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Electrochemical Decontamination of Metallic Wastes Contaminated with Uranium Compounds in a Neutral Salt Electrolyte

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Abstract

Electrochemical decontamination process has been applied for recycle or self disposal with authorization of large amount of metallic wastes contaminated with uranium compounds such as UO_2, ammonium uranyl carbonate (AUC), ammonium di-uranate (ADU), and uranyl nitrate (UN) with tributylphosphate (TBP) and dodecane, which are generated by dismantling the contaminated system components and equipment of a retired uranium conversion plant in Korea Atomic Energy Research Institute (KAERI). Electrochemical decontamination for metallic wastes contaminated with uranium compounds was evaluated through the experiments on the electrolytic dissolution of stainless steel as the material of the system components in neutral salt electrolytes. The effects of type of neutral salt as the electrolyte, current density, and concentration of electrolyte on the dissolution of the materials were evaluated. Decontamination performance tests using the specimens taken from a uranium conversion plant were quite successful with the application electrochemical decontamination conditions obtained through the basic studies on the electrolytic dissolution of structural material of the system components.

I.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 ofenvironmental restoration of the uranium conversion plant at KAERI.

The main internal process components 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.*

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.

Table 1. Main process equipments in uranium conversion facility.

main process	detailed process	process condition*	process equipment	structural materials
ADU process	dissolution, filtration	U_3O_8,HNO_3 ~95℃	dissolver, tanks, pumps, rotary drum filters	stainless steel
	purification (solvent extraction)	UN, HNO_3, TBP, Dodecane, ~60℃	pulse columns, tanks, pumps	stainless steel
	ADU purification	UN, ADU, NH_3, ~90℃	rotary kilns	stainless steel
	ADU calcination/ reduction	ADU, UO_3, UO_2, 40kg-U/hr, ~650℃	rotary kilns	Inconel
	UF_4 conversion	UO_2, HF, UF_4, ~600℃	Rotary Kiln	Inconel
	waste treatment	NO_X, NH_3NO_3, NaOH, $Ca(OH)_2$, ~60℃	Scrubber, tanks, pumps	stainless steel
AUC process	evaporation	UN, HNO_3, ~100℃	evaporator, pumps	stainless steel
	precipitation/ filtration	UN, NH_3, CO_2, MeOH, AUC, ~80℃	precipitator, pumps, rotary filters	stainless steel
	calcination/reduction/ blending	AUC, UO_3, UO_2 ~650℃	fluidized bed reactors, pumps, mixers	stainless steel
	waste treatment	AUC, NH_3, ~90℃	precipitator, tanks, pumps	stainless steel

In the uranium conversion plant at KAERI, concentrated nitric acid was used in the dissolution of uranium compounds including U3O8, 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. With consideration of the compatibility with lagoon wastes, it was evaluated that the chemical decontamination using nitric acid and the electrochemical decontamination in neutral salt electrolyte containing nitrate anion are desirable for application to system components in contact with nitric acid solutions, which are applicable to the system components for recycle or self disposal with authorization of a large amount of metallic waste generated from the decommissioning of the plant at KAERI.

In this study, the applicability of a neutral salt electrolyte solution to the electrochemical decontamination of metallic wastes contaminated with uranium compounds was evaluated through the electrolytic dissolution of stainless steel as the main material of the system components in a neutral salt electrolyte. The electrochemical decontamination performance tests using UO_2, AUC and ADU contaminated specimens taken from the uranium conversion plant were also conducted.

II.EXPERIMENTAL

II.A. Electrolytic Dissolution of Structural Materiasl

The experiment on electrolytic dissolution of SUS-304 specimen was carried out in a conventional three-electrode electrolysis cell under a constant current using potentiostat/galvanostat (JS-P500, Ji Sang Electric Co.). The platinum foil was used as a counter electrode. All electrode potentials were measured with respect to a Ag/AgCl with saturated KCl. The effects of type of neutral salt as the electrolyte, current density, concentration of electrolyte, and electrolysis time on the electrolytic dissolution were evaluated by measuring the weight losses of the specimens and by examining the optical microscopic images of the specimen surfaces before and after electrolytic dissolution.

