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Thermal and X-ray diffraction studies on the phase equilibria in the system $UO_2(NO_3)_2 \cdot 6H_2O$–$NaNO_3$

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Abstract

The interaction between uranyl nitrate hexahydrate and sodium nitrate at high temperatures has been studied using TG–DTA–EGA, infrared spectral and X-ray diffraction (XRD) measurements. Compound formation in the nitrate system was apparent from the differences in dehydration pattern of the nitrate mixtures as the composition was varied and also from the variation in crystallographic nature of the intermediate compounds formed. The results showed that compound formation was favoured in equimolar mixtures and intermediate nitrates of the type $Na[UO_2(NO_3)_3] \cdot H_2O$ and $Na_2[(UO_2NO_3)_2(O)_2]$ were formed. The latter compound which is essentially a dimerised sodium uranyl oxynitrate has been identified for the first time. XRD, infrared spectral and thermal stability data on this compound have been reported. It decomposes above 435°C to sodium diuranate. When the amount of sodium nitrate in the mixture is less than 50 mol%, the excess uranyl nitrate hexahydrate decomposes to U_3O_8 through the formation of hydroxynitrates of uranium and amorphous UO_3 rather than forming a mixed nitrate or oxide of lower sodium-to-uranium ratio. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

The interaction of nitrates of uranium and sodium is of interest in view of its importance in the conversion of nuclear waste from reprocessing plants to glass form [1,2] for immobilization. The high-level liquid waste (HLW) contains nitrates of the fission products cesium, rare earths, ruthenium, palladium, barium, strontium as well as corrosion products, like, zirconium, chromium, nickel and iron. Uranyl nitrate and other actinide nitrates, left over from the reprocessing step, are the other important constituents of HLW. Significant amounts of sodium nitrate are also generated during the reprocessing step. Glass forming additives like silicon dioxide, boric oxide, etc. and manganese oxide which helps to improve leach resistance and lower the pouring temperature of the glass [3] are added to HLW which is dried and calcined to oxide form before conversion to glass form. Interaction between the nitrates and formation of nitrate complexes at elevated temperatures could affect the drying and calcination steps. This, in turn, will affect the nature and composition of glass derived therefrom. Thermoanalytical methods and X-ray diffraction (XRD) measurements have been used extensively for the study of nitrato complexes of rare earths [4,5] and actinides [6]. However, very little information is available in the literature on the equilibria involving mixtures of actinide nitrates with other nitrates of interest in the context of nuclear waste immobilization. The earlier work [2,7,8] did not highlight the possible interaction between the various nitrates. In an attempt to gain insight into the nature of the relevant processes, we have taken up the study of a series of binary mixtures of nitrates of interest. A detailed study of the dehydration and decomposition mechanism of mixtures of

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uranyl nitrate hexahydrate and sodium nitrate is reported in the present paper.

2. Experimental

Uranyl nitrate hexahydrate was prepared from nuclear grade U_3O_8 as described elsewhere [9]. Mixtures of uranyl nitrate and sodium nitrate (BDH, AnalaR grade) containing 30, 40, 50, 60, 70 and 80 mol% of uranyl nitrate hexahydrate were prepared by mixing the required amounts of the two components and grinding gently in a dry glove box using a mortar and pestle to ensure a uniform mixture. The majority of the grains were found to be of 100 μm size when examined under a microscope. However, agglomeration of the powder because of its hygroscopic nature posed problems in obtaining reliable measurements of the particle size.

The TG–DTA–EGA measurements were carried out using 100 mg samples of the mixtures on a simultaneous thermal analyser (Model STA-409, Netzsch Gerätebau, GmbH, Germany) coupled by a heated capillary to a quadrupole mass spectrometer (Model QMG 311, Balzers, Leichtenstein) described elsewhere [9]. The sample environment was of argon (IOLAR-3, Indian Oxygen, Mumbai) maintained at a flow rate of 80 ml min^{-1} and the measurements were carried out at the heating rates of 3 and 10 K min^{-1}. Crucibles made from recrystallized alumina were used as specimen holders. XRD measurements were carried out on an X-ray diffractometer (Model PW1710, Philips, The Netherlands) using nickel-filtered Cu-Kα radiation. The intermediate compounds examined by XRD measurements were prepared by heating the desired mixture of the nitrates in the thermal analyser under the same conditions as used for TG–DTA–EGA measurements and cooling the specimen in argon flow by switching-off the furnace power. Infrared spectra were recorded in Nujol mull as well as KBr pellet in the range 200–4000 cm^{-1} on FTIR spectrometer (Model MB102, Bomem, Canada) using CsI windows.

