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Separation of uranium from $(U,Th)O_2$ and $(U,Pu)O_2$ by solid state reactions route

Meera Keskar, K.D. Singh Mudher *, V. Venugopal

Fuel Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India

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Abstract

Solid state reactions of UO_2, ThO_2, PuO_2 and their mixed oxides $(U,Th)O_2$ and $(U,Pu)O_2$ were carried out with sodium nitrate upto 900 °C, to study the formation of various phases at different temperatures, which are amenable for easy dissolution and separation of the actinide elements in dilute acid. Products formed by reacting unsintered as well as sintered UO_2 with $NaNO_3$ above 500 °C were readily soluble in 2 M HNO_3, whereas ThO_2 and PuO_2 did not react with $NaNO_3$ to form any soluble products. Thus reactions of mixed oxides $(U,Th)O_2$ and $(U,Pu)O_2$ with $NaNO_3$ were carried out to study the quantitative separation of U from $(U,Th)O_2$ and $(U,Pu)O_2$. X-ray diffraction, X-ray fluorescence, thermal analysis and chemical analysis techniques were used for the characterization of the products formed during the reactions.

1. Introduction

Fuel reprocessing and re-fabrication are the essential steps for sustained operation of the nuclear power program. Reprocessing has an important objective of recovering the valuable actinide materials from the irradiated fuel discharged from the reactors, with the aim of recycling and thus increasing the overall utilization of the fuel materials. THOREX (Thorium–Uranium Extraction) and PUREX (Plutonium–Uranium Extraction) are the well known aqueous processes used worldwide for the separation of a fissile U^{233} from the fertile Th^{232} and fissile Pu^{239} from fertile U^{238}, respectively [1,2]. However, both the processes are time consuming, involve many steps and thus produce a lot of highly radioactive liquid waste, disposal of which is a major problem. In addition, the THOREX process produces the hazardous high gamma active nuclides, like U^{232} in the separated U^{233} product and Th^{229} and Th^{228} in the separated Th^{232} product [3].

For the recovery and separation of U^{233} from $(U,Th)O_2$ and Pu^{239} from $(U,Pu)O_2$ respectively, the mixed oxides should be brought in the soluble form. Sintered UO_2 is readily soluble in concentrated nitric acid, because it gets easily oxidized to UO_2^{2+} by HNO_3, whereas it is difficult to dissolve sintered ThO_2 and PuO_2, even in concentrated nitric acid due to the difficulty in oxidizing them [4]. These oxides are soluble in concentrated nitric acid only in the presence of fluoride ions, which act as catalyst. As fluoride ions are incompatible with the conventional reprocessing process and also enhance the corrosion of the dissolver vessel [5], it becomes necessary to remove fluoride ions from the

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* Corresponding author. Fax: +91 22 25505151.

E-mail address: kdsingh@apsara.barc.ernet.in (K.D. Singh Mudher).

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dissolved solution. Since UO_2–ThO_2 as well as UO_2–PuO_2 form solid solutions in the full range of 0–100%, the dissolution of these mixed oxides become a difficult task. Heisbourge et al. [6] have studied the dissolution of mixed uranium–thorium dioxide in nitric acid medium as a function of leaching time, acidity of leachate and temperature. High pressure dissolution at high temperature has been tested as one possible method to enhance the dissolution rate of mixed oxides [7].

Non-aqueous or pyrochemical processing is an alternative route to the aqueous extraction process, that can be used for bringing the actinide oxides into the soluble form by fusing them with alkali metal or alkaline earth metal melts [8,9]. The non-aqueous reprocessing route involves few steps and thus producing less radioactive waste.

It is reported that reactions of PuO_2 and/or $(U,Pu)O_2$ with alkali salts or alkaline earth salts, enhanced the solubility of the oxide in mineral acids [10,11]. Solid state reactions of different sulphate salts of potassium with UO_2, ThO_2 and their mixed oxides upto 900 °C showed the formation of various products, which were readily soluble in dilute acids [12]. Identification of various reaction products formed during the solid state reactions of UO_2, ThO_2 and PuO_2 with $(NH_4)_2SO_4$ [13,14] was helpful in knowing the temperature and minimum proportion of the salt required for bringing the oxides into soluble form.

