DEVELOPMENT OF SLUDGE WASTE TREATMENT PROCESS

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ABSTRACT

Korea Atomic Energy Research Institute (KAERI) has launched a decommissioning program of the uranium conversion plant. The treatment of the sludge waste, which was generated during the operation of the plant and stored in the lagoon, was investigated. The treatment process consists of a desalination, liquid-solid separation, solid waste stabilization, and a nitrate solution waste denitration. Desalination was carried out with the adding ratio of water and the denitration of the nitrate solution waste was decomposed thermally with two steps according to the characteristics of the nitrate solution waste. The solid waste stabilization property was analyzed by TG/DTA and XRD. Nitrate salts involved in the sludge were separated over 98 % at the water adding ratio of 1.5. The solid waste was converted into calcium oxide, $3CaO\text{-}UO_3$, $3Na_2O\text{-}7UO_3$ by a calcination at 900 and these are stable compounds for storage. The nitrate solution was denitrated in two steps; ammonium nitrate was decomposed at around 250 and the sodium and calcium nitrate at over 500 . Alumina should be added for stabilizing sodium oxide, which reacts easily with water. The solid waste after decomposing at 900 consisted of calcium oxide and $Na_2O\text{-}Al_2O_3$ and these are stable compounds for storage. As a result, the volume of the sludge waste could be decreased by over 75 % with the sludge treatment process.

INTRODUCTION

The Korea Atomic Energy Research Institute (KAERI) decided to construct a pilot plant of the uranium conversion process for development of the technologies and the localization of nuclear fuels for PWR and HWR in 1976. The final product of the plant was UO_2 powder of a ceramic grade for a HWR and its capacity was 100 ton-U/year. The construction was finished in 1982. After that, a part of the AUC process was added and the process was improved for an automatic operation. 320 tones of UO_2 powder were produced and supplied to the fabrication plant of KAERI for the fuels of the Wolsong-1 CANDU reactor. In early 1992, it was determined that the plant operation would be stopped due to a much higher production cost than that of the international market. The conversion plant has been shutdown and minimally maintained for the prevention of contamination by deterioration of the equipment and the lagoon. In 2000, the decommissioning of the plant was finally decided upon and a decommissioning program was launched to complete the following tasks by 2007: planning and assessment of the environmental impact; decontamination of the pipe, tanks, vessels and equipment for canning or reuse; decontamination of the building for unrestricted reuse, and the treatment of the sludge and the demolition of the lagoon.

The treatment of the sludge waste, which was generated during the operation of the plant and stored in the lagoon, will be one of the most important tasks in the decommissioning program of the plant. The uranium content of the deposit at the bottom of the lagoon is very high and the sludge cannot be treated as a simple industrial waste. The sludge should be canned in drums of

200 liters and managed as low-level radioactive wastes. Because the sludge contains a lot of nitrate compounds, which are easily dissolved in water and are deliquescent, it is not permissible for the sludge to be directly canned after a simple drying. Therefore, the sludge of the lagoon should be economically and safely treated for a reduction of the volume and the removal of the nitrate salts. A proper process should be developed by considering the characteristics of the sludge.

In this study, a treatment process of the sludge was developed as follows based on the results of the sludge characteristics [1]. The treatment process consists of a desalination, liquid-solid separation, solid waste stabilization, and a denitration of the nitrate solution waste. The purpose of the desalination process is to dissolve the nitrate salts with water. After the dissolution of nitrates, the slurry is transferred to the separation system. The nitrate solution is denitrated by a thermal decomposition. And the solid waste is calcined for the stabilization of the solid waste involving uranium.

Characteristics of the Sludge

The lagoon is a series of artificial ponds where all the liquid wastes have gathered. It is located adjacent to the conversion plant building and consists of two ponds. The volume of the liquid waste has decreased by a natural evaporation of the water. So, the concentration of the dissolved salt has increased and some salt has precipitated and deposited on the bottom of the lagoon to form sludge. The sludge consists of three different layers. The upper layer is a saturated solution, but at a low temperature in winter, the solution layer changes to a crystalline phase (part of middle layer) and most of this solution layer disappears. The middle layer is white crystalline and is a very similar feature in both lagoons. The bottom layer of the lagoon is a deposit of particulate materials and very different due to the different compositions. The height and several physical properties of the layers are shown in Table I.

