

《Original》

## Vitrification of Highly Active Liquid Waste(I) (Thermal Decomposition of Nitrates and Additives for Glass-making)

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### Abstract

The decomposition of all the individual chemicals used in the Harwell inactive vitrification pilot plant has been studied by means of a thermal balance. Weight loss curves to 1100°C have been obtained. The four materials (sodium nitrate, cesium nitrate, lithium nitrate and ruthenium nitroso-nitrate solution) showed a greater weight loss than that based on an oxide yield, and hence these compounds of their products of decomposition are volatile below 1100°C. The remaining materials suffered a weight loss no more than that corresponding to a full yield of the oxide, and hence they were not volatile below 1100°C. Most of chemicals begin to decompose at less than 75°C but the nitrates of cesium, strontium, barium and sodium not until 295°C to 590°C.

The results obtained can be used in the analysis of process conditions in the vitrification and calcination of highly radioactive wastes and also of the thermal decomposition behaviour of mixtures containing those materials.

### 요 약

고준위 방사성 폐액의 고화처리 방법들 중 하나인 Vitrification Process의 연구로서 핵연료 재처리 과정에서 유출되는 가상적인 비활성폐액 중에 함유되어 있는 분열 및 부식 생성물들의 질산화물과 유리화시키기 위해 사용되는 첨가제의 열분해에 관하여 연구 조사되었다. 결정수를 갖고 있는 화합물들의 열분해시점은 75°C 이하였지만, 무수화합물들은 비교적 높은 분포를 보였다.

1100°C 까지 가열하여 얻어진 질량손실율을 이론치와 비교하였을 때, 대부분의 화합물은 일치하거나 근사하였지만, Sodium, Cesium, Lithium, Ruthenium 등의 질산화물의 질량손실율은 이론치 보다 훨씬 높았다. 여기서 얻어진 결과는 고준위 폐액의 가소처리과정 또는 조사된 화합물들의 혼합에 따른 열분해를 분석하는데도 이용될 수 있을 것이다.

### 1. Introduction

The general public should be convinced

that the nuclear industry operates, and will continue, to acceptable standards of safety. Economic and technical considera-

Table 1. Summary of Results and Materials investigated

Chemicals	Manufactured Company	Form	Yield (Weight) *			Asso-med Oxide Form	Decom-position Temp. (°C)	Ter-minal Temp. (°C)	Remarks
			Theo-retical	Obtained					
				Therm-obalance	Fur-ance				
Al(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	Sherman	Solid	0.136	0.137	0.136	Al <sub>2</sub> O <sub>3</sub>	53	460	
Ba(NO <sub>3</sub> ) <sub>2</sub>	B. D. H.	"	0.587	0.586	0.586	BaO	296	805	
CsNO <sub>3</sub>	"	"	0.723	No con-st. wt.	0.008	Cs <sub>2</sub> O	522	Volatile	
Cr(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	"	"	0.190	0.189	0.189	Cr <sub>2</sub> O <sub>3</sub>	33	466	
Fe(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	"	"	0.198	0.194	0.194	Fe <sub>2</sub> O <sub>3</sub>	46	367	
Mg(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	Fred Allen	"	0.157	0.157	0.157	MgO	43	502	
Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	B. D. H.	"	0.257	0.256	0.256	NiO	55	665	250°—270° C: Ni(OH)NO <sub>3</sub> ·½H <sub>2</sub> O
R. E. Nitrates	New Metals & Chemical Co.	"	0.386	0.411	0.366	M <sub>2</sub> O <sub>3</sub>	50	836	Composition of R.E. Nitrates La(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O: 11.20%, Nd(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O: 50.37%, Ce(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O: 17.60%, Sm(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O: 2.80%, Pr(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O: 18.00%, Eu(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O: 0.03
Ruthenium Sol.	Johnson Matthey	Aqueous Solution	0.022	0.021	0.010	RuO <sub>2</sub>	37	557	But volatile above 1000° C
Sr(NO <sub>3</sub> ) <sub>2</sub>	B. D. H.	Solid	0.490	0.486	0.477	SrO	339	738	
UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	UKAEA/BNFL	"	0.559	0.559	0.555	U <sub>3</sub> O <sub>8</sub>	40	851	{ 170° C: UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ·3H <sub>2</sub> O 290° C: UO <sub>2</sub> (OH)NO <sub>3</sub> ·½H <sub>2</sub> O
Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	B. D. H.	"	0.274	0.275	0.272	ZnO	74	372	{ 220°—320° C: Zn(NO <sub>3</sub> ) <sub>2</sub>
Zirconium Sol.	Magnesium Electron	Aqueous Solution	0.205	0.202	0.194	ZrO <sub>2</sub>	24	656	
"Gasil WP" Silica	Crossfields	Solid	0.32	0.335	0.306	SiO <sub>2</sub>	25	852	
"Neosyl" Silica	"	"	0.86	0.931	0.923	SiO <sub>2</sub>	45	See Text	
LiOH·H <sub>2</sub> O	Koch-Light Lab. Ltd.	"	0.356	0.365	0.353	Li <sub>2</sub> O	56	900	{ 210°—460° C: LiOH
LiNO <sub>3</sub> ·3H <sub>2</sub> O	"	"	0.122	No con-st. wt.	0.083	Li <sub>2</sub> O	56	Volatile	{ 254°—541° C: LiNO <sub>3</sub>
Na <sub>2</sub> CO <sub>3</sub>	Analar	"	0.585	"	0.962	Na <sub>2</sub> O	(See Text)		
NaNO <sub>3</sub>	Analar	"	0.365	No con-st. wt.	0.070	Na <sub>2</sub> O	588	Volatile	
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·10H <sub>2</sub> O	Borax Consolidated Ltd.	"	0.528	0.541	0.539	Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	38	540	{ 140° C: Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·4·45H <sub>2</sub> O Starting material: Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·9·45H <sub>2</sub> O

\*In thermobalance a sample was heated up to 050°C

In furnace " " " " " " 1100°C

tions will dictate the length of time the highly active wastes, coming from fuel reprocessing, are stored in the aqueous form, and it is proposed these aqueous wastes be solidified to reduce potential for accidental release to the environment.