Fujino et al. [15] have carried out the reactions of unsintered as well as sintered UO_2 with various amounts of sodium nitrates and sodium carbonates in air to determine the minimum amount of salt required to form sodium uranates, which were readily soluble in dilute nitric acid. The formation of sodium thorate is reported by reacting ThO_2 with sodium oxide in the dry box at 770 °C in the argon atmosphere [16]. Sodium plutonates are prepared by reacting PuO_2 with sodium oxide and sodium peroxide in an oxygen atmosphere between 400 and 900 °C [17].

In this study, reactions of UO_2, ThO_2 and PuO_2 and their mixed oxides $(U,Th)O_2$ and $(U,Pu)O_2$ were carried out in the solid state with sodium nitrate in air upto 900 °C, with an aim to study the reactivity of these oxides with sodium nitrate and to examine the dissolution and separation of U, Th and Pu from the respective mixed oxides. Cerium is a structural and chemical homologue of plutonium and also a major fission product [18]. Reactions of CeO_2 and mixed oxide of $(U,Ce)O_2$ were carried out with sodium nitrate as a model for the study of reactions of PuO_2 and $(U,Pu)O_2$, respectively. X-ray diffraction (XRD), X-ray fluorescence (XRF), thermal analysis and chemical analysis methods were used for the characterization of various compounds formed during the reactions and to study the dissolution and separation of the above mentioned oxides.

2. Experimental

2.1. Sample preparation

UO_2 was prepared by equilibrating U_3O_8 (nuclear grade) in an atmosphere of moist Ar + 7%H_2 at 800 °C for 4–5 h. ThO_2, CeO_2 and PuO_2 were obtained by decomposition of oxalates of thorium, cerium and plutonium, respectively at 800 °C in air. The formation of all the oxides was confirmed by powder X-ray diffraction (XRD). Mixed oxides of composition $(U_x,Th_{1-x})O_2$ with $x = 0.25$, 0.50 and 0.75 were prepared by co-precipitating U and Th with NH_4OH from their nitrate solutions mixed in the required proportions. The hydroxides were filtered, dried and heated in moist Ar + 7%H_2 at 800 °C for 4–5 h. Mixed oxide of compositions $(U_y,Ce_{1-y})O_2$ with $y = 0.85$ and 0.90 and $(U_z,Pu_{1-z})O_2$ with $z = 0.50$ and 0.90 were prepared by a co-precipitation method similar to the $(U_x,Th_{1-x})O_2$ precipitation method. The formation of these mixed oxides was confirmed by XRD patterns. All the actinide oxides and their mixed oxides were further mixed separately with $NaNO_3$ (Merck 99.9%) in 1:1, 1:2 and 1:4 molar ratios. The mixtures were well ground using a pestle and mortar and heated in alumina boats in a furnace in air atmosphere at different temperatures.

2.2. Instrumental analysis

X-ray powder diffraction patterns of the heated products at various temperature intervals were recorded on a Diano X-ray diffractometer using nickel-filtered Cu Kα radiation ($\lambda = 0.15418$ nm).

Qualitative analysis of uranium, thorium and plutonium elements was done by XRF method on samples mounted on filter papers in a Diano X-ray fluorescence spectrometer, using tungsten X-ray tube operated at 50 kV and 30 mA, and LiF 200 ($2d = 0.40267$ nm) dispersion crystal and NaI–Tl scintillation counter. Thermograms of the reaction mixtures of UO_2, ThO_2, CeO_2 and their mixed oxides with sodium nitrate were taken on an ULVAC TGD 7000 thermoanalyzer, recording both thermogravimetric (TG) and differential thermal analysis (DTA) curves simultaneously. The samples were heated in alumina cups at a heating rate of 10 °C/min in a flowing air stream. Thermograms of PuO_2 and $(U,Pu)O_2$ with different amounts of $NaNO_3$ were recorded on a Mettler thermoanalyzer enclosed in a glove box especially designed for handling radioactive materials. A stream of dry air was used as cover gas. For DTA studies, pre-heated sintered alumina was used as the reference material.

