High Temperature Interaction Studies for Intermediate Product Characterization and Thermal Decomposition Mechanism

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Abstract:

Present studies have been carried out to understand the high temperature interaction behaviour of fuel material and fission product in stoichiometric, hypo stoichiometric and hyper stoichiometric ratios. Measurements have been performed using simultaneous thermogravimetric – evolved gas analysis and powder diffraction techniques on various molar mixtures (1:1, 3:1, 6:1, 1:3, 1:6) of uranyl nitrate hexahydrate and gadolinium nitrate hexahydrate respectively and the results are being discussed here. The intermediates and / or end products formed have been identified as $(U_{0.5}Gd_{0.5})O_2$, U_3O_8, $GdONO_3$, $(U_{0.25}Gd_{0.75})O_2$ for different molar mixtures of the two nitrates. Dissolution of gadolinium in uranium matrix has been indicated besides proposing the thermal decomposition mechanism of these mixtures at elevated temperatures.

Keywords: Uranyl nitrate hexahydrate, Gadolinium nitrate hexahydrate, Thermogravimetric analysis, Evolved gas analysis, Powder X-ray diffraction, Thermal decomposition mechanism

1. Introduction:

Axial and radial temperature gradients are observed during the burnup of nuclear fuel in a reactor[1]. It alters chemical composition due to interaction of fuel with products generated during fission reaction. The nuclear fuel and fission products interaction chemistry is dependent on many factors like a gradual increase of fission products during irradiation, change in the O/M (M = U or U + Pu) ratio and oxygen potential during burn up with increase in the O/M values of

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fuel. Additionally, chemical interactions between fuel and clad and / or clad and fission products have been observed in the case of failure of cladding materials. In lieu of these factors, thermal studies on these chemical interactions are necessary for the nuclear reactor safety.

Rare earths are one of the fission products during nuclear fission reaction and it has been reported that their oxides form solid solutions with uranium oxide under nuclear reactor operating conditions[2 - 13]. Gadolinium, in particular, is soluble in the uranium dioxide matrix at high temperatures in various concentration ranges[11]. It has been reported[12- 13] that uranium - gadolinium mixed oxide (U, Gd)O_2, containing 2 to 12 weight percent of gadolinium is suitable to make fuel rods. Gadolinium acts as a burnable absorber due to very high neutron absorption cross section of ^{155}Gd (60,700 barns) and ^{157}Gd (254,000 barns) radioisotopes for thermal neutrons and thus, it is commonly used in fresh fuel to compensate an excess of reactivity of reactor core. However, in the 540 MWe Indian Pressurized Heavy Water Reactors (PHWR), gadolinium is employed as the neutron poison by direct injection of a concentrated solution of gadolinium nitrate hexahydrate ($Gd(NO_3)_3 \cdot 6H_2O$) into the heavy water (D_2O) moderator in calandria[14].

Solution based method is attempted for the synthesis of mixed UO_2 - Gd_2O_3 oxides[5]. Solution combustion technique influence the product with carbonaceous material, requires isothermal heating at 800 ^{0}C in air for 4 hours to obtain pure end product. Solid - state reactions necessitate higher temperatures to synthesize desired products in pure form in comparison to sol-gel and solution combustion methods. However, our earlier studies show the preparation of mixed oxide, $(U_{0.5}La_{0.5})O_2$ by 500 ^{0}C from equimolar mixtures of uranyl nitrate hexahydrate (UNH) and lanthanum nitrate hexahydrate through high temperature interaction of intermediate compounds UO_3 and anhydrous lanthanum nitrate[15]. The solid - state reactions between nitrate compounds, UNH and gadolinium nitrate hexahydrate (GDNH) with various mol ratios have been studied using simultaneous Thermogravimetry - Evolved Gas Analysis (TG - EGA) and X-ray Diffraction (XRD) techniques and the results are discussed here.

2. Materials and Methods:

2.1. Materials:

Nuclear grade U_3O_8 was utilized to prepare UNH according to a previously reported method[16]. Analytical reagent grade GDNH was obtained from M/s. Sigma Aldrich.

2.2. Sample Preparation:

Mixtures of UNH : GDNH with mol ratios 1:1, 3:1, 6:1, 1:3 and 1:6 were prepared by mixing the weighed amounts of individual nitrates and grinding gently in a mortar with pestle.

2.3 Characterization:

2.3.1 Simultaneous TG – DTA – EGA measurements:

Netzsch Thermo-balance (Model No.: STA 409 PC Luxx) coupled to Bruker FTIR system (Model No.: Tensor 27) via a heated Teflon capillary (1 m long, 2 mm i.d.) was utilized for simultaneous thermal measurements involving thermogravimetry (TG) and Evolved Gas Analysis (EGA). The further details of instrument are described in our earlier publication[17]. Thermograms for individual binary mixture have been recorded using 100 mg of mixture at heating rate of 10 ^{0}C min^{-1} in the temperature range of 30 – 800 ^{0}C by employing 120 mL min^{-1} flow rate of high purity nitrogen gas.

2.3.2. XRD measurements:

Powder X - ray diffraction measurements were carried out on a X - ray diffractometer (Model PW1710, Philips, The Netherlands) using nickel filtered Cu K_α radiation, in 2θ region of 10^0 to 70^0 with a scanning step of 0.02^0 in 0.8 s, to identify the intermediate and end products of the respective binary mixture. FullProf.2k (Version 7.40 - Jan2021-ILL JRC) Program has been used for multi pattern Rietveld, profile matching & integrated intensity and refinement of X - ray data.