Among solidification methods for long-term storage the vitrification (FINGAL-HARVEST) process<sup>1)</sup> has been preferred in

U.K. as a leading candidate for converting aqueous highly active wastes to solids. This process is being studied in an inactive pilot plant, which produces an alkali borosilicate glass. It consists of feeding the highly active waste with a slurry (of silica, borax and lithium hydroxide or nitrate) into a stainless steel vessel maintained at about 1000°C. Several reactions in the vessel take

place simultaneously: evaporation, denitration and glass formation.

The purpose of the present work is to determine the temperature ranges over which decomposition occurs for each individual nitrate and glass-forming additives contained in the feed solution in order to provide support to the analysis of the behaviour of the complete slurry during vitrification in the pilot plant.

## II. Experimental

Thermogravimetric analyses were obtained using a "Stanton Thermobalance" with an automatic recorder. To get an accurate temperature of the sample, an extra thermocouple was fixed to the top of the crucible. This thermocouple was connected to a digital voltage meter.

The chemicals were thermally decomposed to the oxides using sample sizes ranging in weight from 400 to 1000 mg. Duplicate or in some cases triplicate runs were made on each compound. The furnace heating rate was approx. 3-4°C/min. a slow stream of air was passed through the furnace during the thermal decomposition runs.

The maximum temperature available in the thermobalance is about 950°C. The samples were subsequently heated up to 1000° or 1100°C in a "Carbolite" furnace and held at this temperature for 3 hours.

The materials studies are listed in Table 1. This table also gives the theoretical fractional yield calculated on the basis that decomposition leads entirely to the oxide state. The observed yields are based on the final weights at 950°C (thermobalance) and 1100°C (separate furnace). The "Decomposition Temperature" is that temperature at which loss in weight begins, and the "Ter-

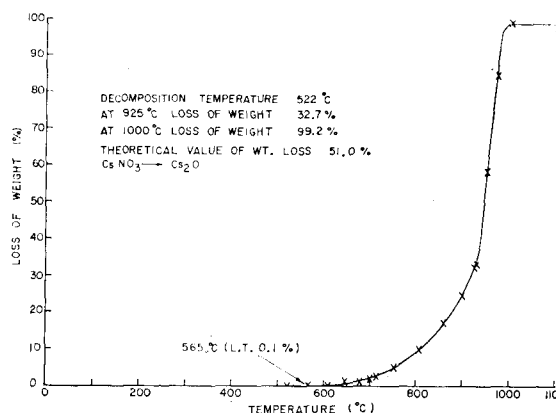


Fig. 1. Thermal Decomposition Curve of Cesium Nitrate

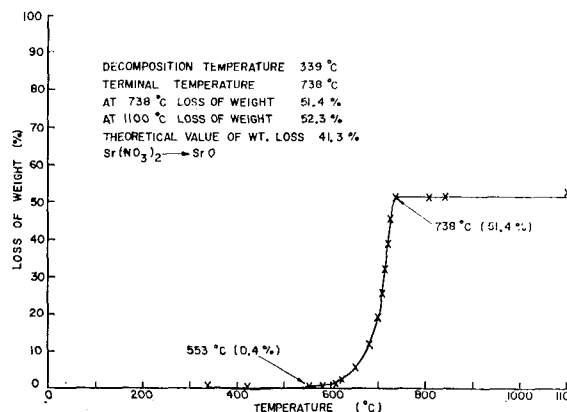


Fig. 2. Thermal Decomposition Curve of Strontium Nitrate

minal Temperature" is that temperature at which loss in weight ceases or the weight loss is within 1% of the theoretical loss.

The weight loss versus temperature data are presented as graphs for each individual compound.

## III. Results and Discussion

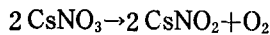
### (a) Nitrates of the principal fission products

#### Cesium Nitrate $\text{CsNO}_3$

The thermal decomposition curve of cesium nitrate is shown in Fig. 1. This shows

that cesium nitrate is very stable up to 522°C and no weight loss was observed. It has been reported that cesium nitrate is very stable and anhydrous at ordinary temperature 490° to 531°C<sup>2, 3)</sup>.

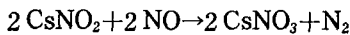
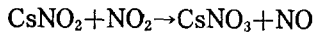
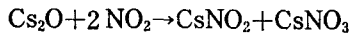
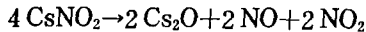
Cesium nitrate lost weight very slowly from, 522° to 600°C and then the loss rate gradually increased according to the reaction<sup>4)</sup>:



At 925°C the weight loss was 32.7%. The results suggest that weight would continue to be lost beyond this point.

When the sample was heated to 1000°C, the weight loss was 99.2%. This is consistent with reports<sup>2, 5)</sup> that the decomposition continues to 970°C and at this temperature it is completely volatilized.