II.B. Decontamination Performance Tests

The specimens contaminated with UO_2, AUC and ADU were prepared to verify an electrochemical decontamination performance in a neutral salt electrolyte. Decontamination efficiencies were evaluated by measuring the gross alpha and beta radioactivity (Tennelec TM Series 5 XLB, Canberra) of the specimens before and after decontamination. SEM images were examined to compare the surface morphology of the specimen before decontamination with that after decontamination.

III.RESULTSANDDISCUSSION

III.A. Electrolytic Dissolution of Structural Materials

In order to choose the adequate electrolyte in electrochemical decontamination of metallic wastes contaminated with uranium compounds generated from a retired uranium conversion plant, the electrolytic dissolution of SUS-304 specimen was carried out in various neutral salt electrolytes under a current density of 50 mA/cm^2 for 1 hour. The weight losses of the specimens after one-hour experiment were given in Fig. 1.

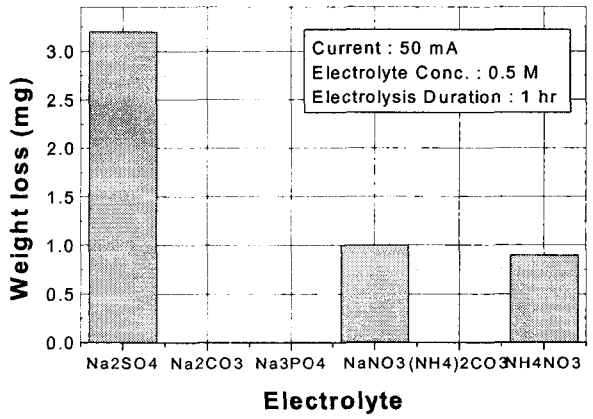


Fig. 1. Electrolytic dissolution characteristics of SUS-304 specimen in neutral salt electrolytes.

The weight loss of SUS-304 was maximized in Na_2SO_4 electrolyte, which means that the electrochemical decontamination in Na_2SO_4 electrolyte can be performed more effectively than that in any other neutral electrolytes. On the other hand, the weight loss of SUS-304 in $NaNO_3$ electrolyte corresponded to 30% of that in Na_2SO_4 electrolyte, while no electrolytic dissolution occurred in any other neutral electrolytes. In this study, a $NaNO_3$ neutral salt solution was selected as an electrolyte for the electrochemical decontamination of metallic wastes with the consideration on the surface of system components contacted with nitric and the compatibility with lagoon wastes generated during the plant operation.

In 0.5 M $NaNO_3$ neutral salt electrolyte, the effect of current density on the electrolytic dissolution of SUS-304 specimen was investigated with variation of current density under the same in cumulative coulombs by controlling electrolysis time. The results are shown in Fig. 2.

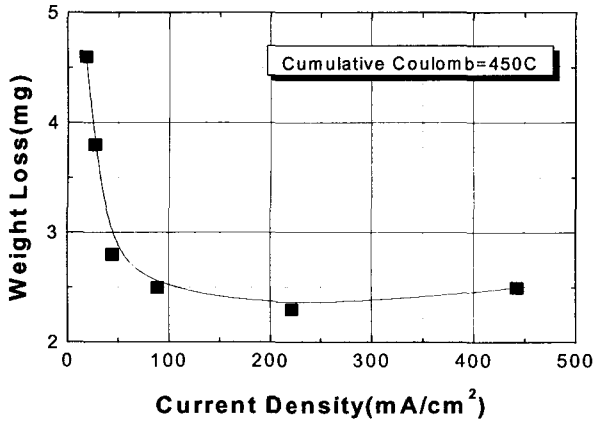


Fig. 2. Effect of current density on the electrolytic dissolution of SUS-304 in 0.5 M $NaNO_3$ solution.