2.3. Chemical analysis

All the heated products obtained during the reaction of oxides and $NaNO_3$ at different temperatures were treated with 2 M HNO_3 and the solutions were warmed on a hot plate.

The analysis for U content in the solutions was carried out by redox titrimetry following Davies and Gray method [19]. In the weighed aliquots of the sample uranium, mainly present as U(VI), was reduced to U(IV) using excess Fe(II) in 10 M H_3PO_4. The excess of Fe(II) was destroyed selectively by adding HNO_3. U(IV) was then titrated against standard $K_2Cr_2O_7$ solution using potentiometric end point detection method.

Thorium in the heated products was anlaysed by chemical analysis using xylenol orange indicator [20]. Thorium content in the weighed aliquot of the reaction products was dissolved in concentrated HNO_3 by adding 2–3 drops of 0.05 M HF solution. NH_4OH was added drop wise in the solution in 1:1 proportion with continuous stirring, to get the pH of solution between 2 and 3. Thorium was then titrated against standard EDTA solution using xylenol orange indicator.

Plutonium and cerium content in the dissolved heated products were analysed following the redox titrimetic method reported earlier [14]. For determining Pu and Ce content, weighed aliquots of the reaction products were dissolved in concentrated HNO_3. Two to three drops of 0.05 M HF were added for the dissolution of plutonium. The aliquots were oxidized using AgO solution. Pu(VI) and Ce(IV) in the solutions were further reduced to Pu(IV) and Ce(III) respectively, using known excess of standard Fe(II) solution and titrated against standard $K_2Cr_2O_7$ solution.

3. Results and discussion

3.1. Thermal study of $NaNO_3$

TG and DTA curves of pure $NaNO_3$ (Merck 99.99%) recorded simultaneously, in air upto 900 °C, are shown in Fig. 1. TG curve of the compound showed a single step mass loss between 520 and 900 °C due to the decomposition of $NaNO_3$ to Na_2O, accompanied with two endothermic DTA peak at 745 °C and 875 °C [21]. DTA curve showed two additional endothermic peaks, at 265 °C and at 306 °C, due to the reversible phase change and melting of the compound respectively. The reversible phase change at 260 °C in $NaNO_3$ is reported earlier by Johnson et al. [22].

3.2. Reactions of the actinide oxides with $NaNO_3$

3.2.1. Reaction of UO_2 with $NaNO_3$

TG and DTA curves of reaction mixture of UO_2 with $NaNO_3$ in 1:1 molar ratio are given in Fig. 2. TG curve showed mass loss in a single step between 300 and 520 °C, along with endothermic DTA peak at 360 °C. DTA curve also showed two additional endothermic peaks at 260 °C and 310 °C, due to the phase change and melting of $NaNO_3$ respectively. TG curves of reaction mixture of $UO_2 + NaNO_3$ in 1:2 and 1:4 molar ratio, recorded upto 900 °C showed decomposition in the temperature ranges of 320–500 °C, 550–750 °C and 760–840 °C. The mass losses are accompanied with three endothermic DTA peaks at 380 °C, 710 °C and 780 °C respectively. Before the decomposition, two more endothermic peaks were observed at 260 °C and 310 °C, as in the case of pure $NaNO_3$, due to the phase change and melting of $NaNO_3$ respectively. Thermogram of the reaction mixture of UO_2 and $4NaNO_3$ is given in Fig. 3. To identify the intermediate products, the reaction mixtures were heated at different temperatures in

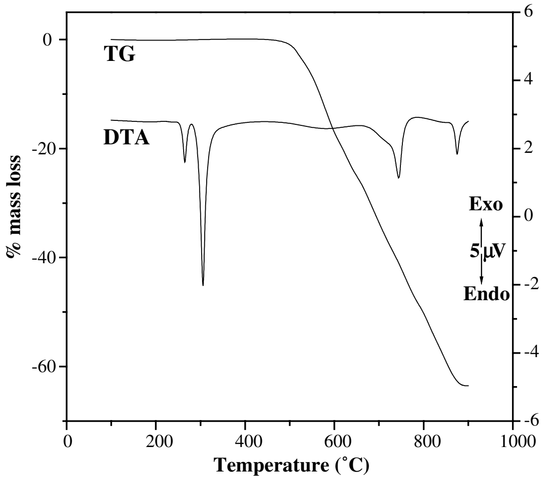

Fig. 1. TG and DTA curves of $NaNO_3$.