The thermal decomposition of the nitrite at elevated temperatures proceeds according to the following equilibria<sup>12)</sup>:



In an open reaction system the nitrite should be converted to the oxide  $\text{Cs}_2\text{O}$ .

When the sample was heated up to 900°C, the colour was completely changed to orange, corresponding to that of the oxide, and the sample was volatilized. This indicates that cesium nitrate is converted to the oxide at less than 900°C and the oxide is volatile. The residue, which was still in the crucible at 1000°C, is probably due to impurities.

#### Strontium Nitrate $\text{Sr}(\text{NO}_3)_2$

Strontium nitrate began to lose weight at 340°C which continued very slowly up to 553°C. This is ascribed to the residual water of hydration<sup>5)</sup>.

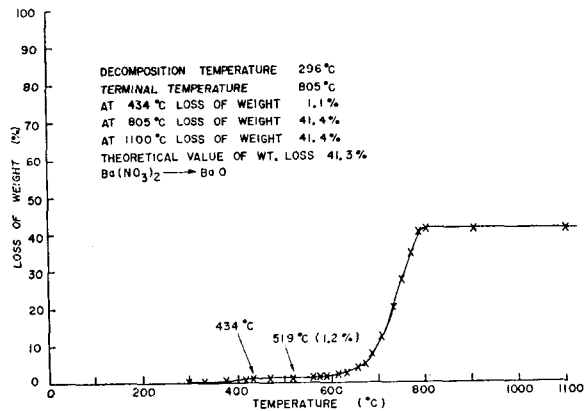


Fig. 3. Thermal Decomposition Curve of Barium Nitrate

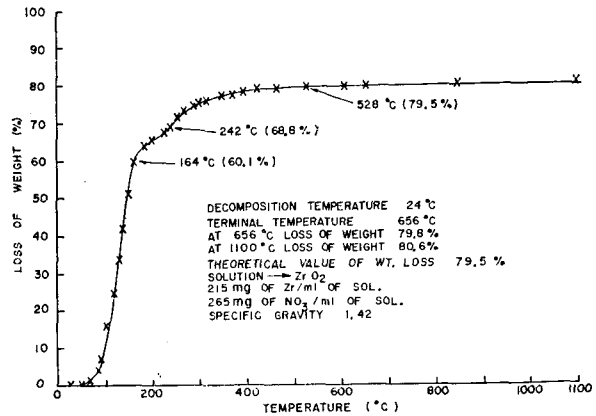


Fig. 4. Thermal Decomposition Curve of Zirconium Solution

As shown in Fig. 2, above 600°C it decomposed rapidly until a constant weight was obtained. At 738°C where a constant weight was reached the weight loss was 51.4%, compared to the theoretical value for the conversion of  $\text{Sr}(\text{NO}_3)_2$  to the oxide  $\text{SrO}$  (Table 1).

#### Barium Nitrate $\text{Ba}(\text{NO}_3)_2$

Barium nitrate began to lose weight at 296°C and then very slowly decomposed up to 434°C. A horizontal level appeared between 434°C and 520°C as shown in Fig. 3. Compared with the previous reports<sup>2, 2)</sup> that barium nitrate is stable up to 592°-600°C, this suggests that some impurities were

contained in the nitrate.

From 520° to 660°C it gently lost weight and then decomposed more rapidly up to 805°C corresponding to the conversion of the salt to the oxide BaO. It has been reported by Mukerji and Kayal<sup>3)</sup> that nitrous fumes start evolving at 661°C and the evolution becomes rapid at 692°C, and that a constant weight due to the oxide is observed at 986°C. It is probably due to the impurities that the complete conversion of the nitrate to the oxide appeared at the lower temperature.

#### Zirconium Solution

The zirconium is supplied as an aqueous solution of the basic nitrate. It started to lose weight at 24°C and then continued very slowly up to 70°C. This is due to vapourizing of free water contained in the solution. An intermediate product, like an anhydrous nitrate compound, should be formed at around 170°C.

As shown in Fig. 4, after a point of inflection at 190°C, its weight loss then increased until about 260°C and then it more slowly decomposed until the oxide ZrO<sub>2</sub> was completely obtained. This is due to the decomposition of the nitrate compound.

A constant weight was reached at 656°C and at this the weight loss was 79.8% very close to the theoretical value (Table 1). But, when the sample was heated to 1100°C, the weight loss increased to 80.5%.

#### Ruthenium Nitroso-Nitrate Solution

The ruthenium sample consisted of a solution of the nitroso-nitrate in water. It started to lose weight at 37°C and then slowly up to 70°C. After this point weight was rapidly lost up to 160°C. This is due to the evaporation of free water and the nitric acid contained in the solution.

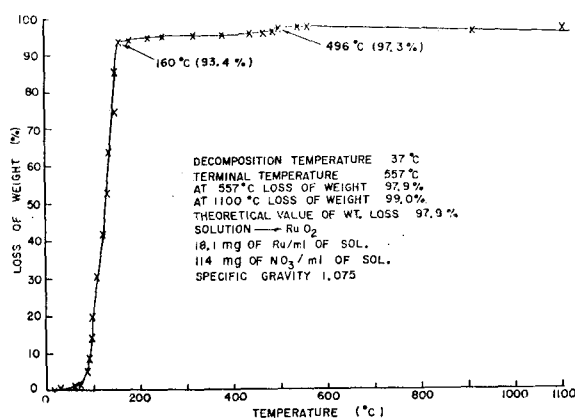
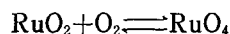


Fig. 5. Thermal Decomposition Curve of Ruthenium Solution

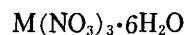
From 160°C to 480°C the thermal decomposition curve is very flat. (Fig. 5). After this there is a short period of decomposition. This is due to the ruthenium nitrate compound to the oxide RuO<sub>2</sub>. A constant weight was obtained at 557°C and the weight loss indicated 97.9% corresponding to the theoretical value for its complete conversion to the oxide RuO<sub>2</sub> (Table 1).

