.8) and further improved by subsequent addition of 0.1 M $K_4Fe(CN)_6$ and 0.1 M $FeCl_3$. The findings demonstrate that optimal removal of both TOC and metal ions was achieved by increasing Ca^{2+} concentrations and maintaining the pH between 8 and 9, confirming the effectiveness of the proposed multi-step chemical precipitation strategy. These results suggest that the proposed method can serve as an efficient and eco-friendly alternative for the pre-treatment of liquid organic radioactive waste in nuclear facilities.

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