Table I. Height and Physical Properties of each Layer of the Ponds

Items	Lagoon-1			Lagoon-2		
	Upper	Middle	Bottom	Upper	Middle	Bottom
Phase	liquid	crystalline	deposit	liquid	crystalline	deposit
Color	yellow	white	brown	yellow	white	white
Density	1.42	1.96	1.81	1.43	1.80	2.12
Height, cm	7	7	23	2	15	12

The chemical composition of each layer is shown in Table II. The major compounds are ammonium nitrate and sodium nitrate, generated from the operation of the conversion plant and calcium nitrate and calcium carbonate which are the reaction products of calcium hydroxide with nitric acid and carbon dioxide in air. The minor compounds are iron, magnesium, aluminum, silicon and phosphorus and are contained in the bottom deposit of the lagoon. Their composition is shown in Table III. They came from filter aids, uranium concentrates, and a decomposed organic solvent.

Table II. Chemical Composition of each Layer in the Lagoon

Sample		NH_4NO_3,	$NaNO_3$	$Ca(NO_3)_2$	$CaCO_3$
Lagoon 1 (wt %)	upper	61.86	28.43	2.07	-
	middle	68.81	25.30	0.30	-
	bottom	53.04	17.98	9.53	-
Lagoon 2 (wt %)	upper	79.84	13.82	1.77	-
	middle	90.31	0.31	0.93	-
	bottom	20.17	3.14	18.94	38.11

Table III. Chemical Composition of other Metals in the Lagoon Sludge

Element	P	Fe	Al	Mg	Si
Lagoon 1 bottom (wt %)	0.27	0.15	0.35	0.03	1.25
Lagoon 2 bottom (wt %)	0.007	0.02	-	0.08	-

Table IV. Radiological Properties of the Sludge

Element	Lagoon 1			Lagoon 2		
	upper	middle	bottom	upper	middle	bottom
U, μg/g	10	586	20300	<0.5	8	305
Th, μg/g	*ND	**Tr	42	ND	ND	18
Ra-226, Bq/g	ND	ND	163	ND	ND	8

*ND: not detected (detection limit; Th: 0.1 μg/g , Ra-226: 0.1 Bq/g)
**Tr: trace

Uranium, thorium and radium-226 contents in the samples of each layer were analyzed and the results are shown in Table IV. As shown in Table 4, except for a trace of thorium in the middle crystalline solid of lagoon 1, thorium and radium-226 were not detected in the upper solution and the middle solids and their uranium contents are also much lower than in the bottom layer sludge. This means that all the heavy radioactive elements were precipitated and deposited at the bottom, and that they were not dissolved in the concentrated aqueous nitrate solution.

Treatment Process

Most chemical salts in the sludge are nitrates as shown in Table 2. Therefore, in order to reduce the volume and to meet the conditions for the storage and final disposal, these nitrates should be removed from the sludge. All nitrates are easily decomposed to oxides by a simple heating or by a heating with reducing agents such as aluminum [2] or carbon powder [3] and they are easily dissolved in water while uranium remains in the solid.

Two concepts of the treatment processes can be proposed: (1) a thermal decomposition at a higher temperature than 800 °C with reducing agents and (2) a liquid-solid separation following the dissolution of the nitrates with water. However, a thermal decomposition has the difficulties of an ammonium nitrate decomposition. Ammonium nitrate is explosive and is decomposed by evolving a great deal of gas. In the range of decomposition temperatures, the sludge was greatly expanded because of many large bubbles. So, a reactor with a large volume was required and this volume was dependent on the decomposition rate. Therefore, we selected tentatively the liquid-solid separation process following the dissolution of the nitrates with water for the sludge treatment. Water is added to the lagoon for the dissolution of the nitrates and the slurry is transferred to a liquid-solid separation system. The solid waste is stabilized for a final disposal or further solidification. The nitrate solution waste is denitrated thermally. Fig. 1 shows this concept. The purpose of each unit process is as follows;