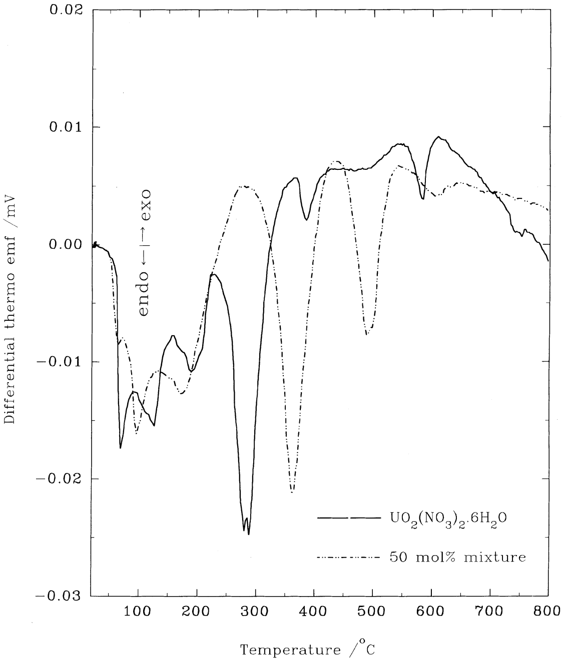


Fig. 1. DTA curves for pure uranyl nitrate hexahydrate and its 50 mol% mixture with sodium nitrate at a heating rate of 10 K min^{-1} in argon flow.

3. Results and discussion

The DTA curve for a mixture containing 50 mol% sodium nitrate is compared with that for pure uranyl nitrate hexahydrate in Fig. 1. The weight of uranyl nitrate hexahydrate in the mixture and that used for measurement with the pure component were the same. Uranyl nitrate hexahydrate is reported to melt at 60°C [10]. The extrapolated onset temperature read from the first endotherm for the pure $UO_2(NO_3)_2 \cdot 6H_2O$ in Fig. 1 corresponds to 60°C and indicates this endotherm to be due to melting. The corresponding peak temperature was in the range of 65–70°C, in close agreement with earlier reports [9,11] using DTA measurements on the melting endotherm for uranyl nitrate hexahydrate. The peak temperature was not significantly affected by the presence of sodium nitrate in the mixture as evident from Table 1. This indicated that interaction between the two nitrates, if any, took place after the melting of uranyl nitrate hexahydrate. The endothermic peaks for the subsequent dehydration reactions were at lower temperatures in the case of the mixture, indicating interaction between $UO_2(NO_3)_2 \cdot 6H_2O$ and $NaNO_3$ during the dehydration step. Another noticeable difference between the thermal decomposition patterns of the pure uranyl nitrate hexahydrate and the mixture of nitrates, evident from Fig. 1, is the significant enhancement in thermal stability of uranyl nitrate in presence of sodium nitrate. The first endotherm for denitration in pure uranyl nitrate hexahydrate (as evidenced by EGA curves discussed later) occurs in the temperature range of 225–365°C with a peak temperature of 290°C. In the case of the mixture containing 50 mol% sodium nitrate, however, the corresponding peak occurs in the higher temperature range of 280–430°C with a peak temperature of 365°C. This is indicative of formation of a more stable nitrate complex, containing both sodium and uranyl ions, as an intermediate during dehydration in the presence of sodium nitrate.

A comparison between the DTA curves for pure sodium nitrate and the mixture containing 50 mol% uranyl nitrate hexahydrate in heating–cooling cycles between

Table 1
Thermal decomposition data for mixtures of uranyl nitrate hexahydrate and sodium nitrate heated at the heating rate of 10 K min^{-1}

