Stabilization of Uranium Sludge from a Conversion Plant Through Thermal Decomposition

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Abstract: The Korea Atomic Energy Research Institute (KAERI) has begun a decommissioning program for a uranium conversion plant. A treatment process for the sludge waste, which was generated during the operation of the plant and stored in lagoons, was proposed based on the results of an analysis of the sludge characteristics and the thermal decomposition properties. The thermal decomposition rate was observed by a load cell at a given heating rate. The solid waste’s stabilization properties were analyzed by TG/DTA and XRD. The nitrate salts in the sludge were decomposed in two steps; the first decomposition occurred at ca. 300 °C and the second at over 600 °C. The low-temperature decomposition was due to ammonium nitrate at 300 °C; the high-temperature decomposition was due to those of sodium and calcium nitrate and calcium carbonate at 900 °C. Alumina should be added for stabilization of the sodium oxide, which arose from decomposition of the sodium nitrate and reacted readily with water. The residual solid waste consisted mainly of Na₂O · 2UO₃, calcium oxide, calcium hydroxide, and Na₂O · Al₂O₃; these materials are stable compounds for storage. As a result, the volume of the sludge waste could be decreased by over 75 % when using this sludge treatment process.

Keywords: uranium conversion, thermal decomposition, nitrate, sludge, stabilization

Introduction

The Korea Atomic Energy Research Institute (KAERI) decided to construct the pilot plant for a uranium conversion process for the development of relevant technology and the localization of nuclear fuel for a pressurized water reactor (PWR) and a heavy water reactor (HWR) in 1976. The final product of the plant was uranium dioxide (UO₂) powder of a ceramic grade for a HWR; its capacity was 100 ton-U/year. The construction was finished in 1982. After that, a part of the ammonium uranyl carbonate (AUC) process was added and the process was improved for automatic operation. A total of 320 tons of UO₂ powder was produced and supplied to the fabrication plant at KAERI for the fuel of the Wolsong-1 CANDU (Canadian deuterium uranium) reactor [1].

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In early 1992, it was decided that the plant operation would be stopped because of its relatively higher production cost than that of the international market. The conversion plant was shut down and minimally maintained to prevent contamination through 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 pipes, tanks, vessels and equipment for canning or reuse; decontamination of the building for unrestricted reuse, and treatment of the sludge and demolition of the lagoon. The treatment of the sludge waste generated during the operation of the plant and stored in the lagoon is one of the most important tasks in the decommissioning 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
Table 1. Physical Properties of Each Layer of Lagoons 1 and 2

<table>
<thead>
<tr>
<th></th>
<th>Lagoon 1</th>
<th></th>
<th>Lagoon 2</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Upper</td>
<td>Middle</td>
<td>Bottom</td>
<td>Upper</td>
</tr>
<tr>
<td>Phase</td>
<td>liquid</td>
<td>crystalline deposit</td>
<td>liquid</td>
<td>crystalline deposit</td>
</tr>
<tr>
<td>Color</td>
<td>yellow</td>
<td>white</td>
<td>brown</td>
<td>yellow</td>
</tr>
<tr>
<td>Density</td>
<td>1.42</td>
<td>1.96</td>
<td>1.81</td>
<td>1.43</td>
</tr>
<tr>
<td>Height, cm</td>
<td>7</td>
<td>7</td>
<td>23</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 2. Chemical Composition of the Lagoon Sludge

<table>
<thead>
<tr>
<th></th>
<th>wt%</th>
<th>NH$_4$NO$_3$ wt%</th>
<th>NaNO$_3$ wt%</th>
<th>Ca(NO$_3$)$_2$ wt%</th>
<th>CaCO$_3$ wt%</th>
<th>U ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lagoon 1</td>
<td>Upper</td>
<td>19.62</td>
<td>61.86</td>
<td>28.43</td>
<td>2.07</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Middle</td>
<td>17.16</td>
<td>68.81</td>
<td>25.30</td>
<td>0.30</td>
<td>586</td>
</tr>
<tr>
<td></td>
<td>Bottom</td>
<td>63.21</td>
<td>53.04</td>
<td>17.98</td>
<td>9.53</td>
<td>20300</td>
</tr>
<tr>
<td>Lagoon 2</td>
<td>Upper</td>
<td>15.38</td>
<td>79.84</td>
<td>13.82</td>
<td>1.77</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td></td>
<td>Middle</td>
<td>47.19</td>
<td>90.31</td>
<td>0.31</td>
<td>0.93</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>bottom</td>
<td>37.42</td>
<td>20.17</td>
<td>3.14</td>
<td>18.94</td>
<td>38.11</td>
</tr>
</tbody>
</table>

Figure 1. Flow diagram for the lagoon sludge treatment (L1, lagoon 1; L2, lagoon 2; U, upper; M, middle; B, bottom layer).