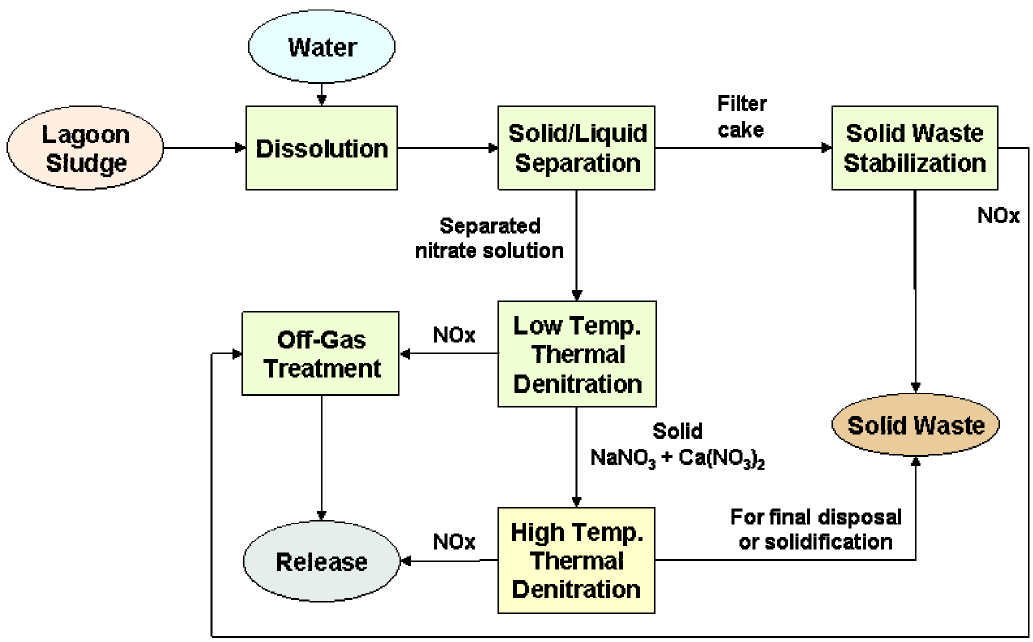

Fig. 1. A flow diagram for the lagoon sludge treatment

Desalination: The dissolution of the nitrate salt and making slurry in order to transfer it by a pump. This operation is carried out in the lagoon by a slurry pump, that is, water is added first and circulated to the other side of the lagoon. After the dissolution of the nitrates, the slurry is transferred to the separation system.

Liquid-solid separation: A continuous drum type vacuum filter is used for this separation. For constant feeding of the slurry, a mixing tank is installed and another slurry pump is used to feed the slurry from this tank.

Solid waste stabilization: For stabilizing the solid waste, a simple muffle furnace is used. The solid cake from the filter was gathered in steel pans and put into the furnace and stabilized by heating. The off-gas is treated by a gas treatment system.

Thermal Denitration: The nitrate solution waste is denitrated thermally. This is denitrated in two steps; the first occurs at around 250 and the second at over 500 . The low temperature denitration is due to the ammonium nitrate and the second is due to the sodium and calcium nitrate.

Experimental

Samples were taken from each layer in the lagoon 1 and 2 and they were used by mixing them at their constitution ratio. Dissolution of the nitrate was performed by varying the amount of water at a regular interval from 1.0 to 3.0 into the sludge of 100 g. The undissolved residue was separated by filter paper (Whatman 42) of 2.5 μm after dissolving it for 30 minutes. The residue, which is a solid waste containing uranium, was dried for 3 hours at 130 °C for investigating the stabilization properties of the solid waste. The nitrate solution was denitrated in two steps; the first was performed at 250 for 5 hours and the second at 900 for 5 hours in the muffle furnace. In the second, alumina was added for stabilizing the sodium oxide, which reacts easily with water. The solid waste was calcined at 900 for 5 hours.

