Thermal decomposition analysis of simulated high-level liquid waste in cold-cap

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Abstract. The cold cap floating on top of the molten glass pool in liquid fed joule-heated ceramic melter plays an important role for operation of the vitrification process. A series of such phenomena as evaporation, melting and thermal decomposition of HLLW (high-level liquid waste) takes place within the cold-cap. An understanding of the varied thermal decomposition behavior of various nitrates constituting HLLW is necessary to elucidate a series of phenomena occurring within the cold-cap. In this study, reaction rates of the thermal decomposition reaction of 13 kinds of nitrates, which are main constituents of simulated HLLW (sHLLW), were investigated using thermogravimetric instrument in a range of room temperature to 1000 °C. The reaction rates of the thermal decompositions of 13 kinds of nitrates were depicted according to composition ratio (wt%) of each nitrate in sHLLW. It was found that the thermal decomposition of sHLLW could be predicted by the reaction rates and reaction temperatures of individual nitrates. The thermal decomposition of sHLLW with borosilicate glass system was also investigated. The above mentioned results will be able to provide a useful knowledge for understanding the phenomena occurring within the cold-cap.

1 Introduction

In the closed fuel cycles, high-level liquid waste (HLLW) is generated from reprocessing of spent nuclear fuel. HLLW possesses intrinsic characteristics such as decay heat, corrosiveness and generation of hydrogen associated with radiolysis [1,2]. Thus, long time storage of HLLW is difficult in terms of confinement and management of radioactive materials because of its liquid state. Therefore, HLLW is immobilized into borosilicate glass matrix for safe long-time storage. The immobilized HLLW is called vitrified waste. Prior to the final disposal in deep geological repository, vitrified waste should be cooled for 30–50 years to achieve decrease of decay heat.

HLLW contains 31 kinds of nitrates which consist of fission products, Na from alkaline rinse, P from TBP degradation products, some insoluble particles such as Zr fines from the cladding of the fuel elements, Mo and platinum group metals (Pd, Ru and Rh) [3].

In the vitrification process, the cold cap floating on top of the molten glass pool in liquid fed joule-heated ceramic melter plays an important role for its operation. A series of such phenomena as evaporation, melting and thermal decomposition of HLLW takes place within the cold-cap.

The contact with glass beads results in further chemical reactions to incorporate all waste constituents, either as oxides of other compounds into the glass structure. The cold-cap formation and conversion to glass take place under non-isothermal conditions in a range of room temperature to 1200 °C. It depends on the processing parameters and properties of the various chemical elements of HLLW. An understanding of the various thermal decomposition behavior of many nitrates constituting HLLW is necessary to elucidate a series of phenomena occurring within the cold-cap. Some works such as developments of simulation model in terms of heat balance, kinetic analysis of reactions, decomposition of individual chemicals used for the UK solution by means of thermal balance and so on have been reported on the study of cold-cap [4–9]. However, there are few studies which investigate interaction among constituents of HLLW for cold-cap reaction. In this study, we investigated thermal decomposition of nitrates constituting HLLW at each temperature region under an elevated temperature process by the mean of reaction rate. In addition, the map of thermal decomposition rate vs temperature for the nitrates constituting sHLLW was depicted according to the composition ratio of each nitrate that was contained in sHLLW in a range of room temperature to 1000 °C in order to simulate the thermal decomposition of sHLLW. Moreover, we investigated effects of addition of borosilicate

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glass for the thermal decomposition behavior of nitrates constituting HLLW in order to simulate practical phenomena occurring in cold-cap. These results lead to further clarification of transport phenomena and reactions occurring over a range of room temperature to 1200 °C in cold-cap.

2 Experimental

Table 1 shows the composition of sHLLW used in this study. Composition of HLLW is determined by private communication with Japan Nuclear Fuel Limited which is Japanese reprocessing company based on the book “Nuclear chemical engineering” written by Benedict et al. [10]. The sHLLW was evaporated to dryness on a hot plate at 70 °C in order to obtain the dried-sHLLW.

