SURFACE DECONTAMINATION OF SYSTEM COMPONENTS IN URANIUM CONVERSION PLANT AT KAERI

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ABSTRACT

A chemical decontamination process using nitric acid solution was selected as *in-situ* technology for recycle or release with authorization of a large amount of metallic waste including process system components such as tanks, piping, *etc.*, which is generated by dismantling a retired uranium conversion plant at Korea Atomic Energy Research Institute (KAERI). The applicability of nitric acid solution for surface decontamination of metallic wastes contaminated with uranium compounds was evaluated through the basic research on the dissolution of UO_2 and ammonium uranyl carbonate (AUC) powder. Decontamination performance was verified by using the specimens contaminated with such uranium compounds as UO_2 and AUC taken from the uranium conversion plant. Dissolution rate of UO_2 powder is notably enhanced by the addition of H_2O_2 as an oxidant even in the condition of a low concentration of nitric acid and low temperature compared with those in a nitric acid solution without H_2O_2. AUC powders dissolve easily in nitric acid solutions until the solution pH attains about 2.5~3. Above that solution pH, however, the uranium concentration in the solution is lowered drastically by precipitation as a form of $U_3(NH_3)_4O_9 \cdot 5H_2O$. Decontamination performance tests for the specimens contaminated with UO_2 and AUC were quite successful with the application of decontamination conditions obtained through the basic studies on the dissolution of UO_2 and AUC powders.

INTRODUCTION

In Korea, there is a retired uranium conversion plant, in which a large number of the internal components and equipments will be completely removed and the concrete building itself will be reused through the national project of environmental restoration of the uranium conversion plant at KAERI..

The main internal process equipment in the uranium conversion plant are listed in Table 1 together with used and/or treated chemical compounds, process temperature, and system materials. It can be seen that there are both particulate contaminants such as U_3O_8, UO_2, AUC, ADU, *etc*. and liquid phase contaminants such as uranyl nitrate and organic compounds (TBP, dodecane) on the surface of the system components such as the dissolver, rotary drum filters, pulse columns, evaporator, precipitators, fluidized bed reactors, pumps, piping, valves, *etc*.

Table 1. Main internal process equipments in the uranium conversion plant (1)

	Main Process	Chemicals Used or Treated	Process Temp.	Process Equipments[a]	Structural Materials
ADU Process	Dissolution and Filtration	U_3O_8, HNO_3	~95 °C	Dissolvers, Tanks, Pumps, Rotary drum filters	Stainless steel
	Purification (Solvent Extraction)	UN, HNO_3, TBP, Dodecane	~60 °C	Pulse columns, Tanks, Pumps	Stainless steel
	ADU Precipitation	UN, ADU, NH_3	~90 °C	Rotary drum filter, Precipitator, Pumps, Tanks	Stainless steel
	ADU Calcination/ Reduction	ADU, UO_3, UO_2	~650 °C	Rotary kilns	Inconel
	UF_4 Conversion	UO_2, UF_4, HF	~600 °C	Rotary kiln	Inconel
	Waste Treatment	NOx, NH_4NO_3, NaOH, $Ca(OH)_2$	~60 °C	Scrubber, Tanks, Pumps	Stainless steel
AUC Process	Evaporation	UN, HNO_3	~100 °C	Evaporator, Pumps	Stainless steel
	Precipitation & Filtration	UN, NH_3, CO_2, MeOH, AUC	~80 °C	Precipitator, Pumps, Rotary filters,	Stainless steel
	Calcination/ Reduction/Blending	AUC, UO_3, UO_2	~650 °C	Fluidized bed reactors, Pumps, Mixers	Inconel
	Waste Treatment	AUC, NH_3	~90 °C	Precipitator, Tanks, Pumps	Stainless steel

[a] In all cases, piping and valves must be included.

During the course of dismantling the contaminated system components and equipment, a lot of uranium contaminated metallic wastes will be generated, so that the effective waste management strategy is required. Decontamination is one of the technologies that promotes workers’ safety and reduces the amount of radioactive waste in the decommissioning of the uranium conversion plant.

