〈Technical Note〉

A PRACTICAL METHOD FOR THE DISPOSAL OF RADIOACTIVE ORGANIC WASTE

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Radioactive organic wastes containing acetone, alcohol, and particularly tributyl phosphate (TBP)/dodecane contaminated with uranium are extracted from the PUREX process and the decontamination of related equipment.

An evaporation method that utilizes existing DU oxidation apparatuses and ventilation systems and a typical muffle furnace installed with an aspirating system are adopted. A separation method using phosphoric acid especially for the TBP/dodecane waste is also studied and evaluated.

The results show that a simple evaporation process is utilizable for wastes containing acetone or alcohol with a lower boiling point. A modified muffle furnace is more appropriate to dispose directly of organic wastes having a higher boiling point, such as TBP/dodecane, without generating a condensed waste solution.

It is recommended that, when the uranium concentration of TBP/dodecane waste is much higher than stipulated levels, separation technology should be applied to remove uranium from the mixture. Each type of solvent after separation can then be considered disposable below the regulatory limit in the modified furnace discussed in this study.

KEYWORDS : Radioactive Organic, Wastes, Uranium, Treatment, Evaporation, Separation, TBP, Dodecane

1. INTRODUCTION

Various types of organic radioactive liquid waste are generated from nuclear fuel cycles and related research laboratories. A strategy for the effective treatment of this waste is needed, as organic radioactive waste requires attention in terms of both its activities and chemical contents, both of which have detrimental effects on public health and on the environment. Several techniques for conditioning organic radioactive waste have been developed.

Incineration[1-2] and wet oxidation[3-4] are attractive techniques, but the combustion of TBP-containing waste solution produces corrosive products, causes corrosion in the machinery utilized, and leads to off-gas purification problems. Moreover, the combustion generates relatively large volumes of radioactive gaseous, liquid and solid wastes. Wet oxidation also generates various undesirable secondary waste byproducts.

In this study, a simple evaporation technique is adopted for the treatment of major organic waste types, such as acetone, alcohol, TBP/dodecane, and cutting oil, in order to utilize an established oxidation apparatus[5] and ventilation system. The utilization of a furnace as a heating device is also studied for TBP/dodecane waste, and the effects of the temperature and the amount of solvents on the evaporation time are described. Furthermore, a separation technique[6-7] is also applied, especially for TBP/dodecane waste, and all results are compared.

2. EXPERIMENTAL METHODS

2.1 Chemicals

- Chemicals: Extra pure grades of organic solvents, such as acetone, alcohol, TBP and dodecane were procured from Showa Chemical Co. Phosphoric acid for the separation of the TBP mixture was also used.

2.2 Experimental Apparatus

- Apparatus: An existing oxidation apparatus for depleted uranium (DU) was utilized for the evaporation of organic solvents. This apparatus utilizes heating elements on the bottom and the wall and is connected to a ventilation system. A typical muffle furnace of a small laboratory scale was utilized as a heating device. It was modified slightly for the direct removal of the generated vapors during evaporation.

2.3 Experimental Procedures

- Evaporation was carried out by utilizing the oxidation apparatus, the muffle furnace, and the solvent separation apparatus depending on the amount of each solvent, the type of solvent, and the evaporation temperature.

The results were compared in order to apply them in the field practically.

3. RESULTS AND DISCUSSION

3.1 Characteristics of the Radioactive Organic Waste

The compositions of radioactive wastes containing organic solvents are presented in Table 1. The acetone and alcohol-containing wastes were generated mainly from decontamination processes related to nuclear fuel cycling, and the TBP/dodecane waste is produced from an extraction process for uranium. Most of the waste types containing uranium are composed of more than 90% of those solvents. The uranium concentration in the waste containing acetone was very low. Compared to the acetone waste from the uranium fabrication process, and TBP and dodecane wastes show fairly high uranium concentrations and activity levels.

3.2 Evaluation of the Evaporation Method depending on the Amount of each Solvent

The evaporation temperature was adapted by considering the boiling point of each objective solvent. Results from the evaporation of acetone, alcohol, and cutting oil as organic wastes were investigated by utilizing a DU oxidation apparatus and the aforementioned ventilation system.

For solvents such as acetone and alcohol that have a low boiling point, only a slight difference was found in terms of the evaporation time as the temperatures and the amount of solvents increased. The entire evaporation process was completed within 2 to 3 hours for 8 L of each solvent (Fig. 1).