The thermal decomposition reaction of 13 kinds of nitrates, which are main constituents of sHLLW (corresponding approximately to 93.3 mol% of sHLLW), with different chemical and physical properties were investigated using thermogravimetric instrument (TG: TGA-50, SHIMADZU). **Table 2** shows 13 kinds of reagents. Ru was omitted in this study due to cost, and Mo was also omitted because thermal decomposition of sodium molybdate dehydrate from room temperature to 1000 °C is only dehydration which is occurring at around 100 °C. NaNO_2 was used as sodium nitrate for the following reasons. Thermal decomposition of sodium nitrate under isothermal conditions at around 600 °C is sequential reaction, which is $\text{NaNO}_3 \rightarrow \text{NaNO}_2 \rightarrow \text{Na}_2\text{O}$. The fractional reaction α is defined as $\alpha = (m_{\text{ini}} - m_t) / (m_{\text{ini}} - m_{\text{fin}})$; where m_{ini} , m_{fin} and m_t are the weight at initial, final and a given time, respectively. The α value is 0.295 for $\text{NaNO}_3 \rightarrow \text{NaNO}_2$ reaction step and 0.705 for $\text{NaNO}_2 \rightarrow \text{Na}_2\text{O}$ reaction. The thermal decomposition of sodium nitrate gradually starts from 550 °C and the sequential reaction cannot be confirmed under non-isothermal (1–10 °C/min) [11,12]. This suggests that $\text{NaNO}_3 \rightarrow \text{NaNO}_2$ reaction proceeds more rapidly than $\text{NaNO}_2 \rightarrow \text{Na}_2\text{O}$ so that $\text{NaNO}_2 \rightarrow \text{Na}_2\text{O}$ reaction step is rate-limiting reaction. For this reason, as the starting reagent, sodium nitrate (NaNO_3) is replaced by sodium nitrite (NaNO_2).

The TG measurements were conducted with heating rate of 5 °C/min in a range of room temperature to 1000 °C at flow rate, 75 cm³/min of N₂ gas in order to evaluate the thermal decomposition occurring under inert atmosphere. The reaction rates of thermal decomposition of the nitrates were calculated on the basis of the TG curves. The map of their reaction rates and reaction temperatures was described over their reaction temperature ranges under heating rate of 5 °C/min. In addition, chemical compounds were described in the map. Their compounds are estimated stoichiometrically based on TG curves.

The thermal decomposition reaction of dried-sHLLW and each nitrate included in the dried-sHLLW with borosilicate glass powder were investigated as well. The composition of used borosilicate glass is listed in **Table 3**, which are determined by private communication with Japan Nuclear Fuel Limited as well. The borosilicate glass beads were ground to powder of 75 μm to 100 μm in

Table 1. Composition of simulated high-level liquid waste.

Element	Concentration [mol/L]	Oxide concentration [g/L]
H	1.38	
Na	1.005	31.1
Nd	0.0615	10.3
Zr	0.0512	6.31
Gd	0.0364	6.6
Ce	0.0363	6.25
Cs	0.0358	5.04
Mo	0.0321	4.62
Fe	0.0307	2.45
La	0.0225	3.67
Ru	0.0219	2.91
Mn	0.0189	1.34
Ba	0.0161	2.47
Pr	0.0159	2.71
Pd	0.0155	1.9
Sr	0.0124	1.28
Sm	0.00898	1.57
Y	0.00815	0.92
Cr	0.0063	0.479
Rh	0.00501	0.636
P	0.0043	0.305
Te	0.00399	0.796
Ni	0.00109	0.814
Ag	0.000966	0.112
Others	0.00483	0.2978

Table 2. Used reagent for 13 kinds of elements (Wako: Wako Pure Chemical Industries, Ltd., Kanto: Kanto Chemical Co., Inc.).

Element	Reagent	Reagent-grade
Na	NaNO_2	>98.5%, Kanto
Nd	$\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	99.5%, Wako
Zr	$\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	>97.0%, Wako
Gd	$\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	99.5%, Wako
Ce	$\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	>98.0%, Wako
Cs	CsNO_3	99.9%, Wako
Fe	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	>99.0%, Wako
La	$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	99.9%, Wako
Mn	$\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	>98.0%, Wako
Ba	$\text{Ba}(\text{NO}_3)_2$	99.9%, Wako
Pr	$\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	99.9%, Wako
Pd	$\text{Pd}(\text{NO}_3)_2$	>97.0%, Wako
Sr	$\text{Sr}(\text{NO}_3)_2$	>98.0%, Wako

Table 3. Composition of borosilicate glass.