There are chemical decontamination methods using aggressive or mild organic and/or inorganic chemical reagents, mechanical methods including brushing, abrasive blasting systems, and high-pressure water jets containing abrasives, and other methods such as electrochemical processes, pastes, gels and foams, strippable coatings, *etc.*(2) in the decontamination technologies applicable to an internal surface of metallic components of the uranium conversion plant. The chemical decontamination has the advantage of *in-situ* application for inaccessible internal surfaces of the process system components such as tanks, piping and pumps in the uranium conversion plant. Complexing agents such as EDTA, HEDTA and DTPA, which form powerful uranium complexities, strong or weak acid, and acid or alkaline salts are used in the chemical decontamination process. Aggressive chemical decontamination processes using acid and/or oxidizing solutions greater than 1 wt% concentration, in which high DFs can be achieved, but special care of the secondary wastes must be taken into account, have been used for systems and components in a reprocessing plant. In a mild chemical decontamination process using below 1 wt% chemical concentration, the contact with the contaminated surface for a longer period has to be kept to get desired DF. The chemical components of mild decontamination agents are the same as for aggressive solutions, but the arising secondary waste, which may be treated easier compared with those in aggressive chemical decontamination, are relatively small due to lower concentration (3).

In the uranium conversion plant at KAERI, concentrated nitric acid was used in the dissolution of uranium compounds including U_3O_8, and the processes including the filtration of impurities and the extraction for purifying uranium were contacted with a nitric acid media containing uranium during the course of the operation. Liquid wastes, which exist currently in the sludge form saturated inorganic salts such as NH_4NO_3, $NaNO_3$, $Ca(NO)_2$, *etc*., generated from the plant during operation have been stored in lagoons(4). With consideration of the compatibility with lagoon wastes, it was evaluated that chemical decontamination using nitric acid is desirable for application to system components in contact with nitric acid solutions.

In this study, a decontamination process using nitric acid was selected as an *in-situ* technology applicable to the system components for recycle or release with authorization of a large amount of metallic waste generated from the decommissioning of the plant at KAERI. The applicability of a nitric acid solution to surface decontamination of metallic wastes contaminated with uranium compounds was evaluated through the dissolution of UO_2 and AUC powders. Decontamination tests using contaminated specimens taken from the uranium conversion plant were also conducted.

EXPERIMENTAL

Dissolution of UO_2 Powder

The basic decontamination performance was evaluated by the dissolution of UO_2 powder, which is one of the contaminated uranium compounds on the metallic surface of the system components in the uranium conversion plant. Dissolution of UO_2 powders was carried out in nitric acid solutions as a decontamination medium with the effect of process parameters such as nitric acid concentration, temperature, and the addition of hydrogen peroxide. The dissolution reaction was commenced by putting 0.1 g of UO_2 powders into 85 mL of the solution in a glass reactor at the desired temperature and the concentration of uranium in liquid samples taken using 0.2 μm syringe filter during the course of dissolution were determined with Arsenazo (III) by a UV-spectrophotometer (CE 2021, Cecil Instrument) at 655 nm(5) to observe the dissolution behavior of UO_2 powders.

Dissolution of AUC Powder

AUC is one of the major uranium compounds contaminated on the metallic surfaces of the system components in the uranium conversion plant. In order to acquire the basic information on the decontamination of AUC contaminated metallic surfaces, dissolution of AUC powders was carried out in 50 mL nitric acid solutions with the addition of AUC powders little by little. With the variation of nitric acid concentration at room temperature, amount of dissolved uranium was determined by the same analytical method as described earlier and pH change in the solution, which occurs with increasing the dissolved amount of AUC, was measured with a pH meter (Fisher Scientific Model 25). After the maximum dissolution is reached, the remainder in the solution was filtered, washed with pure water, dried in a vacuum oven, and analyzed with X-ray diffractometry (Siemens D5000).