Composition (mol% uranyl nitrate hexahydrate)	Temperature range (°C)	Weight loss (%)	DTA peak temperature (°C)	EGA peak temperature (°C)	Reaction
30	25–270	14.9	71,130,170	–	Melting and dehydration accompanied by formation of $Na[UO_2(NO_3)_3]\cdot H_2O$, $UO_2(NO_3)_2\cdot 3H_2O$ and $UO_2(NO_3)_2\cdot 2H_2O$
40	25–270	16.0	71, 106, 125, 167		
50	25–265	14.6	68, 97, 129, 169		
60	25–215	15.3	65, 159		
70	25–215	13.8	70, 101, 144		
80	25–205	14.5	70, 142		
60	225–270	2.8	–		Dehydration and partial decomposition to form hydroxynitrates of uranium and small amounts of $Na[UO_2(NO_3)_3]\cdot H_2O$
70	221–260	4.0	246		
80	205–265	5.0	254		
30	285–435	15.3	387	380	Formation of $Na_2[(UO_2NO_3)_2(O)_2]$
40	285–425	17.1	373	368	
50	265–425	19.0	366	363	
60	275–430	20.8	314, 365	301, 360	Formation of amorphous UO_3, hydroxynitrates of uranium and small amounts of $Na_2U_2O_7$
70	265–370	20.9	314	315	
	370–415	2.4	402	401	
80	265–360	20.9	308	305	
	360–425	1.3	393		
30	450–510	6.9	493	489	Formation of $Na_2U_2O_7$
40	450–505	7.8	493	490	
50	435–525	8.4	495	490	
60	435–520	4.8	470	461	Formation of U_3O_8 and small amounts of $Na_2U_2O_7$
70	420–570	1.9	499	500	
80	430–550	1.1	486	–	
30	520–760	11.4	716,747	712, 745	Decomposition of excess $NaNO_3$
40	515–715	5.5	687	680	
50	540–625	1.1	600	594	

room temperature and 385°C is presented in Fig. 2. The weight of sodium nitrate in the mixture was adjusted to match with its weight for the DTA measurement with the pure component. Hence, in order to maintain the composition for 50 mol% mixture, a larger weight of the mixture than that used for recording Fig. 1 had to be employed for obtaining Fig. 2. The DTA curves for the mixture in Figs. 1 and 2 show general agreement. The differences in detail are due to decreased resolution in Fig. 2 resulting from the use of a larger size of sample. Pure sodium nitrate undergoes a crystalline transition at 276°C and melting at 307°C [10,12]. These are seen as endothermic peaks with extrapolated onset temperatures of 258°C and 300°C, respectively, in the heating cycle of the DTA curve for the pure sample in Fig. 2. Exothermic peaks for the reverse reactions are observed in the cooling cycle of the corresponding DTA curve. The absence of the sharp melting endotherm in the heating cycle and the exothermic peak for solidification of molten sodium nitrate in the cooling cycle of the DTA curve for the mixture is a clear evidence for the occurrence of interaction between the two components of the mixture below the melting temperature of sodium nitrate. In the absence of such interaction, an exotherm of the same magnitude as observed for the curve recorded with pure sodium nitrate should have been observed in the cooling mode of the DTA curve for the mixture.

The results of TG–DTA–EGA measurements for the various mixtures of uranyl nitrate hexahydrate and sodium nitrate examined are presented in Figs. 3(a), (b) and 4(a), (b) and Table 1. It is evident from these figures that the complex nitrate is formed only when uranyl nitrate hexahydrate and sodium nitrate react in equimolar amounts. When the amount of sodium nitrate is relatively small, e.g., mixture containing 80 mol% $UO_2(NO_3)_2\cdot 6H_2O$, the denitration reaction corresponds predominantly to denitration of uranyl nitrate hexahydrate and is initiated at the lower temperature of 225°C

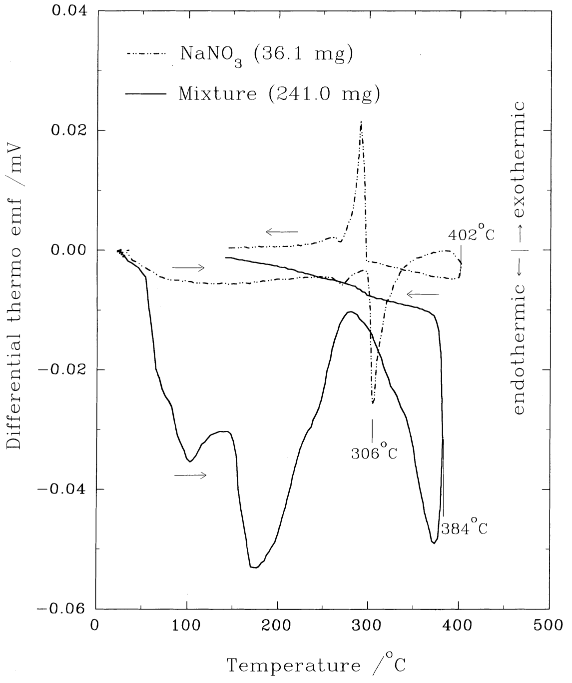


Fig. 2. DTA curves for sodium nitrate and 50 mol% mixture of sodium and uranyl nitrates in heating (→) and cooling (←) modes in argon flow at the heating/cooling rate of 10 K min^{-1}.