3. Results and Discussion:

3.1. Thermal decomposition of pure UNH and pure GdNH:

In order to understand the high temperature interaction behavior of a binary system and to propose its reaction mechanism, it is essential to know the high temperature behavior of individual components. Decomposition behavior of pure UNH and pure GdNH has been

independently studied in detail by our group and the respective decomposition mechanism along with intermediate and/or end products have been reported[18, 19]. Hence, if the need arises, this reported work will be referred to explain or interpret the data/curve obtained during the decomposition of UNH – GdNH binary mixtures. During present studies also, we performed measurements on pure UNH and pure GdNH to check the reproducibility of the high temperature behavior of the respective compounds and found the results to be reproducible. Only the relevant results of the work on these two pure compounds, which are necessary to explain the high temperature behavior of UNH - GdNH system, are being discussed here.

3.1.1 Thermal behaviour of UNH at elevated temperatures:

EGA curves of pure UNH, presented in Fig. 1A, show evolution of water, nitrogen dioxide and nitric acid. The IR absorption bands extracted from Gram Schmidt curve in the region of 1220 - 2095 and 3375 - 4000 cm^{-1} exhibits H-O-H bending and stretching vibrations, respectively[20]. The IR absorption spectra indicate evolution of H_2O in the temperature region of 60 – 220 ^0C.

Simultaneously recorded TG curve in Fig. 1A confirms dehydration with mass loss of 15.5% that corresponds to the release of 4.5 water molecules from UNH in the same temperature region. The IR absorption bands noticed with peak maximum at 1631 and 2919 cm^{-1} along with water bands above 220 ^0C. These IR absorption signatures have been assigned to NO_2 gas evolution[21]. As decomposition of UNH proceeds further, new FTIR absorption peaks with peak maximum at 885, 1309, 1704 and 3560 cm^{-1} confirm the presence of HNO_3 gas due to gas phasic interaction of H_2O and NO_2[22]. Evolution of water, NO_2 gas along with HNO_3 gas suggest simultaneous occurrence of dehydration and denitration reactions above 220 ^0C. The formation and decomposition of hydroxynitrates of uranium from UNH have been reported above 220 ^0C[18, 23]. The mass losses on TG curve [Fig.1A] seen in the temperature ranges of 220 - 350, 350 - 430 and 430 – 540 ^0C are accompanied by the evolution of mixture of HNO_3 and NO_2 gases up to 430 ^0C and only NO_2 gas above 430 ^0C on EGA curve. The hydroxynitrate and nitrato - complexes of uranium decomposes to amorphous uranium trioxide, (UO_3)[18]. The observed experimental mass loss of 42.5 % is in agreement with theorical mass loss for the formation of UO_3, from UNH by 540 ^0C.

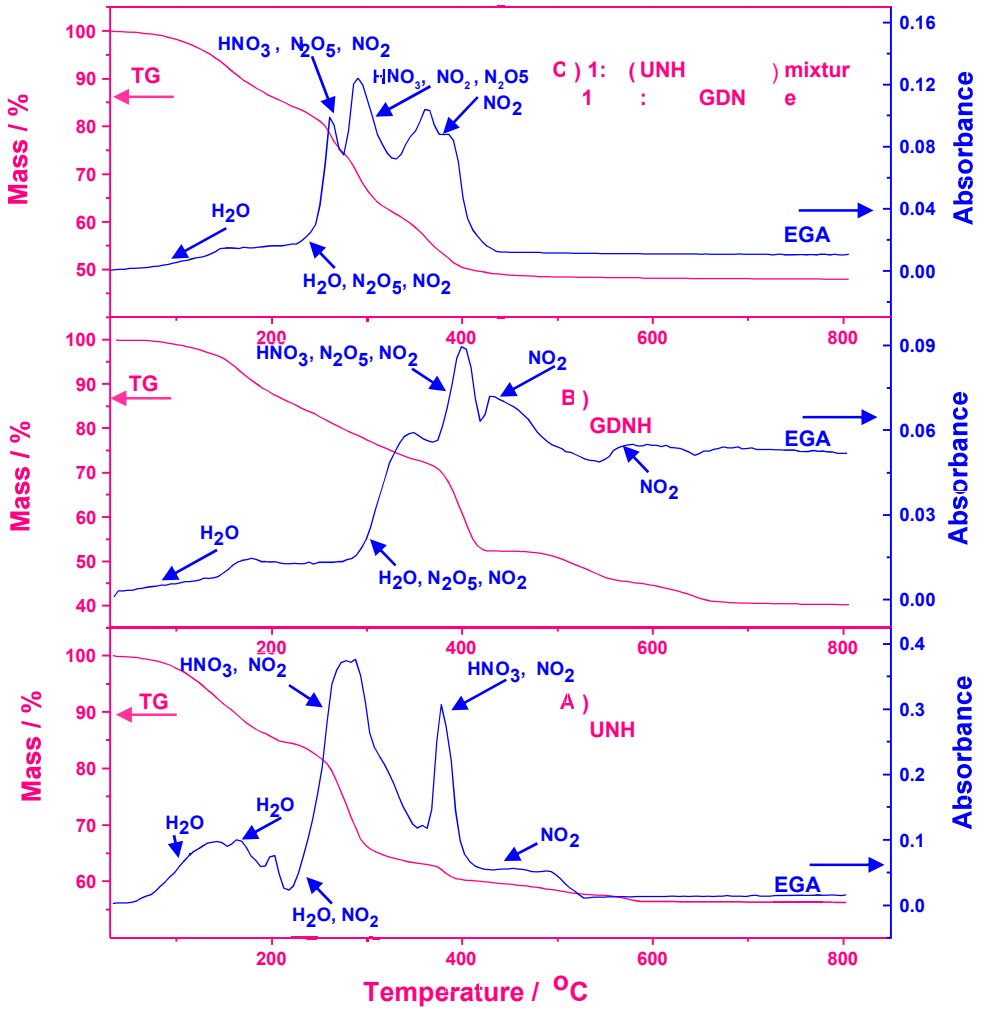

Fig. 1 . TG - EGA (Gram Schmidt) curves for A) Pure UNH ; B) Pure GDNH ; and C) 1:1 (UNH:GDNH) mixture recorded in nitrogen atmosphere

Decomposition of UNH to U_3O_8 occurs by 600 ^{0}C with experimental mass loss of 43.5% and matches well with the theoretical mass loss for the said reaction. These results are in concurrence with the reported work on UNH decomposition[18].