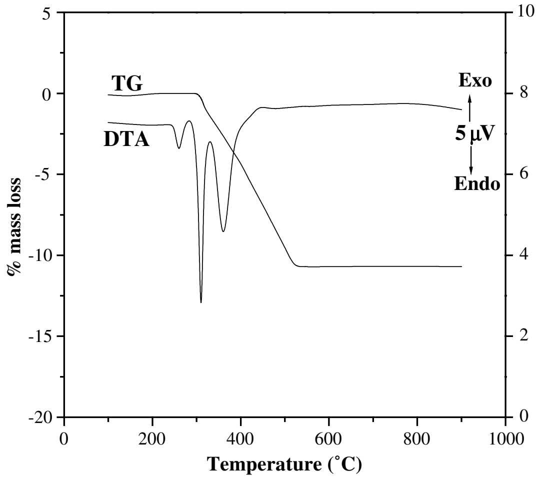

Fig. 2. TG and DTA curves of reaction mixture of $UO_2 + NaNO_3$.

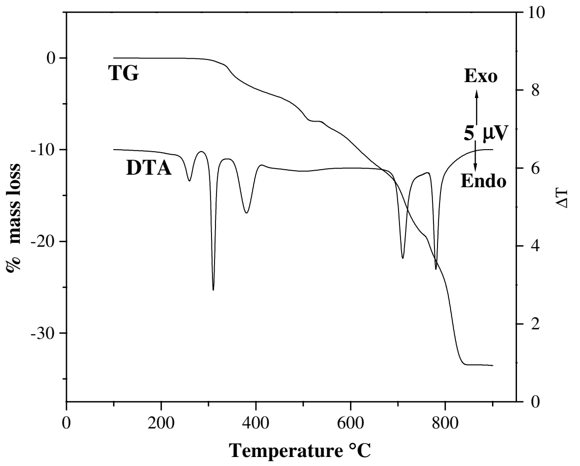

Fig. 3. TG and DTA curves of reaction mixture of $UO_2 + 4NaNO_3$.

the furnace in air in alumina boats. XRD data of the products showed that the reactants in 1:1 molar ratio of UO_2 and $NaNO_3$ led to the formation of $Na_2U_2O_7$ at 500 °C which was found to be stable upto 900 °C. 1:2 and 1:4 molar proportions of UO_2 and $NaNO_3$ reacted to yield $Na_2U_2O_7$ and excess unreacted $NaNO_3$ at 500 °C, mixture of $Na_2U_2O_7$ and Na_2UO_4 at 650 °C and Na_2UO_4 at 900 °C, as confirmed from the XRD data [23]. Though Kovba [24] have reported the formation of Na_4UO_5 at 650 °C during the reaction of UO_2 and $4NaNO_3$, we could not isolate Na_4UO_5 under the reaction conditions mentioned above. Products obtained during the reactions of UO_2 sintered at 1600 °C with $NaNO_3$ at different temperatures were identical with products obtained during the reactions of unsintered UO_2 with sodium nitrate. Products formed during the reactions of UO_2 and $NaNO_3$ in 1:1 and 1:4 molar ratios are listed in Table 1.

All the heated products obtained by reacting unsintered as well as sintered UO_2 with $NaNO_3$ were found to be readily soluble in warm dilute HNO_3.