Decontamination of Uranium Contaminated Specimen

UO_2 and AUC contaminated specimens of dimension *ca*. 20 mm x 20 mm were prepared to verify decontamination performance in nitric acid solutions. UO_2 contaminated specimen was prepared with the piping taken from beneath the fluidized bed reactor, in which UO_2 powders are produced by calcination, reduction and stabilization of AUC powders. AUC contaminated specimen was prepared from the piping that transfers AUC powder produced by concentration and precipitation of uranyl nitrate to the rotary filter. Decontamination performance tests using these specimens were carried out in a glass reactor for 30 minutes under designed test conditions. Decontamination efficiencies were evaluated by measuring the radioactivity (Tennelec^{TM} Series 5 XLB, Canberra) of the specimens before and after decontamination followed by calculating DF. SEM images were examined to compare the surface morphology of the specimen before decontamination with that after decontamination.

RESULTS AND DISCUSSION

Dissolution of UO_2 powder

In preference to the surface decontamination of metallic wastes contaminated with uranium compounds, dissolution behaviors of UO_2 powder in nitric acid solutions as a conventional chemical reagent with variation of nitric acid concentration and temperature were observed. The results are given in Fig. 1.

The dissolution rate of UO_2 powder increases with the increase in nitric acid concentration and the solution temperature. At solution temperature of 25 ^oC, only 4~5 % of UO_2 powders dissolve for 2 hrs independent of nitric acid concentration in the range of 0.1 to 1 M. The rate, however, increases rapidly with the increase in temperature and UO_2 powders dissolve completely within 2 hrs at 80 ^oC. Even though UO_2 powders can be easily dissolved due in large to the specific surface area(6-9) in mild conditions compared with that in the dissolution of a UO_2 pellet for reprocessing of spent fuel, it is expected that effective decontamination of UO_2 contaminated surface can be performed at the solution temperature above 50 °C even in a relatively high concentration of nitric acid.

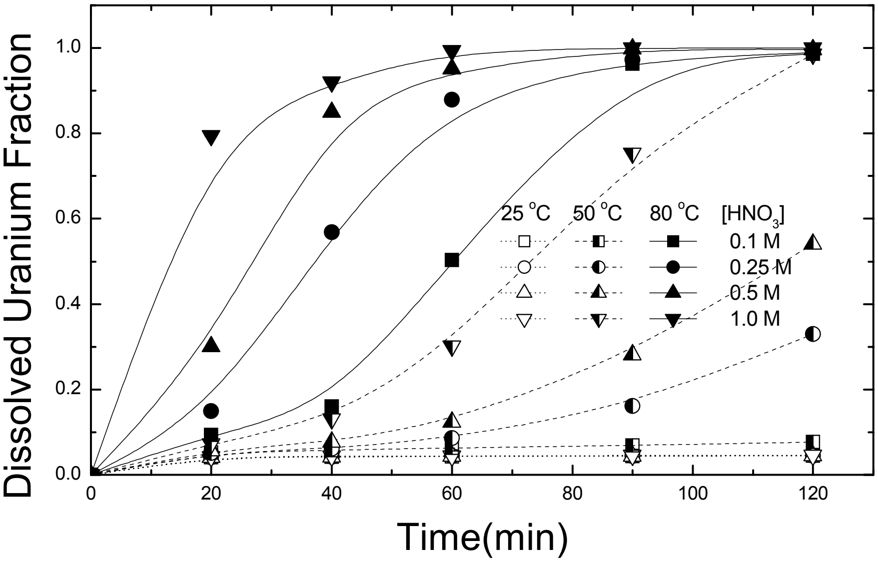

Fig. 1. Dissolution behavior of UO_2 powder in nitric acid solutions.

On the other hand, the effect of H_2O_2 as an oxidant on the dissolution of UO_2 powders was investigated for the purpose of improving the dissolution performance. Dissolution behavior of UO_2 powders in nitric acid solutions containing H_2O_2 are given in Fig. 2 compared with those in nitric acid solutions without H_2O_2.