Calcium and uranium contained in the nitrate solution and the solid waste were analyzed by ICP (inductively coupled plasma spectrometer, model ISA Jobin-Yvon JY 50P), sodium by AA (atomic absorption spectrophotometer, model GBC 906A), nitrate by IC (ion chromatography, model Dionex DX-100), and ammonium by UV (ultra violet visible spectrophotometer, model Varian 3E). The stabilization properties of the solid waste were analyzed using TG/DTA (Thermogravimetry Differential Thermal Analysis, model Setaram TG-DTA 92) and XRD (X-Ray Diffractor, model Siemens D5000).

Results and Discussion

Figure 2 shows the dissolution fraction of each compound with the dissolution time. The dissolution fraction of the nitrate salts generally increased with the adding ratio of the water. Nitrate salts could be removed over 98 wt% from the condition of the adding ratio of 1.5. It is favorable that the nitrate salts in the sludge are dissolved with a small amount of water. So, it is thought that the adding ratio of 1.5 is suitable for a practical process. The chemical composition of the filtrate and the residual solid is shown in Table 5. These are treated in the next processes, which are the solid waste stabilization and the thermal denitration of the nitrate solution waste.

Figure 3 shows the TG-DTA of the solid waste and XRD pattern of the stabilized solid waste at 900 . As shown in the TG-DTA, the solid waste was decomposed in two steps; the first occurred at around 250 and the second in the range of 500 to 750 .

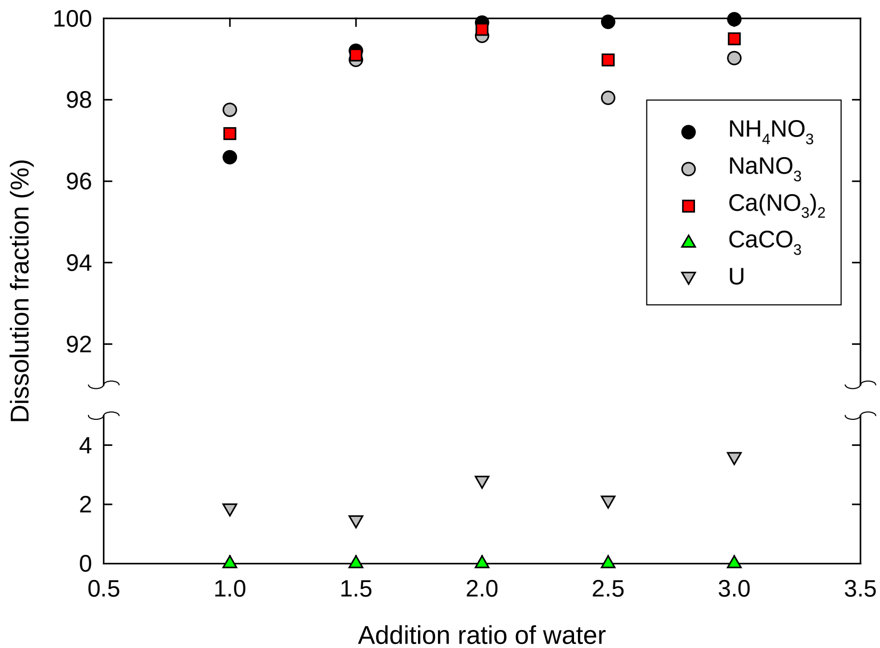

Fig. 2. Dissolution fraction with the addition ratio of the water

Table V. Chemical composition of the filtrate and residual solid

	NH_4NO_3	$NaNO_3$	$Ca(NO_3)_2$	$CaCO_3$	U	Others	H_2O
Filtrate (wt%)	24.7	5.2	1.4	-	0.005	-	68.7
Residual Solid (wt%)	14.3	0.5	0.5	48.1	3.3	3.8	29.5