But when the sample was heated to 1100°C, the weight loss was 99.0%. According to Campbell et al<sup>5)</sup>, no weight is lost up to 1025°C and its weight is slowly lost between 1025° and 1400°C. This suggests that between 950°C and 1100°C the oxidation of RuO<sub>2</sub> to the volatile tetroxide becomes significant:



There is no evidence in our experiments that any RuO<sub>4</sub> is formed as a direct product of the decomposition of the nitroso-nitrate.

#### Rare Earth Nitrate Hexahydrate



The thermal decomposition of mixed rare earth nitrates hexahydrated (Fig. 6) shows that it begins to lose weight at 50°C and decomposes very slowly up to about 200°C. At this temperature the weight loss was

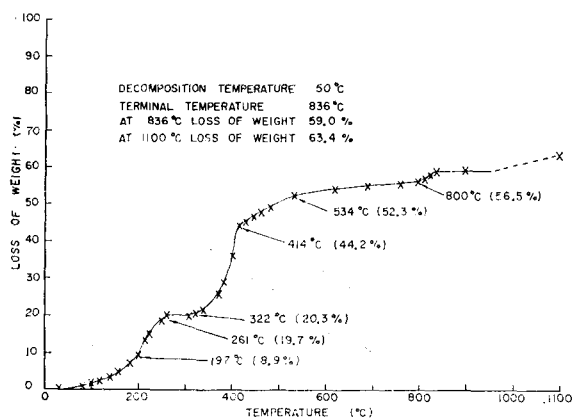


Fig. 6. Thermal Decomposition Curve of Rare Earth Nitrates Hexahydrates

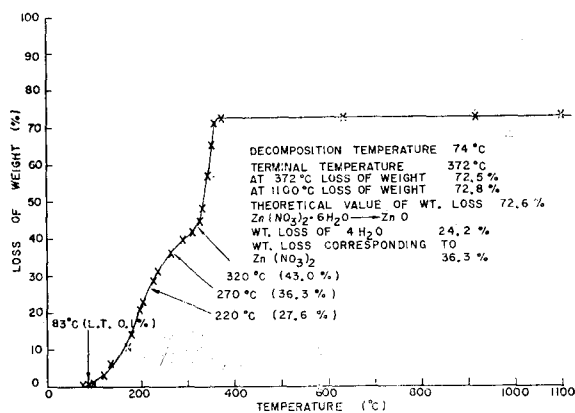


Fig. 8. Thermal Decomposition Curve of Zinc Nitrate Hexahydrate

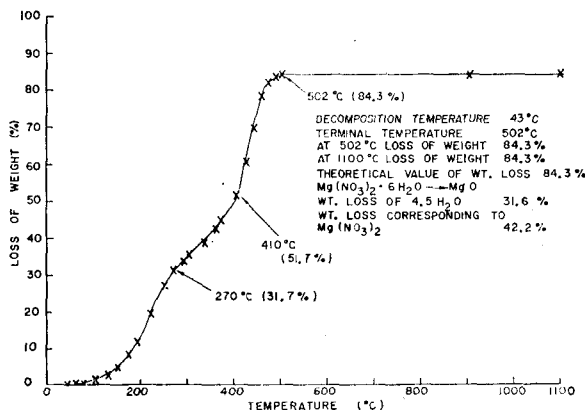


Fig. 7. Thermal Decomposition Curve of Magnesium Nitrate Hexahydrate

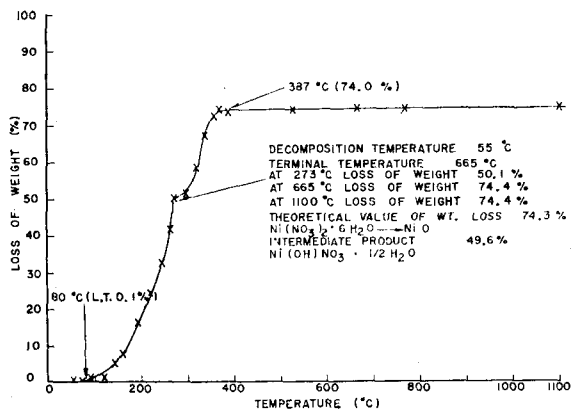


Fig. 9. Thermal Decomposition Curve of Nickel Nitrate Hexahydrate

9.6% which approximately corresponds to the weight loss of 3 molecules of water. And then the rate of weight loss rapidly increased at about 260°C. Between 260°C and 320°C an intermediate horizontal appeared. Presumably this corresponds to an anhydrous nitrate.

After this it decomposed rapidly to 414°C and the weight loss was 44.2%. And then the decomposition was sluggish. This is due to the formation of  $\text{MONO}_3$  as reported by Wendlandt<sup>6)</sup> and Wendlandt and Bear<sup>7)</sup>. As shown in Fig. 6, from about 535°C where the next inflection appeared it very slowly decomposed. This is due to the conversion

of  $\text{MONO}_3$  to the oxides. At about 810°C it began to decompose rapidly, and then the decomposition was completed at 836°C and the weight loss was 59.0%.