3.1.2 Thermal behaviour of GdNH at elevated temperatures:

TG - EGA curves of GdNH in Fig.1B show the formation and decomposition of various intermediate products recorded in the temperature region of 30 – 800 ^{0}C. Water is the only

volatile species in the temperature range of 70 – 220 ^{0}C on EGA curve exhibiting dehydration of GDNH. The additional IR absorption bands to water bands in the wavenumber regions of 817 - 933, 1240 - 1376 and 1376 - 1750 cm^{-1} above 220 ^{0}C indicates the presence of N_2O_5 gas[24]. Denitration of GDNH is initiated along with simultaneous dehydration above 220 ^{0}C[19]. The continued heating of the GDNH above 280 ^{0}C shows evolution of multiple gases involving H_2O, N_2O_5 and NO_2 and HNO_3. The evolution of H_2O or formation of HNO_3 from GDNH is not seen above 430 ^{0}C. The simultaneous evolution of H_2O, N_2O_5 and NO_2 and HNO_3 suggest the formation and decomposition of hydroxynitrate of gadolinium as reported earlier in the temperature range of 220 – 430 ^{0}C[19]. The mass loss of 47.7 % is observed on TG curve in the temperature range of 70 – 430 ^{0}C. It is in agreement with the theoretical mass loss for formation of gadolinium oxynitrate ($GdONO_3$) from the parent compound[24]. The evolution of NO_2 occurs above 450 ^{0}C due to decomposition of $GdONO_3$. A mass loss of 7.3 % from GDNH by 570 ^{0}C confirmed the formation of trimerized gadolinium oxynitrate, $Gd_3O_4NO_3$[18]. The subsequent mass loss of 4.3 % shows the decomposition of $Gd_3O_4NO_3$ to the stable gadolinium oxide, Gd_2O_3 by 680 ^{0}C.

3.2 High temperature interaction studies between uranyl nitrate hexahydrate and gadolinium nitrate hexahydrate in equimolar (1:1) mixture:

Figs. 1A, 1B and 1C show the TG – EGA curves of pure UNH, GdNH and equimolar mixture of UNH and GdNH. TG curve in Fig. 1C for 1:1 (UNH:GDNH) mol ratio mixture indicates the formation of the intermediate product as evidenced by the small plateau around 220 ^{0}C. A mass loss of 15.3 % in the temperature range of 60 – 220 ^{0}C is attributed to the evolution of the 8 water molecules out of 12 water molecules available in the mixture and these results were supported by water evolution from the mixture. It has been confirmed through simultaneously evolved gas curve in Fig. 1C along with the TG curve, depicting the decomposition behavior. Figs. 1A and 1B represent the EGA data on pure UNH and GdNH and indicate simultaneous denitration and dehydration of the respective oxynitrate above 220 ^{0}C[19], which were formed earlier as intermediate products below 220 ^{0}C. It can be seen from the EGA patterns of pure UNH and GdNH, given in Figs 1A and 1B respectively, that the inception temperature for the evolution of NO_2, N_2O_5 and H_2O gases matches well with the evolved gas pattern of the equimolar mixture (Fig.1C) and is in agreement with the inception temperature of simultaneous

denitration and dehydration from equimolar mixture of UNH and GdNH. This observation suggests the absence of interaction between the two nitrates of UNH and GdNH in the mixture up to 220 ^{0}C between the nitrates of UNH and GdNH in equimolar mixture and they independently dehydrate.

IR spectra extracted from Gram Schmidt curve of equimolar mixture confirms the evolution of water, dinitrogen pentoxide, nitrogen dioxide and nitric acid in the temperature range of 220 – 350 ^{0}C. This behavior is similar to the formation and decomposition of hydroxynitrates of pure UNH[18] and GdNH[19], therefore, these results suggest that, there is absolutely no interaction in the temperature range of 60 – 350 ^{0}C between the two nitrates, present in the equimolar mixture, and hence, the formation and decomposition of hydroxynitrates of uranium and gadolinium in the equimolar mixture is evidenced. Fig. 1C shows that TG curve of the equimolar mixture exhibit a single mass loss step in the temperature range of 350 – 470 ^{0}C and indicates the formation of stable compound by the temperature of 470 ^{0}C while the mass loss observed in Fig. 1A for pure UNH above 470 ^{0}C is absent in the case of equimolar mixture. Similarly, the comparison between TG curves of equimolar mixture and pure GdNH as given in Figs. 1C and 1B respectively, show that the mass loss steps involving to the decomposition of GdNH in the temperature ranges of 450 - 570 and 570 – 680 ^{0}C are absent in the mixture. The decomposition of pure UNH and GdNH to their oxides, U_3O_8 and Gd_2O_3, requires heating up to 600 and 680 ^{0}C, respectively[17, 18]. These results suggest that the hydroxynitrates of uranium and gadolinium undergo high temperature interaction above 350 ^{0}C and form thermally stable compound above 470 ^{0}C in equimolar mixture of UNH and GdNH.