Oxide composition	Concentration ratio [wt%]
SiO ₂	60
B ₂ O ₃	18.2
Al ₂ O ₃	6.4
Li ₂ O	3.8
CaO	3.8
ZnO	3.8
Na ₂ O	4.0

diameter using an alumina mortar. The weight ratio of dried-sHLLW or nitrate to the borosilicate glass mixture was 40 wt%.

3 Results and discussion

3.1 Thermal decomposition behavior of constituents of simulated HLLW

Figure 1 shows the reaction rate of thermal decomposition of iron nitrate [Fe(NO₃)₃·9H₂O]. It was dehydrated to produce Fe(NO₃)₃. Then, it reacted to Fe₂O₃ in the low temperature range of 100 to 200 °C.

Figure 2 shows the reaction rate of thermal decomposition of zirconium nitrate [ZrO(NO₃)₂·2H₂O]. It was dehydrated to ZrO(NO₃)₂ in the range of room temperature to 100 °C. ZrO(NO₃)₂ was decomposed to Zr₂O₃(NO₃) and finally to ZrO₂ in the range of 100 to 400 °C.

Figure 3 shows the reaction rate of thermal decomposition of gadolinium nitrate [Gd(NO₃)₃·6H₂O]. It was dehydrated to Gd(NO₃)₃ at around room temperature to 300 °C, Gd(NO₃)₃ was decomposed to GdONO₃ at around 400 °C, finally to Gd₂O₃. Reaction step 1 (Gd(NO₃)₃ → GdONO₃), step 2 (GdONO₃ → Gd₂O₃) proceeded sequentially at around 400 °C (STEP 1), 500 °C to 600 °C (STEP 2), respectively.

Figure 4 shows the reaction rate of thermal decomposition of NaNO₂. It was decomposed to Na₂O in the region above 600 °C. Furthermore, Na₂O is sublimated above a temperature of 800 °C. The thermal decomposition of other 9 kinds of nitrates were also investigated as well. The results are summarized in Table 4. Iron nitrate was decomposed in the temperature region lower than 200 °C. The nitrates of lanthanoid series such as lanthanum, neodymium and gadolinium nitrate were decomposed in the middle range of 200 to 600 °C. Alkali metal and alkaline-earth metal such as strontium, cesium, barium and sodium were decomposed in the high temperature region of 600 to 1000 °C.

In Figure 5, the reaction rates of the thermal decompositions of 13 nitrates were depicted according to composition ratio (wt%) of each nitrate in a range of room temperature to 1000 °C. The presence of Na is dominant in sHLLW as shown in Table 1. The reaction rate curves for 13 nitrates were superimposed on a graph of reaction rates vs temperature, as shown by a red line in Figure 6. The reaction rate curve observed from thermal

Fig. 1. TG curve and reaction rate of the thermal decomposition of Fe(NO₃)₃·9H₂O at heating rate of 5 °C/min. **Fig. 2.** TG curve and reaction rate of the thermal decomposition of ZrO(NO₃)₂·2H₂O at heating rate of 5 °C/min. **Fig. 3.** TG curve and reaction rate of the thermal decomposition of Gd(NO₃)₃·6H₂O at heating rate of 5 °C/min.

decomposition of dried-sHLLW (black line) was also depicted in the same figure. As a result, the characteristic peaks of thermal decomposition of dried-sHLLW were fitted with overlapped reaction rates of thermal decomposition of their nitrates, especially the peaks around 400 °C and 750 °C corresponding to thermal decomposition of lanthanum nitrates and sodium nitrate. However,

Fig. 5. Thermal decomposition rate of 13 kinds of nitrates at heating rate of 5°C/min, which were depicted according to composition ratio of each nitrate in sHLLW.