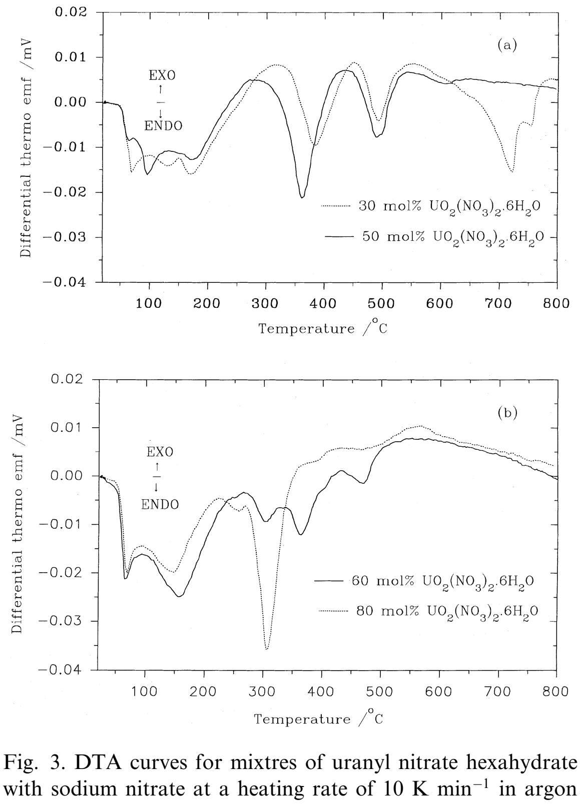


Fig. 3. DTA curves for mixtres of uranyl nitrate hexahydrate with sodium nitrate at a heating rate of 10 K min^{-1} in argon flow.

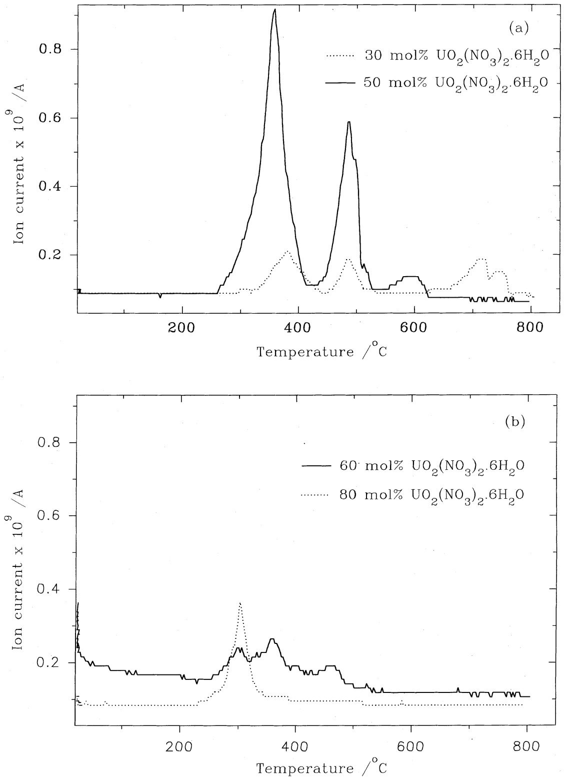


Fig. 4. EGA curves for the evolution of nitric oxide from mixtures of uranyl nitrate hexahydrate and sodium nitrate at a heating rate of 10 K min^{-1} in argon flow.

as observed for pure $UO_2(NO_3)_2 \cdot 6H_2O$ in Fig. 1. In the case of the mixture containing 60 mol% $UO_2(NO_3)_2 \cdot 6H_2O$ (Fig. 3(b)), there is sufficient quantity of sodium nitrate to form significant amount of the complex nitrate of uranium and sodium. However, the amount of sodium nitrate is not sufficient to convert the entire quantity of $UO_2(NO_3)_2 \cdot 6H_2O$. Hence the heated mixture contains both partially dehydrated uranyl nitrate and the complex nitrate which undergo denitration in different temperature ranges. This is indicated by the doublet endotherm for denitration in the temperature range of 225–425°C. The first of these endothermic peaks is due to the decomposition of unreacted uranyl nitrate and the second peak is due to the decomposition of the complex nitrate. For mixtures containing 50 mol% or more sodium nitrate the entire uranyl nitrate reacts to form the complex nitrate and the endothermic peak in the lower temperature range (225–350°C) is absent. When an excess amount of sodium nitrate is present, the complex nitrate is stabilised to higher temperatures in the molten mass containing nitrate ions from the molten sodium nitrate. These facts are also evident from the data presented in Table 1 where the temperature ranges quoted in column 2 correspond to

TG curves (which are less susceptible to heat transfer effects than DTA curves) and the results are average values of duplicate measurements.

