Remediation of Uranium-Contaminated Concrete Coated with Epoxy

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1. Introduction

Many nuclear facilities will have to be decommissioned or dismantled in the next decade. In Korea, a great amount of radioactive concrete waste has been generated from the decommissioning of a research reactor and uranium conversion plant at KAERI. A volume reduction of the concrete waste by appropriate treatment technologies will decrease the amount of waste to be disposed of and result in a reduction of the disposal cost and an enhancement of the efficiency of the disposal site. As decontamination techniques for concrete, biological methods, chemical methods, strippable coating, laser ablation, microwave heating and electrokinetic have been developed.

In this study, decontamination methods for U-contaminated concrete pieces with and without epoxy were examined and the amount of waste sludge generated from the treatment was evaluated. In addition, nitric acid and sulfuric acid were used as the washing solution for the uranium, and their efficiencies were compared each other.

2. Experiment and Results

2.1 Radioactivity measurement of concrete

The concentration of uranium in the solid and solution was indirectly analyzed using γ-spectrometry by measuring the radioactivity of Pa-234m (Energy 1001 KeV, a daughter nuclide of U-238). To observe the proportion of radioactivity of Pa-234m with the uranium concentration, 120 g of soil contaminated with 0.5, 1, 2 and 5 Bq/g of uranium were prepared, and their Pa-234m radioactivities were measured. From the calibration curve, the uranium concentration of concrete was calculated.

2.2 Concrete characteristics

Some of the U-contaminated concrete pieces were coated with epoxy, and their radioactivity was very high. Thus, the concrete pieces were divided into two groups: those with and those without epoxy. To know the distribution of uranium with a concrete depth from the epoxy surface in the concrete pieces coated with epoxy, a concrete piece was analyzed using an EPMA (Electron Probe Micro-Analyzer) The EPMA measurement indicates that there was a high concentration of uranium in the mortar layer under epoxy.

2.3 Decontamination of the concrete pieces without epoxy

The concrete pieces without epoxy were sifted and divided into sizes below 1, 1-5 and 5-25 mm. Most of them that were larger than 1 mm were below 1.0 Bq/g for Pa-234m. 100 g of 5-20 mm concrete pieces, having 0.57±0.07 Bq/g for Pa-234m, was washed in 100 mL of distilled water, 0.1 M sulfuric acid and 0.1 M nitric acid, respectively, for 2 hours at 140 rpm in a shaker. After washing, the concrete solutions were filtered through a sieve with 1 mm pore size and the retained solid was washed 2 times with a small amount of distilled water. Finally the solid was dried in an oven at 105℃ and weighed, and its radioactivity was measured. The sludge passed through the sieve was also dried and weighed.

From the washing and removing of particles below 1 mm size, the Pa-234m radioactivity in the concrete pieces decreased from an initial 0.57±0.07 Bq/g to 0.21±0.04, 0.17±0.03 and 0.17±0.03 Bq/g, and 5.2, 4.6 and 4.2 g of sludge was generated by water, and sulfuric and nitric acids, respectively. This result indicates that the concrete pieces without epoxy can be easily decontaminated to a self-disposal limiting value (0.45 Bq/g for Pa-234m) by washing with 0.1M sulfuric or nitric acid, and even water, and that heating is not necessary.

2.4 Decontamination of the concrete pieces with epoxy

To remove epoxy from concrete pieces with epoxy, the concrete pieces were heated for 0.5 hours at 270, 330, 415 and 600℃, respectively, in a muffle furnace. In addition, we observed the surface change at various heating times: 0.5, 1.5 and 2 hours at 400℃. The heating test results indicate that the concrete pieces have to be heated for longer than 1.5 hours at 400℃ to remove the epoxy.

After heating the concrete pieces for 2 hours at 400℃, following several tests were performed to develop a brief and effective decontamination process for the removal of uranium:

① Concrete pieces were washed with 12% (about 2.0 M) nitric acid for 2 hours at 140 rpm, and the radioactivities of sand broken off from the concrete pieces and the remaining concrete pieces were then measured.

② The remaining concrete pieces produced from ① were successively washed with 12% nitric acid until their radioactivity reached below the limit value for self-disposal.