In this study, a treatment process for the sludge was developed based on the results of the sludge characterization [2]. The sludge was treated using a thermal decomposition process. The sludge decomposed in two steps; the first at low temperature and the second at high temperature. The low-temperature decomposition was due to ammonium nitrate, and the high-temperature decomposition was due to sodium and calcium nitrate and calcium carbonate. The residual solid waste involving uranium was stabilized during the second step.

Characteristics of the Lagoon Sludge

There are two lagoons at KAERI, having dimensions of 3 (H)×10 (W)×40 (L) m and 2.7×8×40 m, respectively. When the uranium conversion plant was constructed, only one lagoon was made. After practical operation began in 1988, the capacity of the lagoon was insufficient and, as such, a second lagoon was constructed. After settlement of the particulates, the solution in lagoon 1 was neutralized with calcium hydroxide. During this step, the heavy metals, including uranium, precipitated. After filtration to remove the solid particles, the solution was transferred to, and stored in, lagoon 2.

The sludge in lagoons 1 and 2 exists in three different layers, respectively. The upper layer is a saturated solution, the middle layer is crystalline, and the bottom layer is the deposited particulate material. Several physical properties of the layers are listed in Table 1. The compositions of the lagoon are very complicated, but the main compounds are ammonium nitrate, sodium nitrate, calcium nitrate, calcium carbonate, and uranium [1]. The chemical composition and the ratio of each layer are shown in Table 2. The uranium content of the deposit at the bottom of the lagoon is very high and the sludge cannot...
Table 3. Chemical Composition of Other Metals in the Lagoon Sludge

<table>
<thead>
<tr>
<th>Element</th>
<th>Al</th>
<th>Si</th>
<th>P</th>
<th>Fe</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lagoon 1 bottom (wt%)</td>
<td>0.35</td>
<td>1.25</td>
<td>0.27</td>
<td>0.15</td>
<td>0.3</td>
</tr>
<tr>
<td>Lagoon 2 bottom (wt%)</td>
<td>-</td>
<td>-</td>
<td>0.007</td>
<td>0.02</td>
<td>0.08</td>
</tr>
</tbody>
</table>

Sludge Treatment Process

Because most of the chemical salts in the sludge are nitrates, as shown in Table 2, to reduce the volume and to meet the conditions for storage and final disposal, the nitrates should be removed from the sludge. All of the nitrates are readily decomposed to oxides through heating with reducing agents, such as alumina [3] or carbon powder [4].

Two concepts of the treatment processes were proposed: (1) a liquid-solid separation following the dissolution of the nitrates with water and (2) a thermal decomposition with reducing agents. The liquid-solid separation process was proposed to dissolve the nitrates with water for the sludge treatment. Water is added to the lagoon for dissolution of the nitrates and the slurry is transferred to a liquid-solid separation system. The solid waste is stabilized for final disposal through a further solidification. The nitrate solution waste is decomposed thermally. However, this process requires an enormous amount of energy to evolve the added water.

The thermal decomposition process has the difficulty of ammonium nitrate decomposition. Ammonium nitrate is explosive and is decomposed by evolving a great deal of gas. In the range of the decomposition temperature, the lagoon 1 bottom layer sludge was expanded greatly because of the presence of many large bubbles. Thus, a reactor with a large volume is required and this volume is dependent on the decomposition rate. This problem was solved by performing a simple filtration of the sludge. Therefore, the thermal decomposition process was selected for sludge treatment. The sludge was decomposed in two steps because of the characteristics of sludge; the first occurred at low-temperature and the second at high temperature. The low-temperature decomposition was due to ammonium nitrate and the high-temperature decomposition is due to sodium and calcium nitrate and calcium carbonate. Sodium nitrate is converted into sodium oxide at 600 °C; it should, however, be created as a stable form because it reacts readily with water. Therefore, alumina is added into the sludge that contains a lot of sodium nitrate, to obtain a stable form. Figure 1 outlines this concept.