Table 1. Characteristics and the Uranium Concentrations of the Investigated Radioactive Organic Wastes

Solvents	Content %	Nuclides	U Concn. μg/ml	Gross-α Bq/ml
Acetone (Refinement)	~99	U/Co/Fe	4.2	0.53
Acetone (Fabrication)	~99	U/I	1,100	10.0
TBP	30	U/Th/	3,300	9.67
Dodecane	70	Pu/Am		

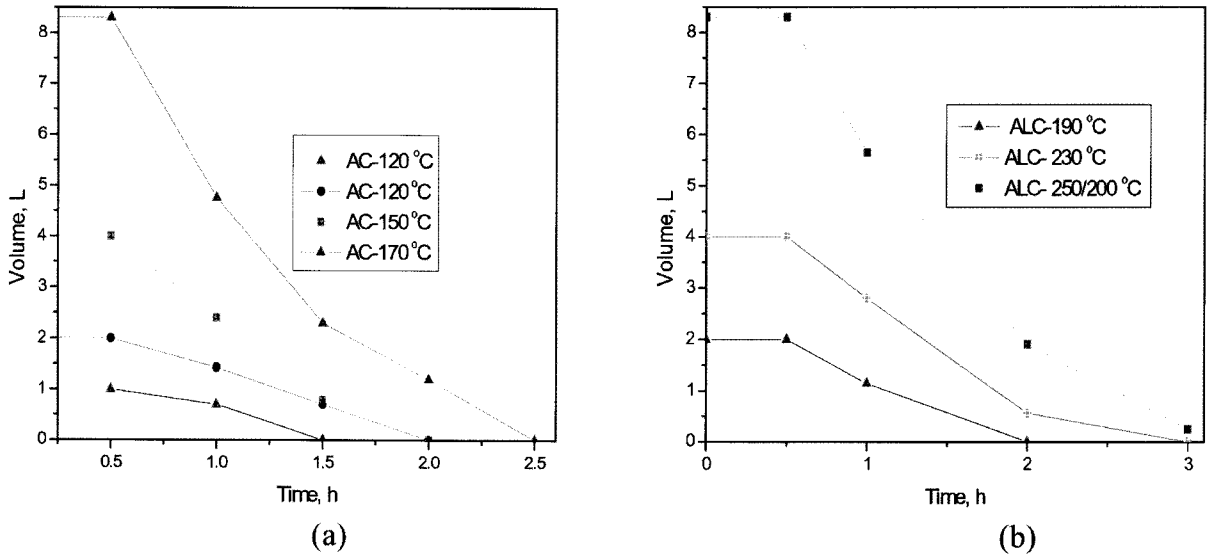

Fig. 1. Evaporation Time for Acetone (a) and Alcohol (b)With Various Amounts of Solvents and at Different Temperatures

In contrast, the evaporation rates of the mixture of TBP and dodecane were very slow, and the entire evaporation process took more than 14 hours for 8 L of the mixture (Fig. 2) due to the high boiling points of 289 °C for TBP and 216 °C for dodecane. Furthermore, the heating temperature was held below 200 °C to exclude any possible spontaneous ignition of the vapor resulting from contact with fresh air at temperatures above 200 °C.

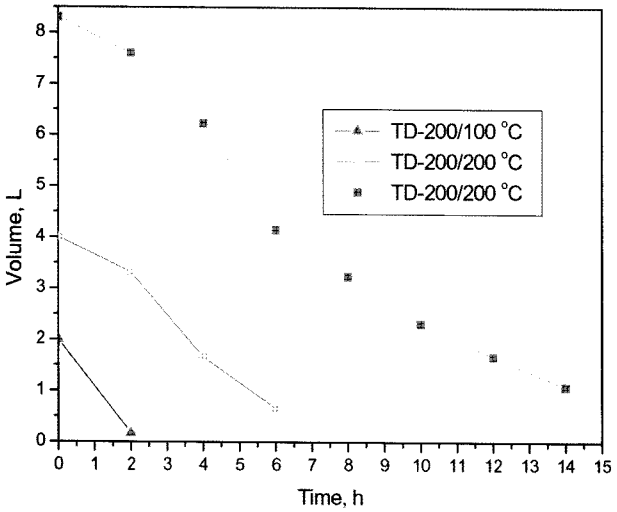

Fig. 2. Evaporation Time for TBP/Dodecane with Different Amounts and at Different Temperatures

It is considered from these results that wastes containing TBP should be treated by another effective heating system.

3.3 Application of a Furnace for the Evaporation of TBP/Dodecane

A general muffle furnace was adopted as a heating device for the evaporation of TBP/dodecane with a high boiling point in order to provide effective heating within a short period of time and to control the evaporation for a relatively small amount. Particularly for the direct removal of the generated vapors, an aspirating system using water was connected to the furnace. With these modifications, the solvent could be treated without any condensation of the vapors during evaporation or unexpected ignition caused by contact with air.