3.2.2. Reaction of ThO_2, CeO_2 and PuO_2 with $NaNO_3$

TG curves of the reaction mixtures of ThO_2 with $NaNO_3$ in 1:1, 1:2 and 1:4 molar ratios showed a single step mass loss between 520 and 880 °C, accompanied with two DTA endothermic peaks at 740 °C and 880 °C, which were due to the decomposition of $NaNO_3$ to Na_2O, as observed in the case of pure $NaNO_3$. DTA curve showed two endothermic peaks at 260 °C and 310 °C, due to phase change and melting of $NaNO_3$ as observed earlier during the reactions of UO_2 with $NaNO_3$. TG and DTA curves of the reaction mixtures of $CeO_2 + NaNO_3$ and $PuO_2 + NaNO_3$, mixed separately in 1:1, 1:2 and 1:4 molar ratios were similar to the TG and DTA curves of the reaction mixtures of

Table 1
Reaction products of MO_2 (M = U, Th, Ce and Pu) and their mixed oxides with $NaNO_3$

Reactants	Temp. (°C)	Weight loss obs. (%)	Cal. (%)	Products identified by TG and XRD
$UO_2 + 1NaNO_3$	300–520	10.7	10.8	$Na_2U_2O_7$
	650–900	–	–	$Na_2U_2O_7$
$UO_2 + 4NaNO_3$	320–500	6.9	6.2	$Na_2U_2O_7 + NaNO_3$
	550–750	19.3	20.1	$Na_2U_2O_7 + Na_2UO_4 + Na_2O$
	760–840	33.5	32.8	$Na_2UO_4 + Na_2O$
$ThO_2 + 4NaNO_3$	500	–	–	$ThO_2 + NaNO_3$
	520–880	34.4	36.0	$ThO_2 + Na_2O$
$CeO_2 + 4NaNO_3$	500	–	–	$CeO_2 + NaNO_3$
	520–880	34.4	36.0	$CeO_2 + Na_2O$
$PuO_2 + 4NaNO_3$	500	–	–	$PuO_2 + NaNO_3$
	520–880	36.24	35.06	$PuO_2 + Na_2O$
$(U_{0.5}, Th_{0.5})O_2 + 4NaNO_3$	320–500	–	–	$Na_2U_2O_7 + ThO_2 + NaNO_3$
	550–740	–	–	$Na_2U_2O_7 + Na_2UO_4 + ThO_2 + Na_2O$
	760–850	–	–	$Na_2U_2O_7 + ThO_2 + Na_2O$
$(U_{0.85}, Ce_{0.15})O_2 + 4NaNO_3$	320–500	–	–	$Na_2U_2O_7 + CeO_2 + NaNO_3$
	550–740	–	–	$Na_2U_2O_7 + Na_2UO_4 + CeO_2 + Na_2O$
	760–850	–	–	$Na_2U_2O_7 + CeO_2 + Na_2O$
$(U_{0.9}, Pu_{0.1})O_2 + 4NaNO_3$	320–500	–	–	$Na_2U_2O_7 + PuO_2 + NaNO_3$
	550–740	–	–	$Na_2U_2O_7 + Na_2UO_4 + PuO_2 + Na_2O$
	760–850	–	–	$Na_2U_2O_7 + PuO_2 + Na_2O$

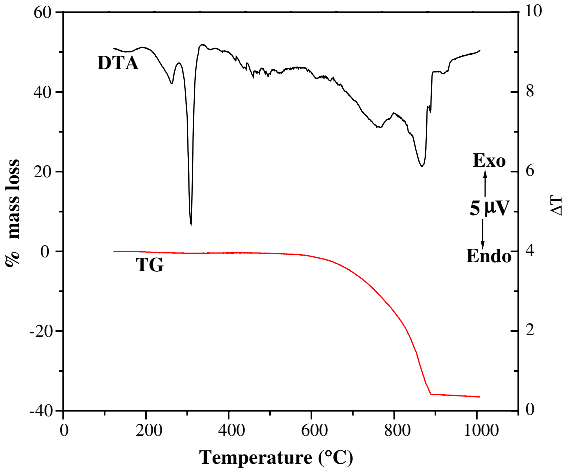

Fig. 4. TG and DTA curves of reaction mixture of $PuO_2 + 4NaNO_3$.