Dissolution of UO_2 in nitric acid undergoes as follows (7, 10, 11):

$$UO_2 + 3\ HNO_3 \rightarrow 2UO_2(NO_3)_2 + HNO_2 + H_2O. \qquad \text{(Eq. 1)}$$

Eary and Cathles(12) reported that the dissolution rate of UO_2 is enhanced in the presence of H_2O_2 and the oxidative dissolution of UO_2 with H_2O_2 proceeds as follows:

$$UO_2 + H_2O_2 + 2H^+ \rightarrow UO_2^{2+} + 2\,H_2O. \qquad \text{(Eq. 2)}$$

It is shown that remarkable enhancement in the dissolution rate of UO_2 powders can be made by the addition of H_2O_2 even in a lower concentration of nitric acid and lower temperature than those in a H_2O_2 free nitric acid solution. From this result, it is inferred that decontamination of UO_2 contaminated metallic surfaces in nitric acid solutions with H_2O_2 can be carried out more successfully resulting in the shortening of decontamination time and the reduction of secondary wastes compared with that in nitric acid solutions without H_2O_2.

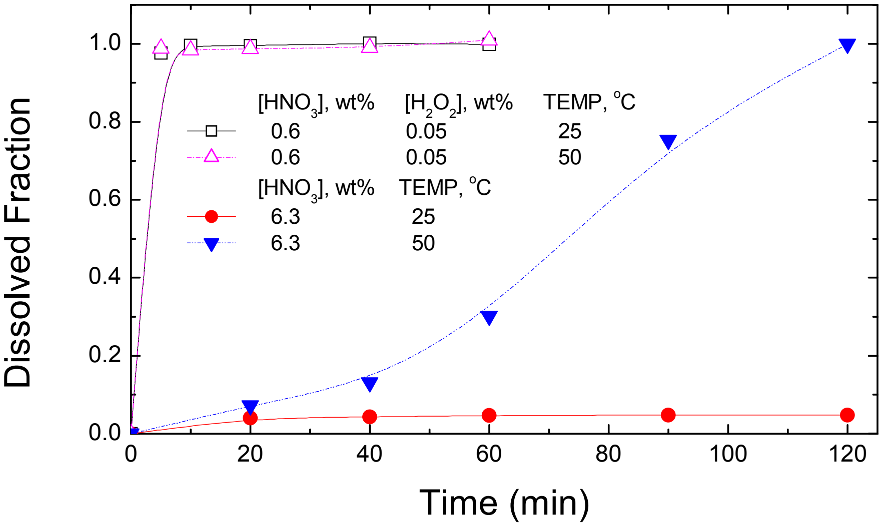

Fig. 2. Dissolution behavior of UO_2 powders in nitric acid solution containing H_2O_2 in comparison with that in nitric acid solution without H_2O_2.

In order to investigate the effect of H_2O_2 concentration on the dissolution of UO_2 tangibly, dissolution tests of UO_2 powders were carried out in 0.1 M nitric acid solution with the variation of H_2O_2 concentration. The maximum dissolved fraction of UO_2 is less than 0.5 in the solution containing 0.5 wt% H_2O_2 and less than 0.8 in 0.2 wt% H_2O_2. It is well known that the addition of a large amount of H_2O_2 causes the formation of $UO_4 \cdot nH_2O$ as a precipitate as follows(12, 13):

$$UO_2 + H_2O_2 + n\,H_2O \rightarrow UO_4 \cdot nH_2O + 2\,H^+. \qquad \text{(Eq. 3)}$$

Consequently, the addition of a small amount of H_2O_2 increases the dissolution rate of UO_2 according to Eq. 2, while a large amount of H_2O_2 leads to the precipitation of $UO_4 \cdot nH_2O$ according to Eq. 3, which may be deposited on the metal surface resulting in the recontamination.

Dissolution of AUC powder

The dissolution of AUC powders was carried out in nitric acid solutions at room temperature with the variation of nitric acid concentration and the results are given in Fig.3.