3.3.1 Modification of the Furnace

Two discharging tubes were inserted into the furnace and were connected to each aspirating system to remove the generated vapors directly during evaporation. A small sus-frame and five trays were placed inside the furnace, as shown in Fig. 3. The dimensions of the inside of the furnace were W120xH90xD250 mm, and the total capacity per batch was estimated as 0.5 L per hour with five trays. Each tray has dimensions of W90xH10x200 mm. The capacity could be extended using a larger commercial furnace measuring W160xH150xD300.

The amount of discharged water was calculated to be 1,500 L per hour from two lines of the aspirating tap. This can be extended to 2,500 L per hour by installing extra lines and pressure pumps.

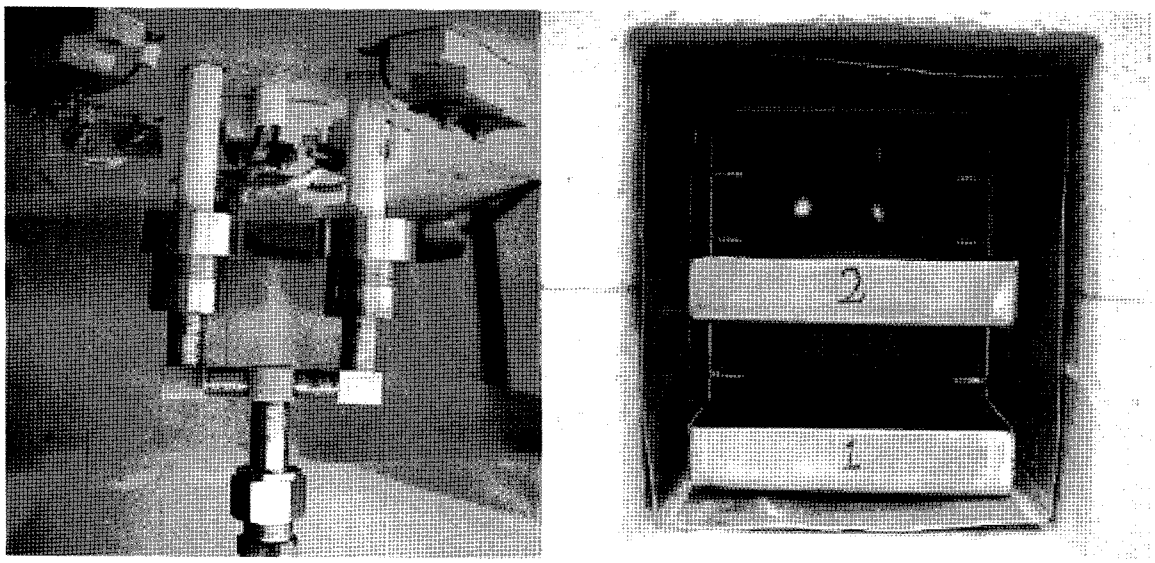

Fig. 3. Establishment of the Discharging Lines Into the Furnace and the Sus-Frame with Trays

3.3.2 Evaporation Time for TBP/Dodecane with Different Temperatures and Amounts.

The evaporation times for TBP/dodecane depending on the amount of the solvent were investigated at different temperatures and the results are summarized in Table 2.

100 ml of the solvent with one tray evaporated within one hour at 130 °C and 140 °C, while the evaporation times were reduced to 30 minutes by increasing the heating temperatures to levels above 150 °C. When increasing the amount to 200 ml and 300 ml of solvent, the solvent was vaporized within one hour at temperatures below 200 °C and 30 minutes at temperatures above 300 °C. The full capacity of the furnace, 500 ml, was also completely evaporated within one hour at 200 °C. It is understood from these results that TBP/dodecane waste can be treated effectively in large amounts by utilizing the modified furnace; moreover, the generated vapors can be cleared out directly by the aspirating system.

It should be noted that the evaporation condition should be optimized between the amount of the solvent and the heating temperature because the vapor is highly flammable when in contact with a fresh air, especially when the vapor becomes dense when a large amount of solvent is used and when it is heated above 250 °C. The heating temperature must be below 250 °C by as much as possible.

The maximum evaporation capacity was evaluated as 3 L for one batch and at least 10 L per a day using a low-cost typical muffle furnace measuring W160xH250xD300 mm.

3.3.3 Estimation of the Level of Radioactivity in the Discharging Water

The concentration of the uranium isotopes should satisfy a minimum concentration of 10 Bq/g for U isotopes in the effluents, as is regulated by the national authority in Korea. The uranium concentration in the mixed water with organic vapors was calculated by considering the dilution effect from the uranium concentration in the waste, 9.6 Bq/ml, the amount of wastes to be treated, and the amount of water to be discharged during evaporation.

The concentration of uranium was estimated as 3.4 Bq/g in the discharged water, as shown in Table 3, which corresponds to one-third of the minimum requirement stipulated in the regulations. It is assumed that, with an additional discharge line and pressure pump, the treatment capacity can be extended to 2 L per hour under the regulatory limit.