ThO_2 with $NaNO_3$. Fig. 4 shows the TG and DTA curves of reaction mixture of $PuO_2 + 4NaNO_3$. To isolate the products, all the reaction mixtures of oxides with $NaNO_3$ in 1:1, 1:2 and 1:4 molar proportions were heated in the furnace at 500 °C, 650 °C and 900 °C. XRD patterns of all the heated products formed during the reactions of ThO_2, CeO_2 and PuO_2 with 4 moles of $NaNO_3$ at different temperature showed the lines of respective oxides. Products obtained by reacting above oxides with 4 moles of $NaNO_3$ are summarized in Table 1. From the XRD analysis and mass loss calculations it was observed that ThO_2, CeO_2 and PuO_2 do not react with $NaNO_3$.

Though many workers have reported the formation of sodium thorates, sodium cerates and sodium plutonates, all the preparations are carried out by reacting ThO_2, CeO_2 and PuO_2 either with sodium oxide or by sodium peroxide in argon filled dry boxes. In Na–Th–O system, a single phase Na_2ThO_3 is reported by Hagenmuller et al. [16], which was obtained by reacting Na_2O with ThO_2 at 770 °C in argon atmosphere. Barker et al. [25] have reported the formation of Na_2CeO_3, by reacting CeO_2 with either Na_2O or Na_2O_2 at 650 °C in vacuum. $NaCeO_2$ is reported to be formed by reacting liquid sodium with cerium oxide in an inert atmosphere [26]. We observe that cerium oxide does not react with $NaNO_3$ in air atmosphere upto 900 °C and thus does not form any of the sodium cerate. Keller et al. [17] have reported several ternary sodium plutonates which were obtained by mixing PuO_2 with either Na_2O or Na_2O_2 in different molar ratios in the argon dry glove box and heating the reaction mixtures in the oxygen atmosphere. As in the case of cerium oxide, it was found that PuO_2 also does not react with $NaNO_3$ in air atmosphere, when heated upto 900 °C.

The heated products obtained by reacting ThO_2, CeO_2 and PuO_2 with different molar proportions of $NaNO_3$ were not soluble in warm 2 M HNO_3.

3.2.3. Reactions of $(U,Th)O_2$, $(U,Ce)O_2$ and $(U,Pu)O_2$ with $NaNO_3$

Synthetic mixed oxide of $(U_x,Th_{1-x})O_2$ with $x = 0.25$, 0.50 and 0.75, $(U_y,Ce_{1-y})O_2$ with $y = 0.85$ and 0.90 and $(U_z,Pu_{1-z})O_2$ with $z = 0.50$ and 0.90 were reacted with $NaNO_3$ in 1:1, 1:2 and 1:4 molar ratios. The reaction mixtures were heated in the furnace at different temperatures and heated products were analyzed by XRD. All the products were found to be mixtures of either sodium mono- or di-uranates depending on the molar ratio of U/Na and unreacted ThO_2, CeO_2 and PuO_2. The products formed during the reactions of $(U_{0.5},Th_{0.5})O_2$, $(U_{0.85},Ce_{0.15})O_2$ and $(U_{0.9},Pu_{0.1})O_2$ with 4 moles of $NaNO_3$ are included in Table 1.

To check the reactivity and solubility of $(U,Th)O_2$ and $(U,Pu)O_2$, 900 °C heated products of both the oxides with $NaNO_3$, were treated with warm 2 M HNO_3 and filtered. Both the residues as well as filtrates were loaded on filter papers and analyzed separately by XRF method. Fig. 5 shows the XRF spectra of the filtrates and residues of the products of $(U,Th)O_2$ and $(U,Pu)O_2$. Filtrate of $(U,Th)O_2$ (scan 1-S) showed only ULα line at $2\theta = 26.14°$ and no line of ThLα whereas scan of residue (1-R) showed only ThLα line at $2\theta = 27.47°$ and no line of ULα, indicating complete solubility of uranium and thorium remaining as insoluble residue. Similarly XRF spectra 2-S and 2-R for the filtrate and residue of the product of $(U,Pu)O_2$ treated with 2 M HNO_3, showed the presence of only U in the filtrate and only Pu (at $2\theta = 24.91°$) in the residue, respectively.