The decompositions of rare earth nitrates except neodymium nitrate are completed at less than 780°C but neodymium nitrate is completed at 830°C<sup>6, 7)</sup>. Then the rapid decomposition at 810°C is due to the conversion of  $\text{NdONO}_3$  to  $\text{Nd}_2\text{O}_3$ .

When the sample was heated up to 1100°C, the weight loss increased to 63.4%. Presumably this is due to the impurities contained in the original sample.

(b) Nitrates of other metals appearing

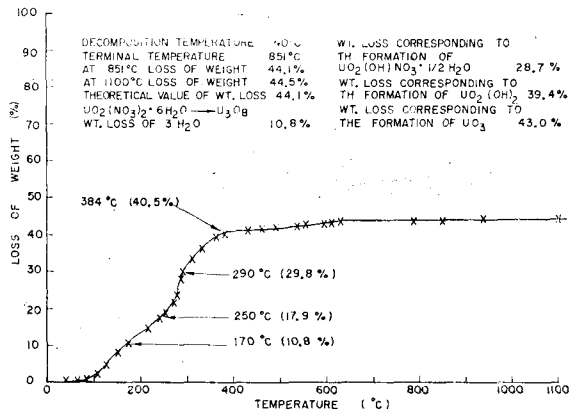


Fig. 10. Thermal Decomposition Curve of Uranyl Nitrate Hexahydrate

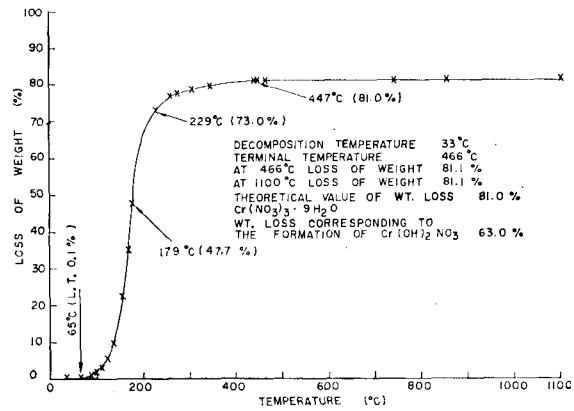


Fig. 12. Thermal Decomposition Curve of Chromic Nitrate Nonahydrate

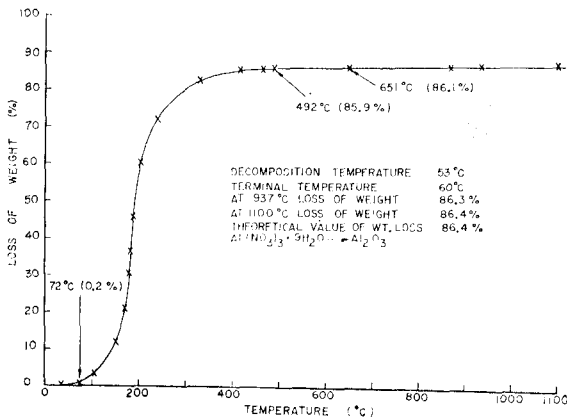


Fig. 11. Thermal Decomposition Curve of Aluminum Nitrate Nonahydrate

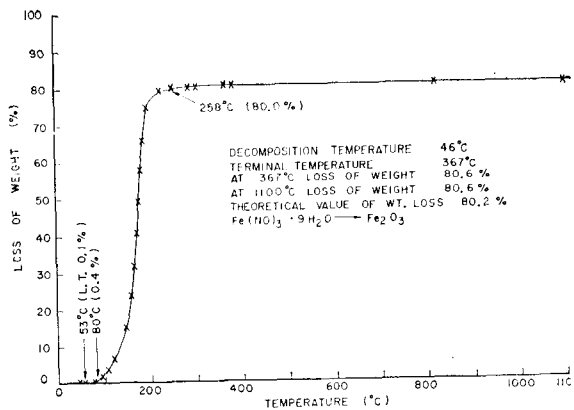


Fig. 13. Thermal Decomposition Curve of Ferric Nitrate Nonahydrate

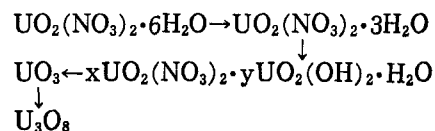
in MAGNOX waste

Magnesium and zinc nitrates, hexahydrated, began to decompose at 43° and 74°C, respectively. As shown in Fig. 7 and 8, their slowdowns occur, due to the formation of the anhydrous nitrates of magnesium and zinc.

Their decompositions were completed at 502° and 372°C, respectively, corresponding to the conversion of their salts to their oxides. As heating continued up to 1100°C, no more weight losses were observed and their weight losses approached their theoretical values (Table 1).

Nickel and uranyl nitrates, hexahydrated,

started to decompose at 55° and 40°C, respectively (Fig. 9 and 10). The thermal decomposition of uranyl nitrate at elevated temperature proceeds according to the following steps, which is similar to the thermal decomposition steps of nickel nitrate<sup>8)</sup>.



But, as shown in Fig 10, between 363°C and 628°C the curve of uranyl nitrate is divided into two steps at around 590°C. The first step is due to the formation of UO<sub>3</sub> and the second to the formation of U<sub>3</sub>O<sub>8</sub>.