The low temperature decomposition is due to ammonium nitrate, which is decomposed by the $NH_4NO_3 = N_2O + 2H_2O$ equation [4]. Ammonium nitrate is completely decomposed to gas and a large amount of gas is evolved. The second decomposition is due to the sodium and calcium nitrate and calcium carbonate. These nitrates are decomposed at a temperature higher than 500 . Calcium nitrate is decomposed according to the $Ca(NO_3)_2 = CaO + 2NO_2 + 1/2O_2$ equation at about 500 , but it is known that the decomposition mechanism is very complicated [5]. Sodium nitrate is decomposed as the following equation at around 600 [6].

$$NaNO_3 = NaNO_2 + 1/2O_2$$

$$2NaNO_2 = Na_2O + NO + NO_2$$

In the decomposition, a brown gas of NO_2 was observed unlike the low temperature decomposition. Calcium carbonate starts a decomposition reaction at 750 and is decomposed according to $CaCO_3 = CaO + CO_2$ [7]. It was confirmed that uranium was stabilized with the forms of 3CaO-UO_3 and $3Na_2O$-$7UO_3$ from the XRD pattern of the stabilized solid waste of figure 3. Therefore, it is predicted that the solid waste can be stored with a stabilized form.

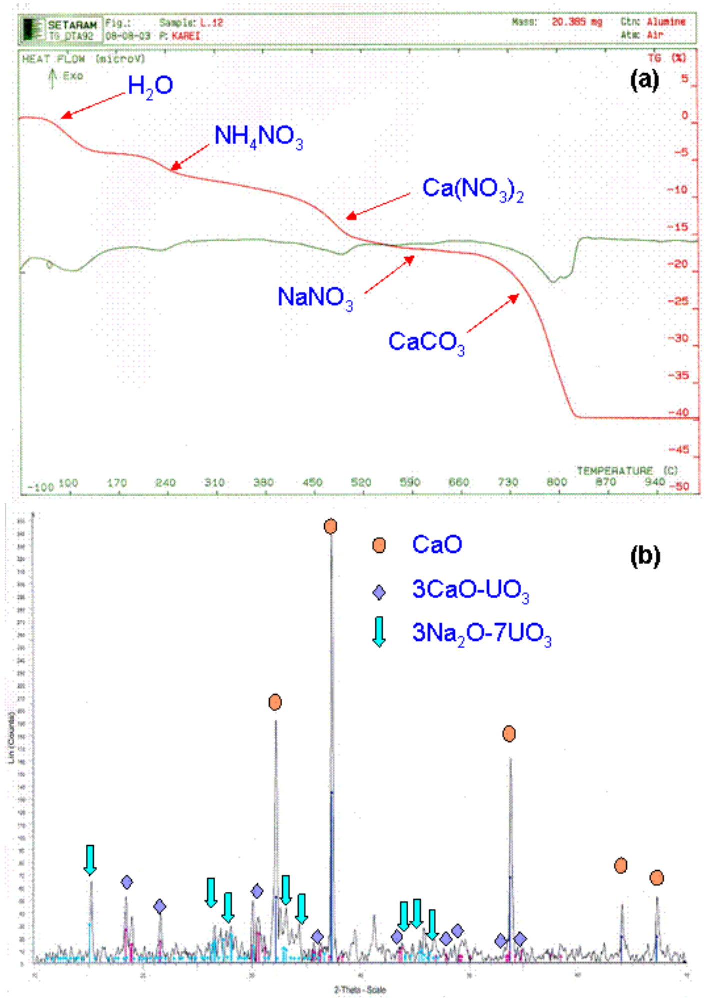

Fig. 3. TG-DTA (a) of the solid waste and XRD pattern (b) of the stabilized solid waste at 900

The nitrate solution was denitrated with two steps as shown above with the thermal decomposition characteristics of nitrate salts. Ammonium nitrate was decomposed at 250 and calcium and sodium nitrate at over 500 . As shown in the TG-DTA of Figure 4, the components of the residual solid after decomposing them at 250 were calcium and sodium nitrate. Sodium nitrate is converted into sodium oxide at 600 . But sodium oxide should be made with a stable form because it reacts easily with water. It is known that when alumina was added it creates a stable form by the $2NaNO_3 + Al_2O_3 = Na_2O.Al_2O_3 + NO_2 + 1/2O_2$ equation. The solid waste after decomposing it at 900 consisted of calcium oxide and Na_2O-Al_2O_3 and these are stable compounds for storage.