3.2 Thermal decomposition behavior of constituents/ borosilicate glass system

In the cold-cap floating on molten glass, HLLW and borosilicate glass coexist. Studying their interaction is necessary to understand a series of phenomena occurring within the cold-cap. Then, the thermal decomposition of

Table 4. Map of reaction property vs. temperature.

Nitrate	Phenomena and Temperature																		
	100°C	150°C	200°C	250°C	300°C	350°C	400°C	450°C	500°C	550°C	600°C	650°C	700°C	750°C	800°C	850°C	900°C	950°C	1000°C
NaNO ₂				Melting							←----- Decomposition→Na ₂ O→Sublimation-----→								
Nd(NO ₃) ₃ • 6H ₂ O			Dehydrating→Nd(NO ₃) ₃				Decomposition→NdO(NO ₃)		Decomposition→Nd ₂ O ₃										
ZrO(NO ₃) ₂ • 2H ₂ O		Dehydrating→ZrO(NO ₃) ₂	Decomposition→Zr ₂ O ₃ (NO ₃)	Decomposition→ZrO ₂															
Gd(NO ₃) ₃ • 6H ₂ O				DehydratingGd(NO ₃) ₃			Decomposition→GdO(NO ₃)		Decomposition→Gd ₂ O ₃										
Ce(NO ₃) ₃ • 6H ₂ O			DehydratingCe(NO ₃) ₃	Decomposition→Ce ₂ O ₃															
CsNO ₃							Melting				←-- Decomposition→Cs ₂ O→Sublimation--→								
Fe(NO ₃) ₃ • 9H ₂ O	DehydratingFe(NO ₃) ₃	Decomposition→Fe ₂ O ₃																	
La(NO ₃) ₃ • 6H ₂ O			DehydratingLa(NO ₃) ₃				Decomposition→LaO(NO ₃)		Decomposition→La ₂ O ₃										
Mn(NO ₃) ₂ • 6H ₂ O	Dehydrating→Mn(NO ₃) ₂		DecompositionMnO(NO ₃)	Decomposition→MnO															
Ba(NO ₃) ₂											←----- Decomposition→BaO-----→								
Pr(NO ₃) ₃ • 6H ₂ O			DehydratingPr(NO ₃) ₃				Decomposition→PrO(NO ₃)	Decomposition→Pr ₂ O ₃											
Pd(NO ₃) ₂		Decomposition→PdO												Decomposition→Pd					
Sr(NO ₃) ₂											←--- Decomposition→SrO-----→								

13 nitrates coexisting with borosilicate glass powder (75 to 100 μm in diameter) was investigated by the same way as that described in the former section.

Figure 7 shows the thermal decomposition rate of NaNO_2 with borosilicate glass powder in a range of room temperature to 800 $^\circ\text{C}$. The weight ratio, the vertical axis in the figure, means the ratio of weight of remaining NaNO_2 to initial weight. Then, it was assumed that the weight of borosilicate glass powder is constant during the reaction. Thermal decomposition of NaNO_2 in the presence of borosilicate glass powder took place at much lower temperature than that of the sodium nitrite itself (Fig. 4). Similar phenomena were reported by Abe et al. [13]. From the viewpoint of thermodynamics, the following chemical reactions can occur in the presence of borosilicate glass. These reactions indicate that the thermal decomposition of sodium nitrite is promoted and occurring at low temperature.

STEP 1

STEP 2

STEP 3

Moreover, Na_2O may not be sublimated in the presence of borosilicate glass as shown in Figure 7. For other alkali metal and alkaline-earth metal nitrates, the thermal decomposition of their nitrates also took place at lower temperatures due to the presence of borosilicate glass powder.

Figure 8 shows the thermal decomposition rate of gadolinium nitrate in the presence of borosilicate glass powder. In this case, the behavior of its thermal decomposition is similar to the case without borosilicate

Fig. 7. TG curve obtained by the thermal decomposition of NaNO_2 in the presence of borosilicate glass powder at heating rate of 5 $^\circ\text{C}/\text{min}$ (solid line) and the thermal decomposition rate calculated from the differential of the TG curve (dashed line).

Fig. 8. TG curve obtained by the thermal decomposition of $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in the presence of borosilicate glass powder at heating rate of 5 $^\circ\text{C}/\text{min}$ (solid line) and the thermal decomposition rate calculated from the differential of the TG curve (dashed line).