The weight loss of SUS-304 decreased with increase in the current density lower than 100 mA/cm^2. Above the current density of 100 mA/cm^2, the weight losses were maintained constantly irrespective of increase in the current density. The current efficiency on the electrochemical decontamination increases with decrease in the current density, but required decontamination time increases as well. With the considerations on the decontamination time and the current efficiency, it is evaluated that the electrochemical decontamination is more effective in the current density more than 50 mA/cm^2.

In order to investigate the effect of $NaNO_3$ concentration, the electrolytic dissolution of SUS-304 specimen was carried out under the application of 100 mA for 1 hour. The results are given in Fig. 3.

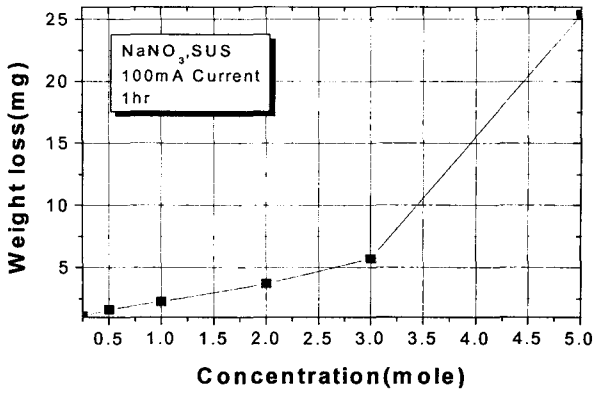
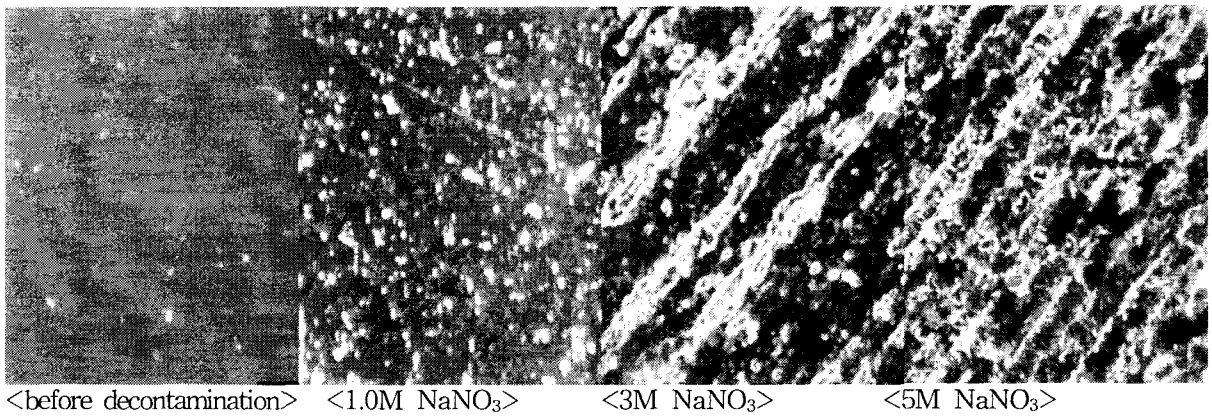


Fig. 3. Effect of $NaNO_3$ concentration on the electrolytic dissolution of SUS-304.

The weight loss of SUS-304 increased slowly with increase in $NaNO_3$ concentration lower than 3 M, while the weight loss increases rapidly above 3 M. With the consideration on the weight loss itself, it is expected that adopting concentrated $NaNO_3$ electrolyte will shorten the decontamination time. The surface irregularity after electrolytic dissolution, which is attributed to pitting, however, increases with increasing $NaNO_3$ concentration as shown in Fig. 4. The localized dissolution does not give a good decontamination effect although the weight loss is enhanced in comparison with that by uniform dissolution and moreover causes recontamination during the course of decontamination. Therefore, it is judged that $NaNO_3$ concentration below 1 M is suitable for electrochemical decontamination of contaminated surface of SUS-304.