③ 100 g of concrete pulverized by a mortar was washed with 100 mL of 20% sulfuric acid for 2 hours at 140 rpm, and the solution was then centrifuged. After drying, the radioactivity of the solid was measured. This concrete was put into 100 mL of distilled water and was washed again. The murky solution was separated from the concrete pieces and dried to produce sludge. The weight, volume and radioactivity of remaining concrete (actually sand) and sludge were measured after drying.

④ 100 g of pulverized concrete was sequentially washed with 100 mL of 0.1, 2.0 and 1.0 M of nitric acid at 140 rpm for 2, 2 and 1 hours, respectively. The washed solid was cleaned with a small amount of water after every washing. The murky solution from every washing was collected and its pH was adjusted to 8-10 by adding NaOH to precipitate the uranium. Finally, the solution was filtered with a Whatman™ 4 filter paper (Particle retention = 20-25 μm). The weight, volume and radioactivity of the washed concrete and filtered sludge were measured after drying. The filtrate was adjusted to pH 8-10, and its radioactivity was also measured.

When the concrete pieces were washed by 12% of nitric acid, the Pa-234m radioactivity of sand broken off from the concrete pieces was very low, 0.29±0.05 Bq/g, while that of the remaining concrete pieces was 2.3±0.4 Bq/g. This result indicates that the concrete pieces have to be pulverized to reduce the radioactivity for self-disposal. When the remaining concrete pieces were additionally washed three times in succession with fresh 12% of nitric acid at 1 g/mL of solid/solute ratio, their radioactivity reached the limit value for self-disposal. However, this process requires too much time and nitric acid.

When 100 g of heated concrete pieces were pulverized and washed with 20% sulfuric acid for 2 hours, the pH of the solution was maintained at 0.8-0.9. After centrifugation, the dried solid still had a radioactivity of 2.2±0.4 Bq/g for Pa-234m. This solid was washed with water again and the murky solution was separated. After drying, the radioactivity of 68 g of the remaining solid, which was almost sand, reached 0.60±0.08 Bq/g for Pa-234m. However, the weight and volume of the sludge were too great at 65 g and 100 mL, which might be contributed by the precipitation of calcium sulfate. This result indicates that nitric acid is preferable to sulfuric acid as a washing solution because of less sludge generation, and the cement paste has to be removed as much as possible by the first washing to reduce the amount of acid required.

Table 1 was obtained from the experiment of ④. In this table, two washing solutions of 12% and 1 M nitric acid after removal of the concrete piece were collected together and adjusted to pH 9.5 by adding NaOH. After washing the concrete pieces with 0.1M nitric acid, the pH of solution was 9.94. When the solution was filtered by a Whatman™ 4 filter paper, Pa-234m radioactivity of filtrate was not detected for 100,000 seconds. When the pulverized concrete powder was washed with water, the pH of the solution increased to higher than 12.0. Since the uranium solubility can be increased in a strong alkaline solution, 0.1M nitric acid would be better than water for the first washing to remove cement paste. The results of the experiment of ④ indicate that about half the weight of the initial concrete pieces with epoxy can be self-disposed. The total weight and volume of sludge were 50 g and 53 mL, respectively. Since the volume of the sludge was still great, a technique for a volume reduction has to be developed in the future to send a small volume of waste to a radioactive waste repository.

Table 1. The experimental results for decontamination of concrete pieces by washing with nitric acid

Step	Washing condition	Concrete pieces		Sludge
		Weight (g)	Pa-234m (Bq/g)	Weight (g)
	Before washing	100	15.1±1.5	
1	0.1M nitric acid	77.4	12.0±1.6	22.2
2	2.0 M nitric acid	55	1.3±0.3	28
3	1.0 M nitric acid	54	0.30±0.1	

3. Conclusions

The concrete pieces produced from the decommissioning of a uranium conversion plant were divided into two groups, concrete coated with epoxy and concrete without epoxy. The concrete pieces without epoxy were easily decontaminated by washing with 0.1M sulfuric or nitric acid and then separation of the cement paste.

In concrete coated with epoxy, a high concentration of uranium exists in a mortar layer under epoxy. When these concrete pieces were heated for 2 hours at 400℃, pulverized and sequentially washed with 0.1, 2.0 and 1.0 M of nitric acid, their radioactivity reached below the limit value of uranium for self-disposal.