Similarly, the endothermic peak in the temperature range of 435–520°C due to the decomposition of the intermediate from the complex nitrate is present as a well-defined peak only when the sodium nitrate content of the starting composition is 50 mol% or more. Further, the area under this peak (Fig. 3) and the corresponding weight loss (Table 1) have maximum values for the mixture with 50 mol% sodium nitrate. This suggested that the complex nitrate present at 265°C and its decomposition intermediate at 425°C are formed by the interaction of uranyl nitrate hexahydrate and sodium nitrate in equimolar ratios.

Excess sodium nitrate, if any present, decomposes endothermically above 520°C. This has also been independently confirmed by TG–DTA–EGA measurements on pure sodium nitrate. With larger samples, this decomposition is indicated by a doublet in the temperature range of 525–760°C. EGA curves for the evolution of nitric oxide, presented in Fig. 4, confirmed the different stages of denitration scheme inferred as above, and the temperature ranges of evolution of nitric oxide were in good agreement with those for the corresponding DTA peaks. A small peak for the evolution of nitric oxide above 520°C from the composition containing 50 mol% sodium nitrate (Fig. 4(a)) and the corresponding endothermic DTA peak (Fig. 3(a)) showed that even for this favourable composition, a small amount of sodium nitrate remained unreacted. This is possibly because of the heterogeneity of the mixture and the localised nature of the solid state reaction.

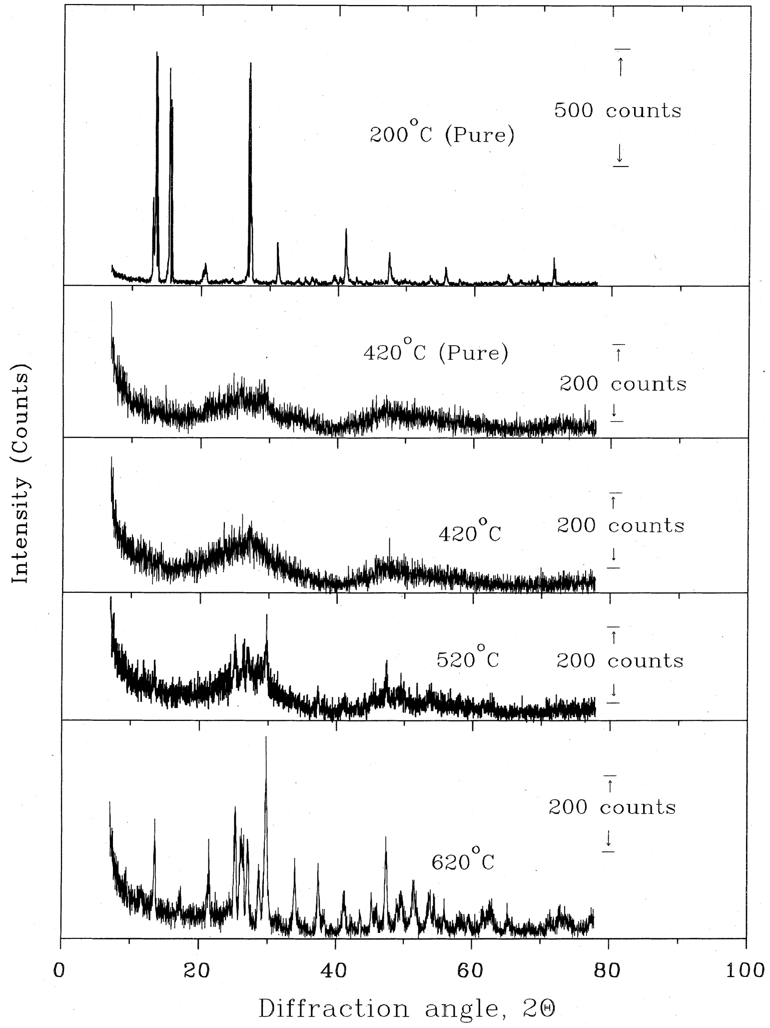


Fig. 5. X-ray diffraction data for heated samples of pure uranyl nitrate hexahydrate and its mixtures with 20 mol% sodium nitrate.