III.B. Electrochemical Decontamination of Uranium Contaminated Metallic Wastes

The electrochemical decontamination tests for the specimen contaminated with uranium compounds taken from the uranium conversion plant were performed in $NaNO_3$ electrolyte with variation of decontamination time under the current density of 100 mA/cm^2. The removal behavior of alpha and beta radioactivity with variation of decontamination time is given in Fig. 5 and Fig. 6.



<before decontamination> <1.0M $NaNO_3$> <3M $NaNO_3$> <5M $NaNO_3$>

Fig. 4. Optical microscopic images of SUS-304 specimen surface before and after electrolytic dissolution with the variation $NaNO_3$ concentration.

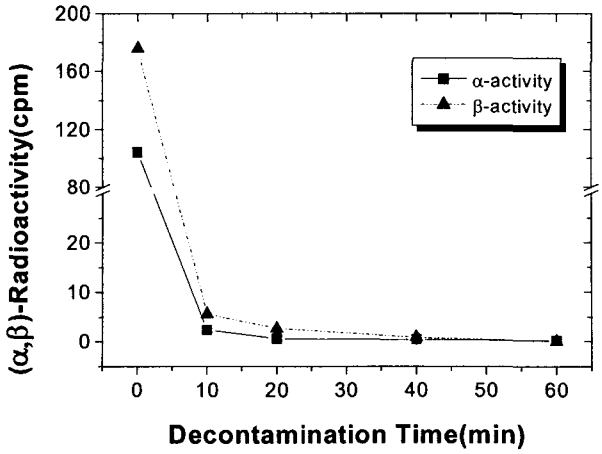


Fig. 5. Electrochemical decontamination behavior of UO_2 contaminated metallic waste.

The alpha and beta radioactivity decreases rapidly with increase in the decontamination time, and it is verified that the electrochemical decontamination of the metallic wastes contaminated uranium compounds was quite successful in a $NaNO_3$ neutral salt electrolyte by reducing alpha and beta radioactivities below the criteria of self-disposal within 10 minutes regardless of the type of contaminants and the degree of contamination.

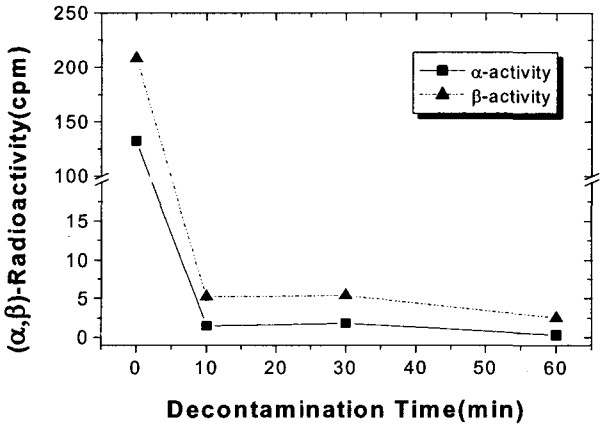


Fig. 6. Electrochemical decontamination behavior of AUC contaminated metallic waste.

IV.CONCLUSIONS

Electrolytic dissolution effectivenessfor SUS-304 was the best with a Na_2SO_4 solution, buta $NaNO_3$ neutral salt solution, in which about 30% for SUS-304 in electrolytic dissolution performance was shown in comparison with that in a Na_2SO_4 solution, was selected as an electrolyte for the electrochemical decontamination of metallic wastes with the consideration on the surface of system components contacted with nitric acid and the compatibility with lagoon wastes generated during the facility operation.

The electrochemical decontamination of the metallic wastes contaminated uranium compounds was quite successful in a $NaNO_3$ neutral salt electrolyte by reducing alpha and

beta radioactivities below the criteria of self-disposal within 10 minutes regardless of the type of contaminants and the degree of contamination.

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