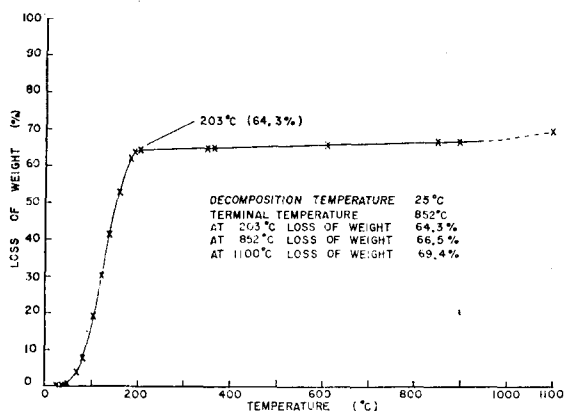


Fig. 14. Thermal Decomposition Curve of Gasil W.P. Silica

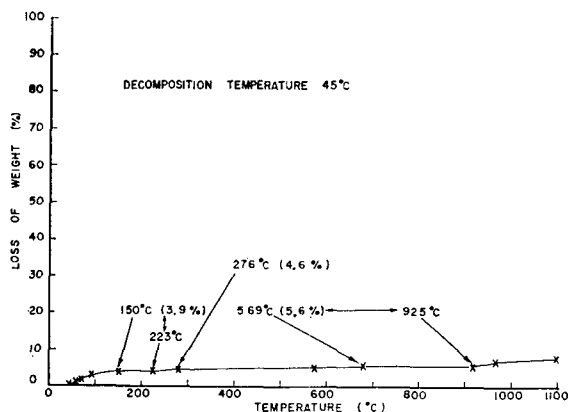


Fig. 15. Thermal Decomposition Curve of Neosyl Silica

The decomposition of nickel nitrates were terminated at 665° and 851°C, and their weight losses were equal to or closely approached their theoretical values (Table 1). When heated up to 1100°C, no more weight of nickel product was lost but the weight loss of uranium product slightly increased, due to the conversion of  $U_3O_8$  to  $UO_2$ .

Aluminum, chromic and ferric nitrates, nonahydrated, started to lose weight at between 33° and 53°C, and then decomposed very slowly to around 80°C, probably due to the moisture absorbed on the starting materials.

Their decompositions were completed at

460°, 466° and 367°C without any transition (Fig. 11 to 13), and their weight losses were equal to their theoretical values corresponding to the conversion of their nitrates to their oxides. By some other reports<sup>2, 9)</sup>, the constant weights were reached between 270° and 400°C, and at 250°C, respectively, due to the formation of intermediate products of chromium and iron, but there are no intermediate horizontals as shown in Fig. 12 and 13.

### (c) Nitrates or other chemicals used as glass formers

#### "Gasil WP" Silica

Gasil WP began to lose weight at very low temperature 25°C. Weight was lost rapidly up to 203°C, due to the removal of absorbed water.

As shown in Fig. 14, after this temperature weight was more remained constant but, when the sample was heated to 1100°C, the weight loss rose to 69.4%. It is considered that small weight losses beyond 203°C represent the removal of traces of tightly bound water and possibly of impurities in the silica.

#### "Neosyl" Silica

Neosyl started to lose weight at 45°C. As shown in Fig. 15, at 150°C 3.9% weight loss was recorded, due to the absorbed water on the silica. A horizontal existed between 150° and 223°C. And then more weight was smoothly lost up to 569°C.

Another horizontal appeared from 569°C and continued to 925°C. After this it lost weight loss for the sample heated to 1100°C was 7.7%, compared to 6.9% at 963°C.

Chemical analysis of the "Neosyl" silica gave the following data:

$$SiO_2 = 85.7\%$$

$$SO_4^{--} = 3.5\%$$



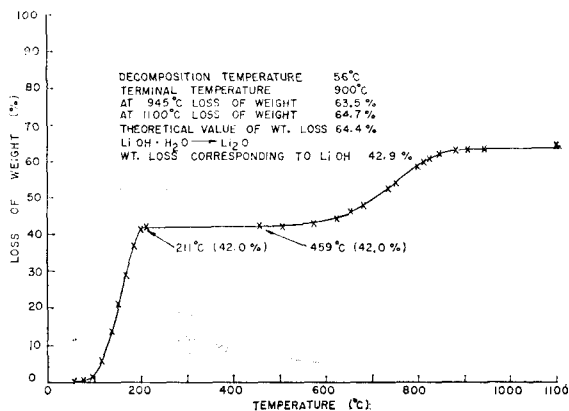


Fig. 16. Thermal Decomposition Curve of Lithium Hydroxide Monohydrate

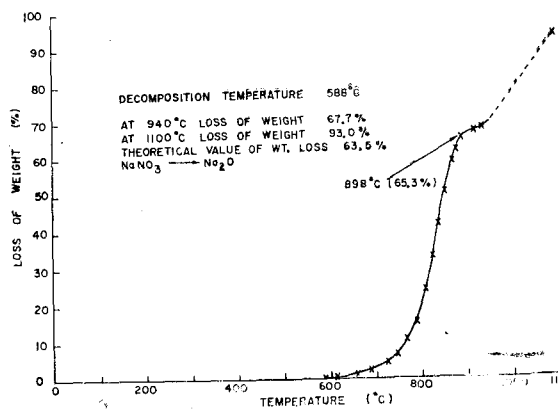


Fig. 18. Thermal Decomposition Curve of Sodium Nitrate

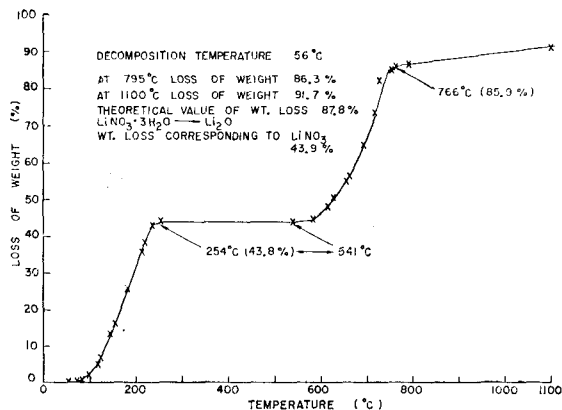
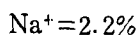


