

## Remediation of Uranium-Contaminated Concrete Using Various Extractants

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### 1. Introduction

A great amount of radioactive concrete waste was produced from the decontamination and decommissioning of a research reactor and uranium conversion plant at KAERI. To reduce the volume of concrete waste, a separation technology of porous fine cement paste from the gravel and aggregate in concrete through a thermal and mechanical treatment was developed [1]. However, since some gravel and aggregates still have higher radioactivity than the limited value for self-disposal, they have to be washed by appropriate decontamination reagents.

Carbonate, because of its ability to be recycled and its tendency to have great selectivity for uranium, was observed to be an effective way to remove uranium from uranium-contaminated soil [2]. However, the use of carbonate for the decontamination of concrete has been little reported. Strong acids have been used to wash soil contaminated with radioactive nuclides.

In this study, carbonate solution, nitric acid and sulfuric acid were used for the extraction of uranium from the concrete contaminated with uranium, and their efficiencies are compared to one another. In addition, the amount of waste sludge produced from the using these extractants was also evaluated.

### 2. Experiment and Results

#### 2.1 Concrete and reagents

Uranium-contaminated concrete was crushed, and particles with sizes of 1-5 and 5-25 mm were separately collected as the concrete samples, respectively. The concentration of uranium in the solution and solid was indirectly analyzed using  $\gamma$ -spectrometry by measuring the radioactivities of Th-234 and Pa-234m. All experiments were duplicatedly performed.

#### 2.2 Washing with carbonate

50 g of concrete particles of 1-5 and 5-25 mm were put into 100 mL of 0.25 M  $\text{Na}_2\text{CO}_3$  solution with 0.1M perhydroxide, respectively. The pH of the solution was then adjusted to 8.5-9.0. For the nitric acid, the pH of the solution was adjusted to pH 1.0 after adding the concrete waste. The solutions were shaken for 2 hours at 60 rpm for the extraction of uranium. The extraction procedure was performed twice under the same condition.

The experimental results are shown in Table 1. While the extraction efficiency of uranium by the carbonate solution is a little lower than that by nitric acid, the activity of Pa-234m in both solutions after extraction for the 5-25 mm sized particles remained below a self-disposal limiting value, 0.48 Bq/g. However, the radioactivity of Pa-234m for the 1.0~5.6 mm sized particles washed by the carbonate solution was higher than 0.5 Bq/g.

Table 1. Comparison of Extraction Efficiency of Uranium Between Nitric Acid and Carbonate Solution

Washing solution	Concrete size (mm)	Con. of Pa-234m of concrete (Bq/g)		Extraction efficiency (%)
		Before washing	After washing	
Nitric acid	1.0~5.6	0.87	0.42	52
	5.6~25	0.80	0.38	53
Carbonate solution	1.0~5.6	1.78	1.04	42
	5.6~25	0.62	0.35	46

#### 2.3 Washing with strong acids

50 g of concrete particles 1-5 mm in size was put into 100 mL of 1.0 M nitric acid and sulfuric acid solutions, and shaken for 1 hour at 60 rpm. The pH of the nitric acid and sulfuric acid solutions reached near 1.0 and 0.3, respectively. The supernatants were collected to measure their radioactivities. After the removal as much of the solute as possible, the washed concrete was washed again under the same conditions. During the second washing time, the pH of both acid solutions remained at 0.4-0.5. The radioactivity of the supernatants was also measured. Finally, the concrete solid was dried after the removal of the solvent, and its activity was measured.

The Pa-234m activities of the supernatants taken from the first and second washings, and of the washed concrete solid, are shown in Table 2. In this table, the amount of uranium extracted from the concrete by washing is double the concentration of the supernatant, since the ratio of solvent/solute was 2. Table 2 indicates that the extraction efficiencies by 1.0 M nitric acid and sulfuric acid are similar to each other.