Fig. 9. Thermal decomposition rate of 13 kinds of nitrates in the presence of borosilicate glass powder at heating rate of 5 $^\circ\text{C}/\text{min}$, which are depicted according to composition ratio of each nitrate in sHLLW.

glass described in Figure 3. Thus, the effects by the addition of borosilicate glass were not observed. For other lanthanides and iron nitrates, the effects of the addition of borosilicate glass were not observed as well.

Figure 9 shows the thermal decompositions rates of 13 nitrates in the presence of borosilicate glass powder, which were depicted according to composition ratio (wt%) of each

Fig. 10. Comparison between the thermal decomposition rate of sHLLW (black line) and that obtained by overlapping the thermal decomposition rates of 13 kinds of nitrates (red line) in the presence of borosilicate glass powder.

nitrate. The temperature range was from room temperature to 800 °C. In order to compare the thermal decomposition of dried-sHLLW and those of 13 nitrates in the presence of borosilicate glass, the overlapping curve of the thermal decomposition rates of 13 nitrates in the presence of borosilicate glass powder is shown with a red line in Figure 10. The thermal decomposition rate of dried-sHLLW in the presence of borosilicate glass powder is shown with a black line in the same figure. The decomposition rates of dried-sHLLW below 500 °C were not changed with and without borosilicate glass. However, the thermal decomposition rates of dried-sHLLW in the presence of borosilicate glass powder above 500 °C is dramatically changed compared to the overlapping of the thermal decomposition rates of 13 nitrates in the presence of borosilicate glass powder, especially the part of the sodium nitrate decomposition with glass powder. In Figure 10, there are no peak corresponding to STEP 3 in Figure 7. It seems that the sodium nitrate decomposition was promoted by the presence of other chemical substances included in sHLLW. Although the thermal decomposition of dried-sHLLW with borosilicate glass powder tends to occur at lower temperature than that of sHLLW above 500 °C, the thermal decomposition rate of dried-sHLLW with borosilicate glass powder could be described by overlapping the thermal decomposition rates of 13 nitrates. Investigation of interaction between sodium nitrate and other chemical substances in the presence of borosilicate glass is also a challenge for the future as well as the former section.

4 Conclusions

The thermal decomposition of 13 nitrates which are main constituents of sHLLW was investigated using thermal-gravimetric analysis in the range of room temperature to 1000 °C. At the low temperature range of room temperature to 200 °C, iron and palladium nitrates decomposed to oxide. At the middle temperature range of 200 to 600 °C, zirconium, manganese and lanthanoid series nitrates decomposed to oxide. At the high temperature range of 600 to 1000 °C, alkali and alkaline-earth metal nitrates

decomposed to oxide. The overlapped curve of the thermal decomposition rates for 13 kinds of nitrates, which includes Na, Nd, Zr, Gd, Ce, Cs, Fe, La, Mn, Ba, Pr, Pd and Sr, was almost fitted with the curve of the thermal decomposition rate of dried-sHLLW. It was also found that iron nitrate, alkali and alkaline-earth metal nitrates are probably decomposed with other chemical substances included in sHLLW. In addition, the thermal decomposition of each nitrate with borosilicate glass powder was investigated as well. As the results, it was observed that the thermal decomposition of alkali metal and alkaline-earth metal nitrates were affected by the borosilicate glass. For other nitrates such as lanthanides, zirconium nitrate, iron nitrate and so on, the effects of their thermal decomposition in the presence of borosilicate glass were not observed. The overlapped curve of the thermal decomposition rates for 13 nitrates with borosilicate glass was fitted roughly with the thermal decomposition rates of dried-sHLLW with borosilicate glass powder. It was found that most of the thermal decomposition behavior of HLLW within the cold-cap is able to be predicted by the thermal decomposition behavior of the individual nitrates which are included in HLLW. The thermal decomposition of sodium nitrate with borosilicate glass powder is promoted due to some reaction with other chemical substances included in sHLLW as well as thermal decomposition of sHLLW. The above results will be able to provide a useful knowledge for understanding the phenomena occurring within the cold-cap.

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