Experiments

Samples were taken from each layer in lagoons 1 and 2. For the sludge of each layer, thermal decomposition was performed in a muffle furnace. The heating rate of the furnace was 10 °C/min. The decreasing weight of the sludge was measured by a load cell (model: CAS MWII-3000) with an indicator (model: CAS NT-501); the data were recorded on a computer. Evolved gas from the thermal decomposition was discharged through two water traps by a vacuum pump. Figure 2 displays the experimental setup.

The stabilization properties of the residual solid waste were analyzed using TG/DTA (thermogravimetry/differential thermal analysis, model Setaram TG-DTA 92) and XRD (X-ray diffractor, model Siemens D5000) systems.

Results

Ammonium Nitrate Decomposition Temperature

The low-temperature decomposition was due to ammonium nitrate, which is decomposed through the several reactions shown in Table 4 [5]. Therefore, a suitable temperature should be chosen to decompose ammonium nitrate safely.

Figure 3 shows the results of the thermal decomposition.
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Table 4. Modes of Thermal Decomposition of Ammonium Nitrate

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Heat evolved (cal/g)</th>
<th>Gas volume (mL/g) at NTP</th>
<th>Temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) NH₄NO₃ → NH₃(g) + HNO₃(g)</td>
<td>-521</td>
<td>840</td>
<td>320</td>
</tr>
<tr>
<td>2) NH₄NO₃ → N₂O + 2H₂O</td>
<td>108</td>
<td>910</td>
<td>860</td>
</tr>
<tr>
<td>3) NH₄NO₃ → 3/4N₂ + 1/2NO₂ + 2H₂O</td>
<td>316</td>
<td>980</td>
<td>950</td>
</tr>
<tr>
<td>4) NH₄NO₃ → N₂ + 2H₂O + 1/2O₂</td>
<td>354</td>
<td>945</td>
<td>560</td>
</tr>
<tr>
<td>5) 8NH₄NO₃ → 5N₂ + 4NO + 2NO₂ + 16H₂O</td>
<td>201</td>
<td>980</td>
<td>945</td>
</tr>
<tr>
<td>6) NH₄NO₃ → 1/2N₂ + NO + 2H₂O</td>
<td>86</td>
<td>980</td>
<td>260</td>
</tr>
</tbody>
</table>

Figure 3. Thermal decomposition of the lagoon 1 upper layer sludge as a function of temperature.

of the lagoon 1 upper layer sludge as a function of the temperature. The heating rate was 10 °C/min up to the target temperature. The sludge decomposed slowly at 250 °C; a small amount of ammonium nitrate remained after 70 min. Although the decomposition rate differed slightly, the ammonium nitrate was completely decomposed within 30 min at 300 and 350 °C. We believe that the sodium nitrate involved in the sludge affects the decomposition rate. The melting point of sodium nitrate is 308 °C. The sludge involving sodium nitrate formed many bubbles because the gases of the decomposed ammonium nitrate are difficult to exhaust from the surface of the sludge. The bubbling phenomena did not appear at temperatures over 300 °C. Therefore, it appears that 300 °C is a suitable temperature for the decomposition of ammonium nitrate in the lagoon sludge.

Thermal Decomposition of the Lagoon Sludge

A sample of 50 g of sludge from each layer was decomposed in the furnace. Figure 4 shows the results of the thermal decomposition of the lagoon 1 and lagoon 2 sludges as a function of time. The temperature was increased at a rate of 10 °C/min and then maintained for 20 min at 300 °C to decompose ammonium nitrate. After increasing the temperature to 900 °C at the same heating rate, this temperature was maintained constant until the decomposition of the sludge was complete. Most of the ammonium nitrate present in the sludge of each layer decomposed during the 20 min at 300 °C in the case of the lagoon 1 sludge. Sodium and calcium nitrate began to decompose at ca. 600 °C, and they decomposed completely within 120 min. Although the amount of ammonium nitrate present in each layer of the lagoon 2 sludge was different, in each case it decomposed within 20 min at 300 °C. Sodium and calcium nitrate also decomposed as they did in the lagoon 1 sludge, while the calcium carbonate involved in the sludge of the lagoon 2 bottom layer decomposed at 700 °C.