The above observations are supported by XRD studies on the residues from different stages of thermal decomposition of the mixture. The XRD patterns for the residue at 420°C from both pure uranyl nitrate hexahydrate and the mixture containing 80 mol% uranyl nitrate hexahydrate (Fig. 5) show amorphous nature indicating the product to be amorphous UO_3 reported [13] as one of the products formed during the decomposition of uranyl nitrate hydrates. It has been observed in our earlier studies [9] that the formation of UO_3 from uranyl nitrate hexahydrate takes place through hydrolysed and polymerised hydroxynitrate species. Apparently, in the absence of sufficient amount of sodium nitrate, the mixture undergoes hydrolysis and polymerisation in the presence of water vapour from the dehydration of uranyl nitrate hexahydrate and forms polymerised hydroxynitrates of uranium. These hydroxynitrates decompose to form amorphous UO_3 above 420°C. Continued heating of this residue in the thermal analyser under argon flow resulted in the self-reduction of amorphous UO_3 to α-U_3O_8 [14] as evidenced by the XRD patterns of the residues obtained at 520°C and 620°C. On the other hand, the patterns for residues at 302°C and 420°C of mixtures containing 50 mol% uranyl nitrate hexahydrate (Fig. 6) showed the formation of new crystalline phases on the attainment of these temperatures. The intermediate compound at 302°C shows an XRD pattern identical to that for $UO_2(NO_3)_2 \cdot 6H_2O$ indicating that dehydration and interaction between the two nitrates have not significantly altered the structure up to 300°C. The structure of uranyl nitrate hexahydrate is known [15] to correspond to the formula $[UO_2(NO_3)_2 \cdot 2H_2O] \cdot 4H_2O$. Apparently, the complex nitrate is formed by replacing the two water molecules in the inner coordination sphere of this structure with a bidentate nitrate group maintaining

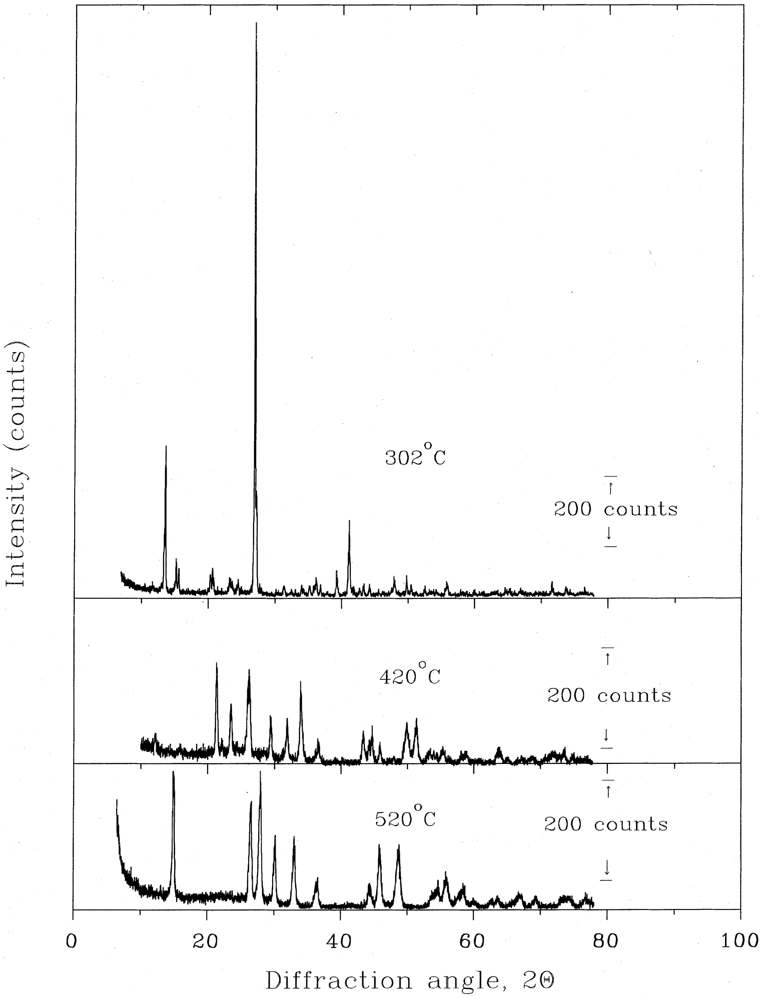
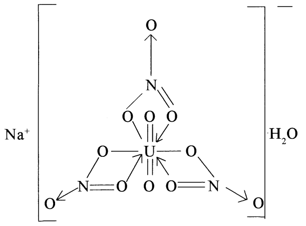
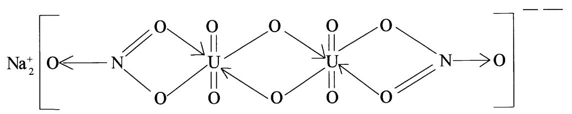