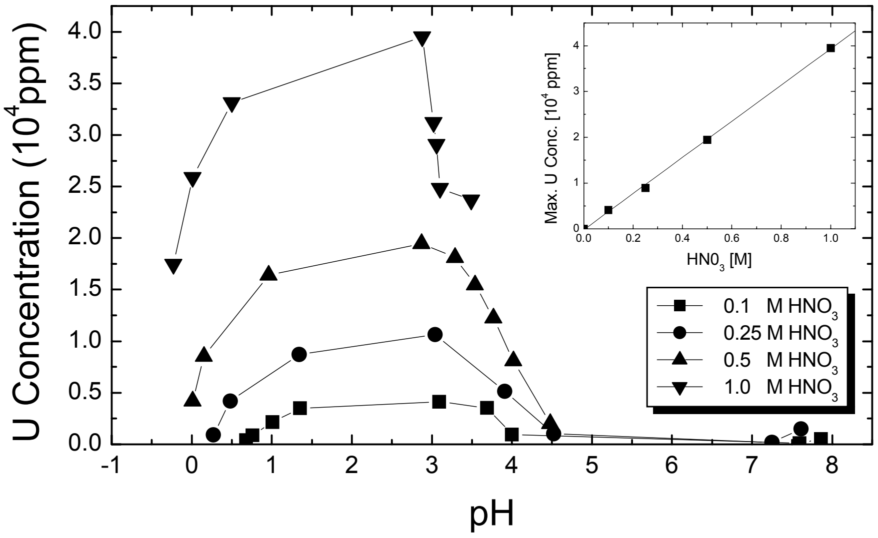

Fig. 3. The change of uranium concentration and solution pH during the dissolution of AUC powders with the variation of initial nitric acid concentration at room temperature.

AUC powders dissolve easily in nitric acid solutions. On putting AUC powders into nitric acid solutions, the bubbles considered to be CO_2 are generated vigorously and the change of the solution pH occurs at the same time. AUC powders dissolve continuously until the solution pH attains about 2.5~3. Above that solution pH, however, the uranium concentration in the solution is lowered drastically by precipitation as a form of $U_3(NH_3)_4O_9 \cdot 5H_2O$. The maximum uranium concentration in the solution was linearly proportional to the initial concentration of nitric acid. It can be drawn that nitric acid solution can be used repeatedly in the decontamination of AUC contaminated metallic wastes below the solution pH of about 2.5~3 without the precipitation of uranium amine oxide hydrate.

Decontamination of specimen contaminated with uranium compounds

The decontamination tests for the specimen contaminated with uranium compounds taken from the uranium conversion plant were performed in nitric acid solutions for 30 minutes. In the decontamination of a UO_2 contaminated specimen, the effects of nitric acid and H_2O_2 concentration on DF were investigated and the results are shown in Table 2.

Table 2. Decontamination test results for UO_2 contaminated specimens

Sample No.	Decon. condition (at 25□)		α-radioactivity [cpm]			β-radioactivity [cpm]		
	HNO_3 [M]	H_2O_2 [wt%]	before	after	DF	before	after	DF
1	0.1	0	181.00	85.27	2.1	483.00	262.33	1.8
2	0.25	0	253.60	93.80	2.7	489.40	213.53	2.3
3	1	0	306.00	174.47	1.8	566.60	290.90	1.9
4	0.1	0.1	312.60	5.07	61.7	628.60	30.37	20.7
5	0.1	0.05	352.60	1.80	195.9	675.40	22.73	29.7
6	0.1	0.02	392.80	3.33	118.0	679.20	20.03	33.9
7	0.25	0.1	232.20	1.90	122.2	709.40	34.77	20.4
8	0.25	0.05	391.40	3.03	129.2	728.40	24.27	30.0
9	0.25	0.02	362.80	1.67	217.3	738.20	27.83	26.5
10	1	0.1	255.80	1.27	201.4	752.00	12.80	58.7
11	1	0.05	334.60	1.60	209.1	891.60	21.87	40.8
12	1	0.02	440.00	1.30	338.5	926.80	10.03	92.4

The DFs in nitric acid solutions without H_2O_2 are 1.8□2.7 and 1.8□2.3 for α and β-radioactivity, respectively, while 61.7□338.5 and 20.4□92.4 for α and β-radioactivity, respectively, could be achieved in nitric acid solutions containing H_2O_2. An obvious enhancement in DF can be obtained in nitric acid solutions with H_2O_2 and it exhibits a tendency to increase the decontamination efficiency with an increase in nitric acid concentration and a decrease in H_2O_2 content.