1:1 (UNH:GDNH) mixture is heated independently to 800 ^{0}C and 470 ^{0}C in thermal analyzer, cooled to room temperature in inert atmosphere in order to characterize the residues by X - ray diffraction measurements. The mixture was heated isothermally to 800 ^{0}C and XRD pattern (Fig. 2A) was recorded in the 2Θ range of 20 – 90^0 for indexing purpose. It shows the absence of formation of either U_3O_8[26] and/or Gd_2O_3[27] as was found earlier in the case of pure UNH or GdNH. In the present case of equimolar mixture, fluorite type (CaF_2) of structure was obtained, resembling with the reported structure of UO_2[28]. Multipattern Rietveld, profile matching and integrated intensity refinement of X - ray data are given in Table 1. The decrease in lattice parameter to 0.5394 nm may be seen from Table 1 as compared to the reported value of 0.5467 nm for pure UO_2 lattice parameter. These results indicate the substitution of gadolinium in UO_2

lattice to form $(U_{0.5}Gd_{0.5})O_2$ mixed oxide[11]. Some of uranium atoms from existing +4 state are converted to +5 state in mixed oxide, $(U_{0.5}Gd_{0.5})O_2$, to maintain electrical neutrality. XRD pattern recorded in the 2Θ range of 10 – 70 ^{0}, for the equimolar mixture, heated to 470 ^{0}C, is given in Fig.2B. It resembles to Fig. 2A and indicate the formation of microcrystalline mixed oxide, $(U_{0.5}Gd_{0.5})O_2$ (marked as ▼), at 470 ^{0}C. It can be seen from Fig. 1C that the experimental mass loss of 51.8 %, obtained for 1:1 mixture in the temperature region of 60 – 470 ^{0}C is in good agreement with theoretical mass loss of 51.9 % for the formation of $(U_{0.5}Gd_{0.5})O_2$ as shown in Table 2. L. Pagano et.al.[29] have reported incomplete dissolution of gadolinium oxide in UO_2 matrix below 900 ^{0}C in the mixture of precursors containing oxides, UO_2 and Gd_2O_3. Our results indicate that solid state route can be utilized for preparation of phase pure mixed oxide $(U_{0.5}Gd_{0.5})O_2$. It should be mentioned here that present studies confirm the phase pure mixed oxide $(U_{0.5}Gd_{0.5})O_2$ formation at much lower temperature than reported by earlier workers[29] using different precursors for U and Gd during solid state route synthesis, as well as, by solution combustion synthesis[5].

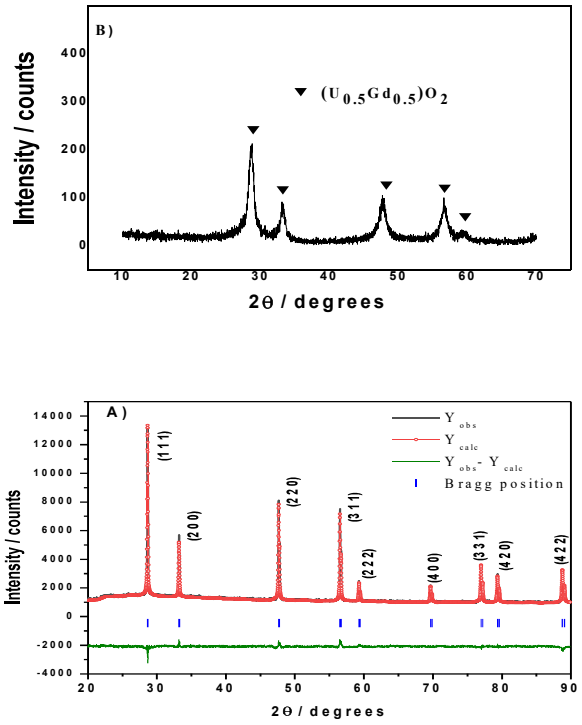

Fig.2. XRD patterns of A) 1:1 (UNH : GDNH) mixture isothermally heated at 800^{o}C for 2 hrs B) 1:1 (UNH : GDNH) mixture heated at 470 ^{o}C

Table 1. Multipattern Rietveld, profile matching and integrated intensity refinement of X - ray data

Molecular formula	$Gd_{0.5}U_{0.5}O_2$
Density$_{Theoretical}$	9.717 g/cm^3
Space Group	*F m 3 m*
Unit cell parameters: *a* (Å), *b* (Å), *c* (Å)	5.3944 (3), 5.3944 (3), 5.3944 (3)
Volume (Å^3)	156.97(7)
Refinement	Rietveld refinements (Fullprof-2K) (Rodriguez-Carvajal, 2000)
Profile	Pseudo -Voigt
Goodness-of-fit (χ^2)	2.38
R_p, R_{wp}, R_{exp}	3.50, 4.28, 2.78
R_F	3.37

Table 2. High temperature interaction mechanism for different UNH : GDNH mixtures