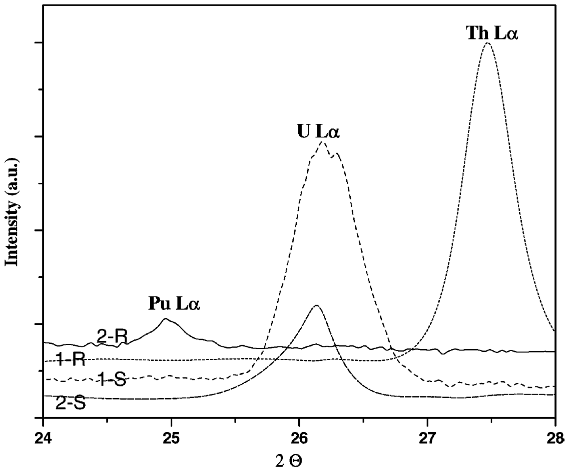

Fig. 5. XRF spectra of solution (1-S) and residue (1-R) of the heated product of $(U_{0.5},Th_{0.5})O_2$ and solution (2-S) and residue (2-R) of the heated product of $(U_{0.9},Pu_{0.1})O_2$.

Table 2
Quantitative dissolution of uranium from the products obtained by reacting UO_2, $(U,Th)O_2$, $(U,Ce)O_2$ and $(U,Pu)O_2$ with 4 moles $NaNO_3$ at 900 °C

Oxide	U content in the oxide (mg)	U content analysed from the dissolved product (mg)	% of U recovered
UO_2	434.30	432.16	99.5
UO_2[a]	211.80	209.60	98.9
$(U_{0.5},Th_{0.5})O_2$	190.40	190.18	99.9
$(U_{0.85},Ce_{0.15})O_2$	239.63	236.24	98.6
$(U_{0.9},Pu_{0.1})O_2$	266.40	261.89	98.3

[a] Sintered at 1600 °C.

3.3. Dissolution and separation of uranium

In order to study the quantitative dissolution of uranium in unsintered and sintered UO_2 as well as in the mixed oxides, the weighed amount of UO_2 and mixed oxides with the composition $(U_{0.5},Th_{0.5})O_2$, $(U_{0.85},Ce_{0.15})O_2$ and $(U_{0.9},Pu_{0.1})O_2$ were mixed separately with 4 moles of $NaNO_3$ and heated in the furnace initially at 300 °C for 3 h and then at 900 °C for 6 h. The heated products of unsintered as well as sintered UO_2 showed complete solubility in 2 M HNO_3. The dissolution data obtained by chemical analysis of uranium are given in Table 2. The reaction products of mixed oxides with $NaNO_3$ were treated with 2 M HNO_3 and warmed on a hot plate for 10–15 min. The solutions were filtered and the filtrates of all the dissolved heated products were analysed for uranium content, and the results are included in Table 2. The unreacted residues of ThO_2, CeO_2 and PuO_2, separated from the solution were analyzed using standard chemical analysis methods as discussed in the experimental part. The results of analysis show that uranium could be separated quantitatively from its mixed oxides with Th, Ce and Pu, by reacting them with $NaNO_3$ above 500 °C.

4. Conclusion

UO_2, ThO_2, CeO_2, PuO_2 and mixed oxides $(U,Th)O_2$, $(U,Ce)O_2$ and $(U,Pu)O_2$ were reacted with $NaNO_3$ in different molar proportion at various temperatures. Unsintered as well as 1600 °C sintered UO_2 react with $NaNO_3$ to form mono and di- sodium uranates and the products were readily soluble in 2 M HNO_3. ThO_2, CeO_2 and PuO_2 do not react with $NaNO_3$ upto 900 °C and remain insoluble when treated with dilute HNO_3. When $(U,Th)O_2$, $(U,Ce)O_2$ and $(U,Pu)O_2$ were reacted with sodium nitrate upto 900 °C, only uranium reacted and could be brought into the soluble form where as ThO_2, CeO_2 and PuO_2 remained insoluble. Thus, solid state reactions of mixed oxides $(U,Th)O_2$, $(U,Ce)O_2$ and $(U,Pu)O_2$ with sodium nitrate can be used to dissolve and separate uranium selectively from other actinide oxides.

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