Fig. 17. Thermal Decomposition Curve of Lithium Nitrate Trihydrate



The residue (8.6%) is probably water. At 1100°C the weight loss was 7.7%. It appears that water is the only species removed up to 1100°C. However the water is bound to the silica with different degrees of firmness. 3.9% is removed by 150°C, the next 1.7% is removed between 223°C 569°C, and then no more is released until 925°C is reached and a further 2.1% is driven off by 1100°C. The other impurities ( $\text{SO}_4$  and Na) are still present at 1100°C.

Lithium Hydroxide Monohydrate  $\text{LiOH} \cdot \text{H}_2\text{O}$

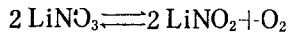
Lithium hydroxide monohydrate began to

dehydrate at 56°C. As shown in Fig. 16, between 90°C and 210°C the curve is steep and then a perfectly horizontal level exists between 210°C and 460°C. This is due to the complete dehydration of the water of crystallisation and the formation of the anhydrous hydroxide  $\text{LiOH}$ .

After this point the anhydrous hydroxide decomposed slowly up to around 340°C and the further weight was lost more slowly. At 945°C the weight loss was 63.5%. This shows that it was not quite completely converted to the oxide. When the sample was heated to 1100°C, the weight loss became 64.7% corresponding to the theoretical value for the complete conversion of the hydroxide to the oxide  $\text{Li}_2\text{O}$  (see Table 1).

Lithium Nitrate Trihydrate  $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$   
Lithium nitrate trihydrate began to dehydrate at 56°C. As shown in Fig. 17, an intermediate horizontal existed between 254° and 541°C, which corresponds to anhydrous salt  $\text{LiNO}_3$ . From 541°C to around 960°C the anhydrous salt decomposed rapidly and then sluggishly up to 1100°C at which a constant weight was reached. At this temperature the weight loss was 91.7% which is higher than theoretical value (see Table 1).

As mentioned in the sections on cesium nitrate and sodium nitrate, this nitrate can decompose to lithium nitrite:



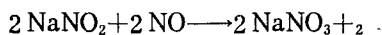
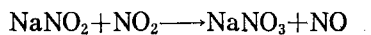
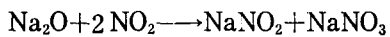
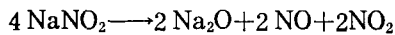
The yield at 1100°C is much less than expected for  $\text{Li}_2\text{O}$ . This is probably due not to the volatilization of the oxide itself, but to the volatilization of lithium nitrite.

#### Sodium Nitrate $\text{NaNO}_3$

The thermal decomposition curve of sodium nitrate (Fig. 18) shows that it begins to lose weight at 588°C and then smoothly decomposed up to 740°C. Above this to around 900°C where a point of inflection appeared its decomposition became rapid. At 900°C the weight loss was 65.3% somewhat more than the theoretical value corresponding to the conversion of the nitrate to the oxide  $\text{Na}_2\text{O}$  though it has been reported that this is completely vaporized<sup>10</sup>). A slowing-down occurs between 900°C and 940°C, and also the curve shows that the tendency to lose weight continues as illustrated in Fig. 18. When the sample was heated to 1100°C, the weight loss rose to 93.0%.

The thermal decomposition of sodium nitrate results in the formation of sodium nitrite and oxygen and the reaction is reversible<sup>4, 11</sup>).

The thermal decomposition of nitrites at elevated temperatures proceeds according to the following equation<sup>12</sup>):



Sodium monoxide has been reported that it begins to vaporize at 1350°C and sublimes at 1295°C at 600 mmHg<sup>10</sup>). Sodium peroxide has been reported that it decomposes to sodium monoxide and oxygen at 510-545°C<sup>10</sup>).

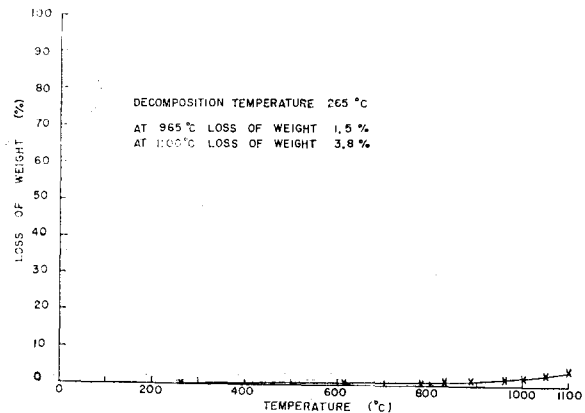


Fig. 19. Thermal Decomposition Curve of Sodium Carbonate

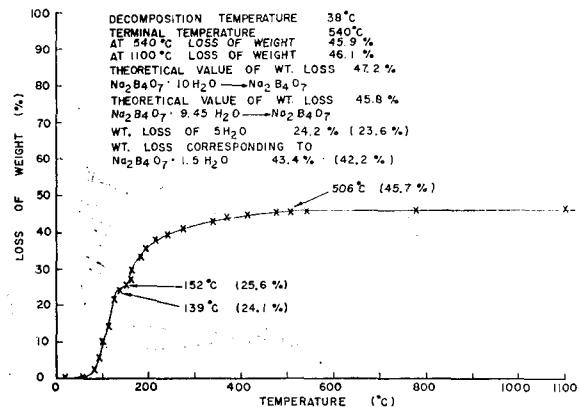


Fig. 20. Thermal Decomposition Curve of Borax

As reported by Newby and Dickerson<sup>11</sup>), sodium nitrate and nitrite are volatile and so this could account for the greater than theoretical weight loss.