Composition (UNH : GDNH)	Temp. range (^{o}C)	Expt. mass loss (%)	Thero. mass loss (%)	Reactions
1 : 1 mixture	60 - 470	51.8	51.9	$UO_2(NO_3)_2.6H_2O + Gd(NO_3)_3.6H_2O \longrightarrow 2(U_{0.5}Gd_{0.5})O_2 + 11H_2O + 2HNO_3 + 3NO_2 + O_2$
3 : 1 mixture	60 - 660	46.9	47.9	$3UO_2(NO_3)_2.6H_2O + Gd(NO_3)_3.6H_2O \longrightarrow 2(U_{0.5}Gd_{0.5})O_2 + 2/3U_3O_8 + 22H_2O + 4HNO_3 + 5NO_2 + 11/6\ O_2$
1 : 3 mixture	60 - 410	50.3	49.9	$UO_2(NO_3)_2.6H_2O + 3Gd(NO_3)_3.6H_2O \longrightarrow 2(U_{0.5}Gd_{0.5})O_2 + 2GdONO_3 + 22H_2O + 4HNO_3 + 5NO_2 + 3/2O_2$
	410 - 670	4.6	4.9	$2(U_{0.5}Gd_{0.5})O_2 + 2GdONO_3 \longrightarrow 4(U_{0.25}Gd_{0.75})O_2 + 2NO_2$
1 : 6 mixture	60 - 410	50.0	49.1	$UO_2(NO_3)_2.6H_2O + 6Gd(NO_3)_3.6H_2O \longrightarrow 2(U_{0.5}Gd_{0.5})O_2 + 5GdONO_3 + 41H_2O + 8HNO_3 + 7NO_2 + 1/2O_2$
	410 - 670	6.2	7.1	$2(U_{0.5}Gd_{0.5})O_2 + 5GdONO_3 \longrightarrow 7(U_{0.143}Gd_{0.857})O_2 + 5NO_2$

3.3 Thermal studies on uranyl nitrate hexahydrate rich (3:1) and (6:1) mixtures at high temperatures:

Fig. 3A displays the simultaneously recorded TG and EGA curves for (3:1) (UNH: GDNH) mixture and the water evolution peak can be seen in the temperature region of 60 – 220 ^{0}C. TG

curve exhibits the perceptible break at 220 ^{0}C, with a mass loss of 15.8 % corresponding to loss of

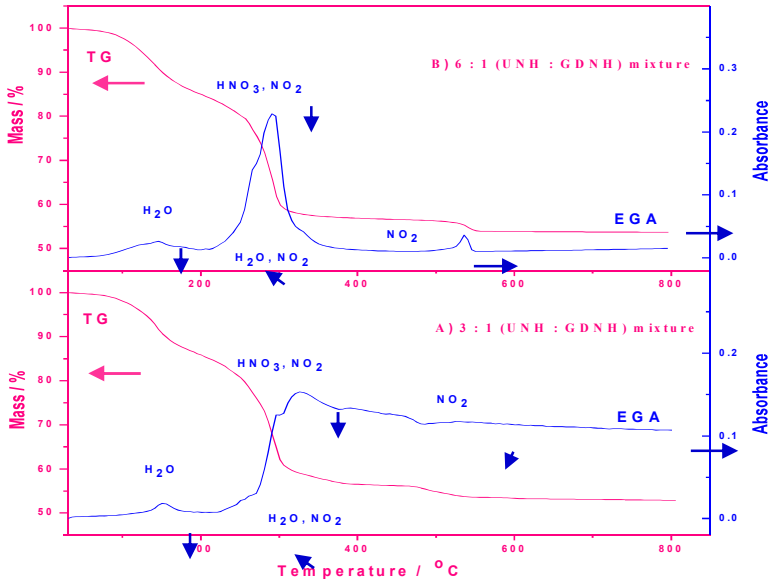

Fig. 3. TG – EGA (Gram Schmidt) curves for A) 3:1 (UNH: GDNH) mixture and B) 6:1 (UNH: GDNH) mixture in nitrogen atmosphere

seventeen water molecules out of twenty four water molecules available in the mixture. TG curves of the UNH rich mixture (3:1) has a small plateau at 220 ^{0}C corresponding to the formation of hydroxynitrates of gadolinium and uranium, during dehydration. Simultaneous evolution of H_2O, NO_2 and HNO_3 in the temperature region of 220 – 400 ^{0}C confirms the decomposition of hydroxynitrate intermediates. The evolution of H_2O, NO_2 and HNO_3 gases was confirmed through IR spectra extracted from Gram Schmidt curve, recorded simultaneously with TG curve and shown in Fig.3A.

XRD pattern shown in Fig. 4A recorded by heating UNH rich mixtures independently and maintaining identical conditions to that of TG-EGA measurements, confirmed the formation of