Fig. 4 shows the SEM images of UO_2 contaminated surface before decontamination and the surface after decontamination for 30 minutes in 0.1 M HNO_3 solution containing 0.02 wt% H_2O_2 at 25 ^{o}C. Most of UO_2 particulates depicted as white colored debris are deposited along by corroded grain boundaries as shown in Fig. 4(a). After decontamination, it can be seen that there is no UO_2 particulate on the specimen surface and the surface is quite clean.

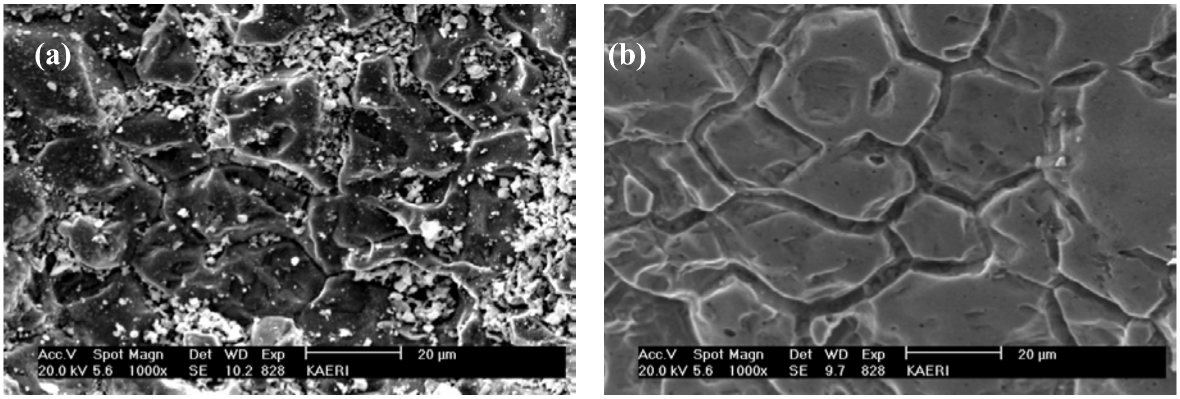

Fig. 4. SEM images of specimen surfaces: (a) UO_2 contaminated surface before decontamination, and (b) the surface after decontamination.

Consequently, it is concluded that the surface of system components contaminated with UO_2 can be decontaminated effectively in a nitric acid solution with adequate content of H_2O_2 even though the decontamination is performed in a low concentration of nitric acid at room temperature.

On the other hand, the decontamination test results for AUC contaminated specimens with the effects of nitric acid concentration and solution temperature on DF are shown in Table 3.

Table 3. Decontamination test results for AUC contaminated specimens

Sample No.	Decon. condition		α-radioactivity [cpm]			β-radioactivity [cpm]		
	HNO_3 [M]	Temp. (□)	before	after	DF	before	after	DF
1	0.1	25	10.0	0.33	30.4	28.90	5.57	5.2
2	0.25	25	10.1	0.30	33.7	32.97	4.70	7.0
3	0.5	25	11.2	0.50	22.4	32.47	4.60	7.1
4	1.0	25	11.8	0.23	51.3	40.77	4.37	9.3
5	0.1	50	12.0	0.50	23.9	37.07	6.70	5.5
6	0.25	50	12.4	0.63	19.6	31.70	2.77	11.4
7	0.5	50	12.7	0.33	38.5	34.43	3.80	9.1
8	1.0	50	13.1	0.40	32.7	40.07	3.57	11.2
9	0.1	80	13.2	0.43	30.6	45.80	3.43	13.4
10	0.25	80	13.2	0.27	48.8	43.63	3.50	12.5
11	0.5	80	21.7	0.27	80.3	53.17	3.40	15.6
12	1.0	80	23.2	0.57	40.6	61.40	3.57	17.2

The effect of nitric acid concentration on the decontamination of AUC contaminated specimen is negligible. It shows a tendency toward an increase in DF with an increase in temperature. AUC contaminated surfaces can be decontaminated easily and it is the case that even decontamination in a low concentration of nitric acid at room temperature can meet the requirements for recycle and release with authorization of AUC contaminated metallic wastes.