Sodium nitrate is converted into sodium oxide at 600 °C. This sodium oxide should be created in a stable form because it reacts easily with water. It is known that a
stable form is obtained when alumina is added, as in the following equation [3]:

\[ 2\text{NaNO}_3 + \text{Al}_2\text{O}_3 = \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 + \text{NO}_2 + \frac{1}{2}\text{O}_2 \]

A stoichiometric amount of alumina was added into the lagoon 1 upper and middle layer sludges and the lagoon 2 upper layer sludge, which contain comparatively large amounts of sodium nitrate. Figure 5 shows the thermal decomposition of the lagoon 1 upper layer sludge in the presence and absence of alumina. In both cases, the sludge decomposed similarly. Therefore, we confirmed that the presence of alumina did not affect the decomposition rate of the nitrate salts. The residual solid waste must be stored in a stable form.
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because it involves uranium. The stabilization properties of the residual solid waste were tested using TG/DTA and XRD. Figure 6 shows the TG/DTA trace and XRD pattern of the residual solid waste obtained after thermal decomposition of the lagoon 1 upper layer with alumina. No compounds in the solid waste were further decomposed. The solid waste consisted mainly of calcium oxide and Na₂O · Al₂O₃, which are stable compounds for storage.

The XRD patterns of the residual solid wastes obtained after thermal decomposition of the lagoon 1 middle, lagoon 1 bottom, lagoon 2 upper, and lagoon 2 middles layer sludges are shown in Figure 7. For the lagoon 1 middle and lagoon 2 upper layer sludges, the thermal decomposition was conducted in the presence of alumina because of the considerable amounts of sodium nitrate present. Sodium nitrate in the lagoon 1 middle layer sludge decomposed to Na₂O · Al₂O₃ with alumina as it had in the lagoon 1 upper layer sludge. The lagoon 1 bottom layer sludge decomposed without alumina being added. Comparatively large amounts of uranium became stabilized as a form of Na₂O · 2UO₃. A minor composition of Fe in the lagoon 1 bottom layer was detected in the form of Fe₃O₅. For the lagoon 2 upper layer sludge, the thermal decomposition was conducted with alumina added. Small amounts of alumina that had not reacted

Figure 8. TG/DTA trace and XRD pattern of the residual solid waste after thermal decomposition of lagoon 2 bottom layer in the presence of alumina.

with sodium nitrate were detected in the XRD analysis as shown in Figure 7(c). The XRD pattern of the residual solid waste obtained after thermal decomposition of the lagoon 2 middle layer is shown in Figure 7(d). Only calcium oxide was detected in the residual solid waste. For all the residual solid wastes considered in Figure 6, the same TG/DTA diagrams were obtained as that from the lagoon 1 upper layer.

Figure 8 shows the stabilization properties of the residual solid waste of the lagoon 2 bottom layer sludge. In the TG/DTA diagram, weight loss occurred at ca. 400 and 600 °C, respectively. A relatively large amount of calcium was found in the lagoon 2 bottom layer. Calcium carbonate is decomposed as follows [6]:

\[
\text{CaCO}_3 = \text{CaO} + \text{CO}_2
\]

Calcium oxide can be transformed into calcium hydroxide in the atmosphere as follows [7]:

\[
\text{CaO} + \text{H}_2\text{O} = \text{Ca(OH)}_2
\]

Figure 9 shows the TG/DTA diagram of calcium hydroxide. The specific weight loss occurred at around the same temperature as that shown in Figure 8. This result suggests that the calcium oxide involved in the solid waste is converted into calcium hydroxide. We confirmed that calcium hydroxide was created from the XRD pattern in Figure 8. These are stable compounds for storage [8].

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

Conclusion

A process for treating lagoon sludge waste was investigated. The treatment process of the sludge was
proposed based on the sludge characteristics and the thermal decomposition properties. The sludge waste was decomposed through thermal decomposition. The nitrate salts in the sludge were decomposed in two steps: the first decomposition removed ammonium nitrate and the second removed sodium and calcium nitrate and calcium carbonate. Most of the ammonium nitrate involved in each layer of the sludge decomposed within 20 min at 300 °C. Sodium and calcium nitrate began to decompose at ca. 600 °C; they decomposed completely within 120 min. Alumina was added to stabilize sodium oxide, which formed through the decomposition of sodium nitrate, and reacts readily with water. The residual solid waste consisted mainly of Na₂O · 2UO₃, calcium oxide, calcium hydroxide, and Na₂O · Al₂O₃; these materials are stable compounds for storage. As a result, the volume of sludge waste could be decreased by over 75 % when using this sludge treatment process.

Acknowledgments

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References