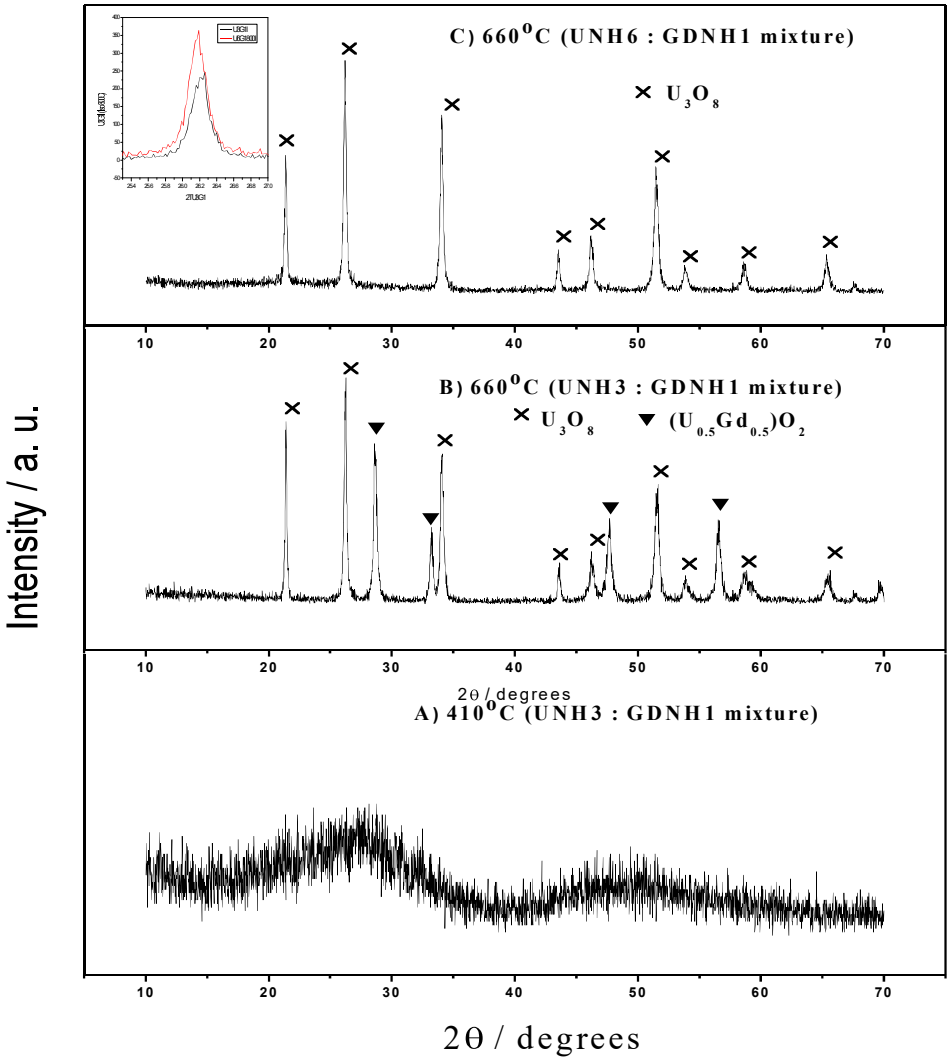

Fig. 4 . XRD patterns of A) 3:1 (UNH: GDNH) mixture heated to 410 ^{0}C; B) 3:1 (UNH: GDNH) mixture heated to 660 ^{0}C; and C) 6:1 (UNH: GDNH) mixture heated to 660 ^{0}C

amorphous phase at 410 ^{0}C. The formation of UO_3 has been reported at 540 ^{0}C in the case of pure UNH[18], therefore, the amorphous nature of residue can be attributed to the signatures of hydroxynitrates of uranium[23] at 410 ^{0}C. Probably due to small amounts and masking effect of amorphous phase the microcrystalline mixed oxide $(U_{0.5}Gd_{0.5})O_2$, could not be seen on XRD pattern. XRD pattern shown in Fig. 4B on the residue obtained at 660 ^{0}C evidenced the

formation of $(U_{0.5}Gd_{0.5})O_2$ and U_3O_8. The recorded XRD patterns matches well with the reported[11] pattern of $(U_{0.5}Gd_{0.5})O_2$ and JCPDS Card nos - 47 - 1493[26]. Excess UNH, remaining after 1:1 mol reaction between UNH and GdNH, leads to the formation of U_3O_8 on decomposition. A mass loss of 46.9 % indicated in Table 2 from initial mixture in the temperature range of 60 – 600 ^{0}C is in agreement for the formation of $(U_{0.5}Gd_{0.5})O_2$ and U_3O_8 . The chemical composition of formed mixed oxide, $(U_{0.5}Gd_{0.5})O_2$, is unaltered even with additional two mols of UNH in the initial mixture.

Water evolution from Gram Schmidt curve in Fig. 3B in the temperature range of 60 – 220 ^{0}C and corresponding mass loss of 16.7 % on TG curve suggest the release of 30.5 water molecules from available 42 molecules of 6:1 (UNH:GDNH) mixture. TG curve of 6:1 mixture has the similar decomposition behavior as of pure UNH, given in (Fig. 1A). This is possible due to higher concentration of UNH in 6:1 mixture. The evolution of H_2O, NO_2 and HNO_3 gases and associated mass loss of 46.1 % from the mixture is observed in the temperature range of 60 – 660 ^{0}C.

Figure 4 depicts the XRD patterns recorded for uranium rich mixtures. It can be seen from Figure 4C that only U_3O_8 phase is formed at 660 ^{0}C in (6UNH:1GdNH) mixture. Probably due to the dissolution of gadolinium oxide in U_3O_8 matrix, the presence of mixed oxide, $(U_{0.5}Gd_{0.5})O_2$ is not seen in the XRD pattern. It has been reported by Ohmichi et al.[30] that if O/M (where M= U + R) ratio is around 2.00, then there is a decrease in lattice parameters due to the dissolution of trivalent rare earth oxides in UO_2 matrix. It can also be seen from the Figure 4 inset, that 2θ value decreases as the UNH concentration in mixture increases from (3:1) to (6:1) or we may say that there is an increase in d spacing which suggests the hypo stoichiometric compound formation and gadolinium getting dissolved in U_3O_8 matrix at higher temperatures in excess of U_3O_8. It has been reported[18] that during UNH decomposition, the intermediate UO_3 is formed at 470 ^{0}C which release oxygen to give U_3O_8 as final product. During this in-situ generated oxygen rich environment, destabilization of hypo stoichiometric mixed oxide is possible which may lead to release of gadolinium from mixed oxide and its dissolution in U_3O_8 matrix. According to Ho and Radford[31], the increase in the oxygen potential reduces the oxygen vacancies concentration and also allow the creation of oxygen interstitials, which would counterbalance the formation of the small size cations ($U^{5+}$and U^{6+}). In general, the sintered density of UO_2 pellet decreases and

pore becomes coarse by the addition of U_3O_8 or we can say that U_3O_8 acts as a density controller and pore former[32]. The decrease in the density of samples, sintered under high oxygen potential atmosphere was explained by Nishida and Yuda[33] on the basis of closed porosities formation. They have mentioned that despite the enhanced diffusivity of U and Gd ions with oxygen potential, under oxidizing atmospheres, the effective diffusion length necessary to form solid solution is slightly elongated due to a barrier effect of closed porosities formation. This may be the reason of destabilization of $(U_{0.5}Gd_{0.5})O_2$ in the presence of excess U_3O_8 at higher temperatures.