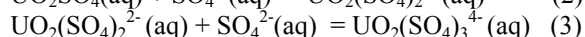
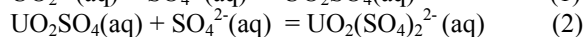
Table 2. The Radioactivities of Pa-234m in the Supernatants and Washed Concrete

	Radioactivity (Bq/g)	
	Nitric acid	Sulfuric acid
Unwashed concrete	0.80	
Supernatant from 1 <sup>st</sup> washing	0.12	0.16
Supernatant from 2 <sup>nd</sup> washing	0.07	0.04
Washed concrete	0.35	0.34

To precipitate the uranium in the solute after washing, the pH of the washing solution was adjusted to 11 by adding NaOH, and 0.1 g of alum and 0.1 g of magnetite were then added into the solution. After 2 hours of shaking, the solution was centrifuged for 10 minutes at 3500 rpm, and the precipitant was dried and weighted. The activity of the solution was also measured to know the concentration of uranium remaining.

From the uranium precipitation treatment, the weight of the dried sludge produced from the washing by nitric acid and sulfuric acid was 5.03 and 3.58 g, respectively. The activities of Th-234 and Pa-234m in both acid solutions were not detected using  $\gamma$ -spectrometry for a measuring time of 50,000 seconds, which means they were below 1 mg/L of the uranium.

A. Rahmati, et al. [3] reported that uranyl sulfate anion complexes are formed by the following reactions, (1)~(3), and 70~80% of these complexes were adsorbed by IRA 910, a strong anion exchanger, in 0.02~9.0 M of sulfuric acid.

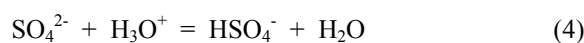


Since 1.0 M sulfuric acid was used for the extraction of concrete in this work, 1.0 g of IRA 910 resin was put into 50 mL of a concrete washing solution to adsorb the uranium dissolved in sulfuric acid and to reuse sulfuric acid without any precipitation treatment. However, the activities of Th-234 in the solution after the sorption by IRA 910 were not significantly changed, unlike the result of A. Rahmati, et al. Though sulfuric acid was additively put into the concrete solution to make 2 M sulfuric acid for the further progress of reaction (2) or (3), the result was not changed. Even when the pure uranyl solution dissolved in 1.0 M sulfuric acid was used, the uranium concentration was not remarkably reduced by the IRA 910.

A. C. Q. Ladeira, et al. [4] insisted that sulfate is the most interfering ion for the sorption of the uranyl sulfate ions onto an IRA 190U. The IRA 190U is also a strong anion exchanger, and has almost identical functional groups as IRA 190. Thus, the uranyl nitrate was dissolved in 0.1M sulfuric acid, and the solution was used for the uranium sorption test by IRA 910. However, no decrease in the Th-234 concentration was

found in this test. While Ag1x8 (100-200 mesh) manufactured BioRad Co., as another strong anion exchanger, was also examined, uranium was not significantly adsorbed onto this resin.

The little sorption of uranium onto the strong anion exchange resins in 0.1-2.0 M sulfuric acid may be due the equilibrium constants for reaction (1), (2) and (3) above. While A. Rahmati [3] insisted that most uranyl ions form  $\text{UO}_2(\text{SO}_4)_2^{2-}(\text{aq})$  and  $\text{UO}_2(\text{SO}_4)_3^{4-}(\text{aq})$  in a sulfuric acid solution, A. Burneau, et al. [5] found equilibrium constants for reaction (1), (2) and (3) at 1M ionic strength and ordinary temperature to be about 1400, 11 and very small, respectively. Moreover, he showed that at below pH 1.3, the uranyl sulfate complex is decomposed by acidification and the formation of  $\text{SO}_4^{2-}$  competes with that of  $\text{HSO}_4^-$  by the following equation:



Therefore insignificant sorption of uranium onto IRA 910 in a sulfuric acid solution might be due to the small formation of  $\text{UO}_2(\text{SO}_4)_2^{2-}(\text{aq})$  and  $\text{UO}_2(\text{SO}_4)_3^{4-}(\text{aq})$ .

### 3. Conclusions

The extraction efficiency of uranium from contaminated concrete by a carbonate solution is a little lower than that by nitric acid, and similar between nitric acid and sulfuric acid. However, the amount of sludge produced by the treatment of precipitation at high pH was less in sulfuric acid than in nitric acid. In addition, domestic sulfuric acid is cheaper than nitric acid.

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