Fig. 6. X-ray diffraction data for 50 mol% mixtures of uranyl nitrate hexahydrate and sodium nitrate heated to various temperatures.

eight co-ordination for uranium to give a uranyl trinitrate complex [16], viz.,



The complex nitrate, $Na[UO_2(NO_3)_3]\cdot H_2O$, decomposes on further heating to form another crystalline complex nitrate stable up to 435°C. The XRD pattern (Fig. 5) of this new complex nitrate is found to be significantly different from that of $Na[UO_2(NO_3)_3]\cdot H_2O$. The infrared spectra of the residue at 420°C (Table 2) indicated the presence of both covalent (absorption peaks at 1563–1510, 996 and 781–684 cm^{-1}) and ionic (peaks at 1400–1328, 837 and 826 cm^{-1}) nitrates in the complex. The ionic character may also be attributed to unreacted sodium nitrate, if any, present in the residue. The peaks in the range 661–500 cm^{-1} are in the range of metal–oxygen stretching vibrations reported [17] for several hydroxyl-bridged complexes. These may therefore be assigned to the U–O–U stretching vibrations of the oxygen bridged dimeric species shown below. The metal–oxygen vibrations involving oxygen atoms of the nitrate groups occur in the range below 500 cm^{-1} [17]. The residue obtained from this mixture at 520°C had XRD pattern matching with that for sodium diuranate, $Na_2U_2O_7$ [21] which is known to be stable up to 1300°C [22]. These results and the weight loss data in the temperature range of 435–520°C from TG studies (Table 1) indicate the residue formed at 420°C to be a complex nitrate with uranium in six co-ordination, viz.,



Based on the above results and the weight loss percentages observed in the various temperature ranges for the mixture containing 50 mol% uranyl nitrate hexahydrate (Table 1), the following reaction scheme is proposed:

$$[UO_2(NO_3)_2(H_2O)_2]\cdot 4H_2O + NaNO_3 \overset{>60^\circ C}{\rightarrow} Na[UO_2(NO_3)_3]\cdot H_2O + 5H_2O, \tag{1}$$

$$2Na[UO_2(NO_3)_3]\cdot H_2O \overset{265^\circ C}{\rightarrow} Na_2[(UO_2NO_3)_2(O)_2] + 2H_2O + 2NO_2 + 2NO + 2O_2, \tag{2}$$

$$Na_2[(UO_2NO_3)_2(O)_2] \overset{435^\circ C}{\rightarrow} Na_2U_2O_7 + NO_2 + NO + O_2. \tag{3}$$

Table 2
Infrared absorption peaks for the residue obtained by heating a 50 mol% mixture of uranyl nitrate hexahydrate and sodium nitrate to a temperature of 420°C

Wave number (cm^{-1})	Peak assignment	Refs.
229 237	Metal–oxygen vibrations	[17]
248 254 282 303	UO_2^+ deformation	[18]
316 341 366 394 419 443 472	Metal–oxygen vibration (M–O–N)	[17]
502 527 546 576 661	Metal–oxygen vibrations (M–O–M)	[17]
684 709	ν_6 – out-of-plane rocking ($O–NO_2$)	[17]
740	ν_5 (NO_2 asym. bend)	[17]
781	ν_3 (NO_2 sym. bend)	[17]
826 837	ν_2 – out of plane (NO_3^- ion)	[19]
906 951	UO_2^{2+} asym. stretch	[18,20]
997	ν_2 – NO_2 sym. stretch	[17]
1296	ν_1 – symmetric stretch ($O–NO_2$)	[19]
1328 1357 1400	ν_3 – NO_2 stretch of NO_3^- ion	[19]
1510 1527	ν_4 – NO_2 asym. stretch	[17,19]
1542 1563	ν_1 – N–O stretch	[17]
1639	O–H bend (H_2O); ν_1 – N–O stretch	[17]

The lack of agreement between the theoretical and experimental weight losses is not significant considering that the reaction between the two nitrates might not have been complete in view of the localised nature of the solid state reactions. The peaks for the decomposition of sodium nitrate observed in the temperature range of 540–625°C in DTA and EGA curves and constituting a weight loss of 1.1% (Table 1) for the mixture containing 50 mol% uranyl nitrate hexahydrate support this conclusion.