3.4 Thermal studies on uranyl nitrate hexahydrate deficient (1:3) and (1:6) mixtures at high temperatures:

Simultaneous TG - EGA curves for 1:3 (UNH:GDNH) and 1:6 (UNH:GDNH) mixtures are given in Figs. 5A and 5B, respectively. The experimental mass losses of 15.0 and 14.8 % are observed only for dehydration of mixtures in the temperature region of 60 – 220 ^{0}C for 1:3 and 1:6 mixtures respectively. The observed mass loss is in agreement with theoretical mass for evolution of 15 water molecules from 1:3 mixture and 25.5 water molecules from 1: 6 mixture. The evolution of H_2O, N_2O_5, NO_2 and HNO_3 gases indicate simultaneous dehydration and denitration of mixtures in the temperature range of 220 – 410 ^{0}C. The peak maxima (Tp) for evolution of HNO_3, N_2O_5 and NO_2 gases noticed at 390 ^{0}C, in Fig. 5B, matches well with Tp for HNO_3, N_2O_5 and NO_2 gases of pure GDNH due to high concentration of GDNH in 1:6 mixture.

TG curves for both the mixtures show a perceptible break around 410 ^{0}C in Figs. 5A and 5B, corresponding to the formation of the intermediate product.

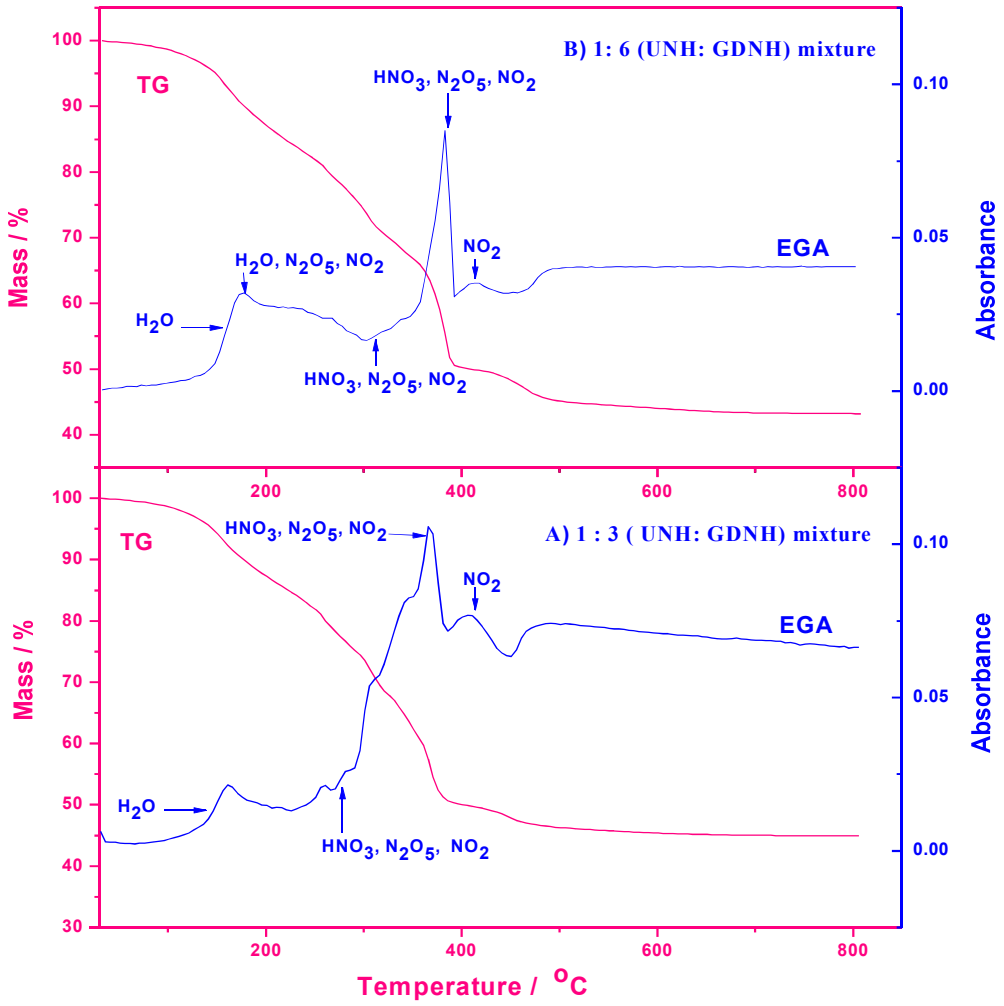

Fig. 5. TG – EGA (Gram Schmidt) curves for A) 1:3 (UNH: GDNH) mixture and B) 1:6 (UNH: GDNH) mixture in nitrogen atmosphere

1:3 mixture is heated to 410 ^{0}C to identify the compounds using XRD measurement and the results are given in Fig. 6A. The formation of $(Gd_{0.5}U_{0.5})O_2$ and $GdONO_3$[34] is shown from the XRD pattern. These results confirm the interaction between hydroxynitrates of gadolinium and uranium in equimolar ratio to form mixed oxide, $(Gd_{0.5}U_{0.5})O_2$. The formation of gadolinium oxynitrate, $GdONO_3$, is the result of decomposition of remaining GDNH present in the 1:3 and 1:6 mixtures, after formation of $(Gd_{0.5}U_{0.5})O_2$.