The amount of sodium monoxide left in the crucible (~7%) will therefore depend on how decomposition of the nitrite occurs before it is completely volatilized.

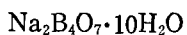
#### Sodium Carbonate Anhydrous $\text{Na}_2\text{CO}_3$

Sodium carbonate anhydrous began to lose weight at 265°C. As shown in Fig. 19, the weight was very smoothly lost at elevated temperatures. At 965°C the weight loss was 1.5% and, even when the sample was heated up to 1100°C, it was 3.8%. Sodium car-

bonate is expected to be very stable below the melting point.

The loss of sodium carbonate in weight<sup>13)</sup> has been reported not to exceed 1.57% on heating at 1000°C for 3 hours in platinum crucible.

#### Sodium Tetraborate Decahydrate



Sodium tetraborate decahydrate began to lose weight at 38°C as shown in Fig. 20. The Decahydrate has been to be stable up to 35°-38°C<sup>2)</sup>. And then it very slowly dehydrated up to around 70°C. After this it was rapidly dehydrated up to around 140°C where an intermediate horizontal was formed and at this the weight loss was 24.2% corresponding to the loss of 5 molecules of water.

After a point of inflection appeared at about 152°C (Fig. 9), its dehydration became rapid to about 200°C. It then smoothly dehydrated until an anhydrous salt was obtained. A constant weight was reached at 540°C which marked the completion of dehydration. The last stages of dehydration are very slow. This is in agreement with the report<sup>2</sup> that the last molecule of water is very firmly attached and it is necessary to carry the temperature to at least 500°C or even 525°C.

The weight loss at 540°C was 45.9% which was slightly below the theoretical value (Table 1). But, on an assumption that the starting material contains 9.45 H<sub>2</sub>O<sup>2)</sup>, the final weight loss closely approached the theoretical. It is expected that the decahydrate is not stable at the room temperature but rather Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> · 9.45 H<sub>2</sub>O is stable as previously reported<sup>2)</sup>.

#### IV. Conclusion

The above discussions indicate that oxides

of nitrogen are released due to the decomposition of the nitrates of fission products and other metals appearing in MAGNOX waste, and other nitrates used as glass former.

The nitrates hydrated begin to decompose at the range of 33° to 74°C but anhydrous nitrates above 290°C. All the nitrates, except alkali nitrates, are completely converted to their oxides below 850°C. The nitrate compounds of Ru, Cs, Na and Li or their products of decomposition are volatile below 1100°C. During the thermal decomposition when gradually heated in air, their intermediate products may be formed as the following:

- (1) Mg(NO<sub>3</sub>)<sub>2</sub>
- (2) Zn(NO<sub>3</sub>)<sub>2</sub>
- (3) UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> · 3H<sub>2</sub>O
- (4) Ni(OH)NO<sub>3</sub> · ½H<sub>2</sub>O
- (5) LiOH
- (6) LiNO<sub>3</sub>
- (7) Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> · 4.45H<sub>2</sub>O

The results obtained can be used in the analysis of process conditions in the vitrification and calcination of highly radioactive wastes and also of the thermal decomposition behaviour of mixtures containing those materials.

#### Acknowledgement

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#### References

1. J. B. Morris and B. E. Chidley, Preliminary Experience with New Vitrification Inactive Pilot plant. "Management of Radioactive Wastes from the Nuclear Fuel Cycle", Proceedings

- of Symposium March 1974, IAEA and NEA, Vienna, Vol. 1, p. 241
2. C. Cuval, Inorganic thermogravimetric Analysis, Elsevier Pub. Co. (1963)
  3. J. Mukerji and P.B. Kayal, J. Scient. Ind. Res., Vol. 34, p.457 (1975)
  4. M.C. Sneed and R.C. Brasted, The Alkali Metals-Comprehensive Inorganic Chemistry, Vol. 6, p. 130 (1957)
  5. P.F. Campbell et al, Anal. Chem., Vol. 33, p. 58 (1961)
  6. W.W. Wendlandt, Anal. Chim. Acta, Vol. 15, p. 435 (1956)
  7. W.W. Wendlandt and J.L. Bear, J. Inorg. Nucl. Chem., Vol. 12, p. 276 (1960)
  8. I.I. Kalinichenko and A.I. Purtov, Russian J. Inorg. Chem. Vol. 11, p. 891 (1966)
  9. E.M. Vander Wall, IDO-14597, USAEC (1962)
  10. J.W. Mellor, Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. I, Supl. II, Li, Na, John Wiley & Sons, Inc., p. 147 (1961)
  11. B.J. Newby and E.S. Dickerson, ICP-1008, USAEC (1972)
  12. T.M. Oxa and R.R. Walawalker, J. Indian Chem. Soc., Vol. 22, p.243 (1945)
  13. M.A. Bezborodov, J. Appl. Chem. U.S.S.R. Vol. 7, p. 517 (1934)
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