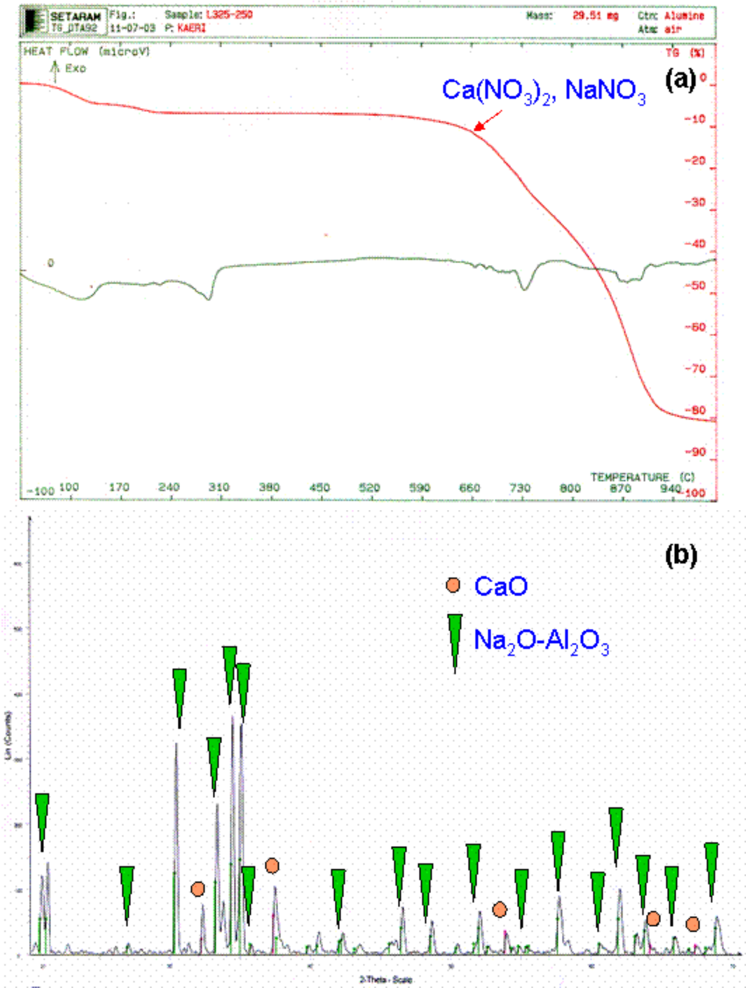

Fig. 4. TG-DTA (a) of the residual solid after the 1st thermal denitration and the XRD pattern (b) of the solid waste after the 2nd denitration

As a result, the volume of the sludge waste could be decreased by over 75 % through the sludge treatment process.

CONCLUSION

The treatment process of a lagoon sludge waste was investigated. The treatment process consisted of a desalination, liquid-solid separation, solid waste stabilization, and a nitrate solution waste denitration. Nitrate salts involved in the sludge were separated over 98 wt% at the water adding ratio of 1.5. The solid waste consists of a small quantity of calcium and sodium nitrate and undissolved solids such as calcium carbonate, uranium, and others in the sludge. These nitrate compounds were decomposed at over 500 and the calcium carbonate was decomposed into calcium oxide at over 750 . The stabilized solid waste consisted mainly of calcium oxide, $3CaO\text{-}UO_3$, $3Na_2O\text{-}7UO_3$ and these are stable compounds for storage. The nitrate solution was decomposed in two steps; the first occurred at around 250 and the second at over 500 . The low temperature decomposition is due to ammonium nitrate and the second is due to the sodium and calcium nitrate. Alumina should be added for the stabilizing sodium oxide, which reacts easily with water. The solid waste after a decomposing at 900 consisted mainly of calcium oxide and Na_2O-Al_2O_3 and these are stable compounds for storage. As a result, the volume of the sludge waste could be decreased by over 75 % through the sludge treatment process.

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