3.4 Application of Separation Technology for the TBP/dodecane Mixture

3.4.1 Separation Process

The separation process of TBP and dodecane from their mixtures is based on the fact that TBP forms adducts with phosphoric acid, which have a high density and are insoluble in hydrocarbons.[6] This involves TBP dealkylation, i.e., transformation of TBP into nonvolatile

Table 2. Evaporation Time for TBP/Dodecane Using a Furnace with Increased Temperatures

Organics (ml)		Evaporation Time (min)					
		130 °C	140 °C	150 °C	200 °C	300 °C	400 °C
TBP + Dode -cane	100	60	60	35	40	30	25
	200	60	60	60	60	30	30
	300	120	60	-	60	30	30
	400	-	-	-	60	-	-
	500	-	-	-	60	-	-

Table 3. Estimation of the U Concentration in the Discharged Water

Exempn. Level Bq/L	Waste Concn. Bq/L	Treatmt. Capacity L/H	Water Discharge L/H	Dilution Ratio*	Final Concn.Bq/L
10	10,000	0.5 (2.0)**	1,500 (2,500)	3,000 (1,250)	3.4 (8.0)

* Dilution Ratio: Water Discharge / Treatment Capacity

** ( ): Extended capacity with an extra line and pressure pump

phosphoric acids, and volatile hydrocarbon-type organic compounds, which contain all of the radioactivity types.

The first step consists of saturating the solvent with concentrated phosphoric acid. Phosphoric acid was added to TBP/dodecane at a molar ratio of TBP and H_3PO_4 of 1:2. The mixture was agitated for one hour and allowed to stand for an additional hour. After settling, the phases were separated.

The mixture was separated into two or three phases. Hydrocarbons were contained in the upper phase, and the TBP was located in the middle or lower phase with phosphoric acid. The hydrocarbon phase was subject once more to the aforementioned treatment to be free of TBP and radioactive substances, and the lower phase was washed with H_3PO_4 solution, after which it was separated into TBP and diluted phosphoric acid..

3.4.2 Separation of the TBP/Dodecane Mixture and Estimation of the Radioactivity Levels

Both the TBP and dodecane were mixed in a typical volume ratio of 30% and 70%, and 15.1 ml of phosphoric acid was added to 100ml of the mixture. Following this, the standard uranium solution was added to verify the residual concentration of the uranium after separation in each phase. The TBP phase was washed again with the H_3PO_4 solution using the same amount used in the organic step to check for a further separation effect. The results of the separation from the mixture as well as an analysis of the uranium concentration are summarized in Table 4.

From the first separation, more than 95% of the dodecane was recovered, and only minute amounts of uranium were present in the hydrocarbon phase. The TBP and H_3PO_4 phases showed a ratio of 123% and 67.5% in volume, respectively, which showed that parts of the dodecane and H_3PO_4 remained in the TBP.

10 ml of the TBP phase was washed again with the same amount of water or H_3PO_4 solution. The effect of a further separation was not significant, but the uranium was removed from the TBP phase and the H_3PO_4 solution had a better effect on uranium removal compared to water.

The separated TBP and separated dodecane after the separation and removal of uranium can be disposed of directly using the furnace modified with an aspirating system. The inorganic residue including uranium and H_3PO_4 can also be disposed of by the modified furnace under the exemption level without condensation occurring. It can also be treated by an established evaporator.

4. CONCLUSION

Am evaporation method was adopted that treated radioactive organic waste by utilizing an existing DU oxidation apparatus and an established ventilation system to remove vapors and radioactive nuclides simultaneously. A typical muffle furnace and an aspirating system were applied as a heating device to remove the evaporated vapors directly before condensation. Furthermore, a separation technique was adopted particularly for a TBP/dodecane mixture.

The results show that the established evaporating apparatus and the ventilation system are applicable for solvents with lower boiling points, such as acetone and alcohol. A modified muffle furnace with an aspirating system is more appropriate to dispose of wastes with a higher boiling point, such as a TBP/dodecane mixture, directly within a relatively short time and without the generation of condensed waste.

If the uranium concentration of TBP/dodecane waste greatly exceeds given exemption levels, it is recommended that the proposed separation method be applied to remove uranium from the mixture. Each solvent after separation can then be disposed of by utilizing the modified furnace.

Table 4. Separation Characteristics of Uranium From the TBP/Dodecane Mixture

Chemicals	Volume	Separation			Washing			
					Water		H_3PO_4	
	ml	ml	%	U μg/ml	ml	U μg/ml	ml	U μg/m
Dodecane	70	66.7	95.3	<2	-	-		
TBP	30	37	123.2	18	9.1	<2	10.6	<2
H_3PO_4	15.1	10.2	67.5	174	11	12	9.2	12
Total	115.1	113.9	99.0	-	20.1	-	19.8	-

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