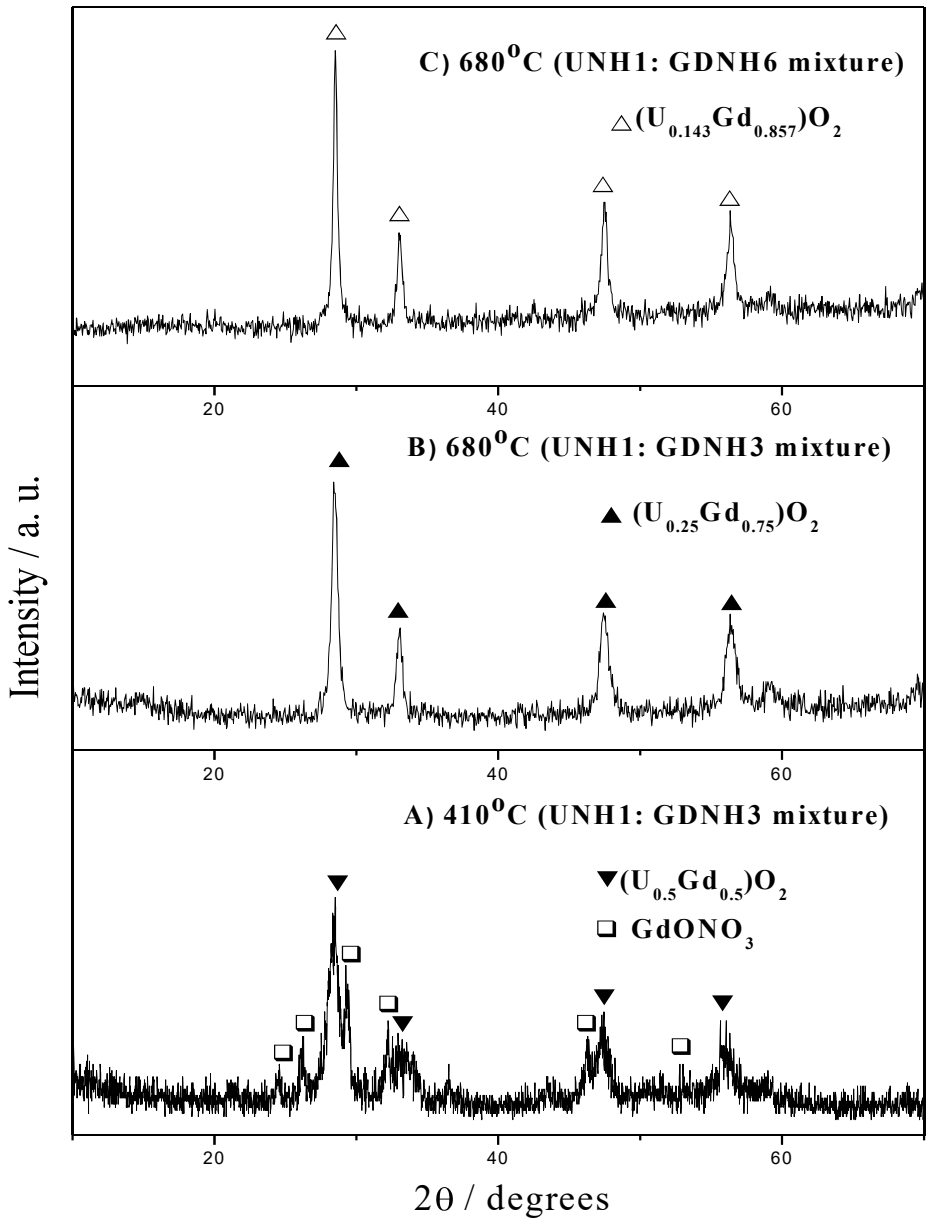

Fig.6 . XRD patterns of A) 1:3 (UNH: GDNH) mixture heated at 480 ^{0}C; B) 1:3 (UNH: GDNH) mixture heated at 680 ^{0}C; and C) 1:6 (UNH: GDNH) mixture heated at 680 ^{0}C

TG curves show the mass losses from 1:3 and 1:6 mixtures in the temperature range of 410 to 680 ^{0}C which are attributed to the denitration as evidenced from NO_2 evolution in Figs. 5A and 5B. XRD patterns in Figs. 6B and 6C show the formation of $(U_{0.25}Gd_{0.75})O_2$ and $(U_{0.143}Gd_{0.857})O_2$ for 1:3 and 1:6 mixtures, respectively. The oxynitrate complex, $GdONO_3$ reacts

with mixed oxide $(Gd_{0.5}U_{0.5})O_2$, to form abovementioned oxides. Our results are in agreement with published work of M. Durazzo et.al.[11], suggesting substitution of gadolinium in uranium dioxide. The reaction mechanism is proposed based on the agreement between experimental and theoretical mass losses for 1:3 and 1:6 mixtures in Table 2, supported by evolved gas analysis and XRD data.

Conclusions

Present studies confirm that the mixtures of UNH and GdNH decompose to form the hydroxynitrates of uranium and gadolinium, without any interaction between two nitrates upto 220 ^{0}C. The hydroxynitrates intermediates in equimolar mixture of UNH and GdNH, interact together to give $(Gd_{0.5}U_{0.5})O_2$ by 470 ^{0}C. Uranium rich binary mixture (3:1) decomposes to give U_3O_8 and $(Gd_{0.5}U_{0.5})O_2$ as the end product by the temperature of 660 ^{0}C. It has been established that 6:1 mixture results in the formation of U_3O_8 only, suggesting the dissolution of gadolinium in the presence of five excess mols of uranium in the mixture. In the case of gadolinium rich 1:3 mixture, formation of $(U_{0.25}Gd_{0.75})O_2$ could be seen by the temperature of 680 ^{0}C while in 1:6 gadolinium rich mixtures, $(U_{0.143}Gd_{0.857})O_2$ is formed.

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