4. Conclusions

It is evident from the present studies that uranyl nitrate hexahydrate and sodium nitrate interact above 60°C in equimolar amounts to form a complex nitrate, $Na[UO_2(NO_3)_3] \cdot H_2O$. This complex nitrate decomposes above 265°C to give another nitrato complex, $Na_2[(UO_2NO_3)_2(O)_2]$, which forms the stable compound sodium diuranate above 435°C. When the amount of sodium nitrate present is 30 mol% or less, the amounts of complex nitrates and sodium diuranate formed are not significant possibly because of hydrolysis of uranyl nitrate hexahydrate during dehydration, and most of the uranyl nitrate decomposes to U_3O_8. Unreacted sodium nitrate, if any, decomposes above 500°C. These factors have to be paid due attention while designing the calciner for the HLW.

Acknowledgements

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References

[1] J. Mukerji, A.S. Sanyal, Ann. Nucl. Eng. 3 (1976) 275.

[2] N. Jain, D.P. Pande, in: B. Bhattacharjee, B.M. Misra, V.K. Tangri, M.S. Krishnan, S.K. Ghosh, S.K. Malhotra (Eds.), Proceedings of Symposium on Advances in Chemical Engineering, BARC, Mumbai, Bhabha Atomic Research Centre, Mumbai, 1997, p. 181.

[3] G.A. Vaswani, P.B. Jahagirdar, R.C. Rastogi, N.S. Sunder Rajan, Bhabha Atomic Research Centre Report BARC-1028, 1979.

[4] A.-E. Gobichon, J.P. Auffredic, D. Louer, J. Solid State Chem. 144 (1999) 68.

[5] M. Karppinen, P. Kylakoski, L. Niinisto, C. Rodellas, J. Therm. Anal. 35 (1980) 347.

[6] S.R. Bharadwaj, M.S. Chandrasekharaiah, M.S. Gill, S.C. Jain, Thermochim. Acta 71 (1983) 247.

[7] K.S. Chunn, Studies on the thermal decomposition of nitrates found in highly active waste and of chemicals used to convert the waste to glass, Atomic Energy Research Establishment Report AERE-R8735, 1977.

[8] M.S. Sonavane, T.P. Valsala, R.G. Yeotikar, Kanwar Raj, in: S.R. Dharwadkar, H.S. Ray, S.B. Kanungo, S.R. Bharadwaj, A.C. Momin (Eds.), Proceedings of the Eigth National Symposium on Thermal Analysis, Regional Research Laboratory, Bhubaneswar, Dec. 19–21, 1991, Indian Thermal Analysis Society, Bombay, 1991, pp. 491.

[9] K.V. Rajagopalan, P.V. Ravindran, T.P. Radhakrishnan, J. Therm. Anal. 44 (1995) 89.

[10] D.R. Linde, H.P.R. Frederikse, Handbook of Chemistry and Physics, 76th Ed., CRC, Boca Raton, FL, 1985.

[11] W. Lodding, L. Ojamaa, J. Inorg. Nucl. Chem. 27 (1965) 1261.

[12] M.J. Harris, J. Phys.: Condens. Mater. 5 (1993) 5773.

[13] R.S. Ondrejcin, T.P. Garrett Jr., J. Phys. Chem. 65 (1961) 470.

[14] JCPDS International Centre for Diffraction Data, Powder Diffraction File, 1995, Card Nos. 24–1172, 43–1014.

[15] J.C. Taylor, M.H. Mueller, Acta Crystallogr. 19 (1965) 536.

[16] G.A. Barclay, T.M. Sabine, J.C. Taylor, Acta Crystallogr. 19 (1965) 205.

[17] J.R. Ferraro, Low Frequency Vibrations of Inorganic Coordination Compounds, Plenum, New York, 1971.

[18] A. Anderson, C. Chieh, D.E. Irish, J.P.K. Tong, Can. J. Chem. 58 (1980) 1651.

[19] B.M. Gatehouse, S.E. Livingstone, R.S. Nyholm, J. Chem. Soc. (1957) 4222.

[20] B.M. Gatehouse, A.E. Comyns, J. Chem. Soc. (1958) 3965.

[21] E.H.P. Cordfunke, B.O. Loopstra, J. Inorg. Nucl. Chem. 33 (1971) 2427.

[22] H. Kleykamp, Assessment of the Physico-chemical properties of phases in the Na–U–Pu–O system, Kernforschungszentrum Karlsruhe Report KfK 4701, 1990.