CONCLUSIONS

The dissolution of UO_2 and AUC powders was carried out to evaluate the applicability of a nitric acid solution to surface decontamination of metallic wastes contaminated with uranium compounds for recycle or release with authorization of a large amount of metallic waste generated from the decommissioning of the uranium conversion plant at KAERI and the decontamination performance tests were performed to verify the decontamination efficiencies using the specimens taken from the plant. Through these basic experiments and the performance tests, the following conclusions can be drawn.

1. Dissolution rate of UO_2 powders can be enhanced by the addition of H_2O_2 even in the condition of low concentration of nitric acid and low temperature compared with that in a nitric acid solution without H_2O_2. It was evaluated that a nitric acid solution of low concentration with an adequate content of H_2O_2 can be applied to the surface of the system components contaminated with UO_2.

2. AUC powders dissolve more easily and continuously until the solution pH attains about 2.5~3, where the maximum uranium concentration in the solution is linearly proportional to the initial concentration of nitric acid. It can be concluded that nitric acid solution can be applied to the decontamination of AUC contaminated metallic wastes and used repeatedly below the solution pH of about 2.5~3 without the precipitation of uranium amine oxide hydrate.

3. Decontamination performance tests using the specimens contaminated with such uranium compounds as UO_2 and AUC taken from the uranium conversion plant were quite successful with the application of decontamination conditions obtained through the basic studies on the dissolution of UO_2 and AUC powders.

REFERENCES

1. W. Z. Oh, W. K. Choi, and C. H. Jung, "Studies on Decontamination for uranium Conversion Plant decommissioning", in Proceedings of the 1st International Symposium on Supercritical Fluid Technology for Energy and Environment Applications, Kyung Hee Univ., Suwon, Korea (2002).
2. International Atomic Energy Agency, "State of the Art Technology for Decontamination and Dismantling of Nuclear Facilities", Technical Report Series No.395, IAEA, Vienna (1999).
3. International Atomic Energy Agency, "Decommissioning of Nuclear Facilities Other Than Reactors", Technical Report Series No.386, IAEA, Vienna (1998).

4. Y. D. Choi, *et al.*, "Decommissioning of Uranium Conversion Plant", in Proceedings of Korea Nuclear Society, 2001 Fall Meeting, Kyung Hee Univ., Suwon, Korea (2001).
5. Z. Marcenko, "Spectrophotometric Determination of the Elements", Wiley, New York (1976).
6. Y. Ikeda, Y. Yasuike, K. Nishimura, S. Hasegawa, and Y. Takashima, *J. Nucl. Mater.*, **224**, 266-272 (1995).
7. T. Fukasawa, Y. Ozawa, and F. Kawamura, *Nucl. Tech.*, **94**, 108 (1991).
8. E.H. Kim, D.S. Hwang, W.M. Cheong, J.H. Park, J.H. Yoo, and C.S. Choi, *Radiochimica. Acta.*, **83**, 147 (1998).
9. T. Fukasawa and Y. Ozawa, *J. Radioanal. Nucl. Chem. Lett.*, **106**, 345 (1986).
10. L.M. Ferris and A.H. Kibbey, "Sulfix-Thorex and Darex-Thorex Processes for the Dissolution of Consolidated Edison Power Reactor Fuel : Laboratory Development", ORNL-2934 (1960).
11. A. L. Uriarte and R.H. Rainey, "Dissolution of High-Density UO_2, PuO_2, and UO_2-Pu O_2 Pellets in Inorganic Acid", ORNL-3695 (1965).
12. L.E. Eary, L.M. Cathles, *Metall. Trans.*, B**14**, 325(1983).
13. R. A. Brown, *Soc. Min. Eng. AIME*, Preprint No. 80-63 (1980).