



Solid state reactions of CeO_2 , PuO_2 , $(\text{U,Ce})\text{O}_2$ and $(\text{U,Pu})\text{O}_2$ with $\text{K}_2\text{S}_2\text{O}_8$

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Abstract

Solid state reactions of CeO_2 , PuO_2 and mixed oxides $(\text{U,Ce})\text{O}_2$ and $(\text{U,Pu})\text{O}_2$ containing different mol.% of Ce and Pu, were carried out with $\text{K}_2\text{S}_2\text{O}_8$ at different temperatures to identify the formation of various products and to investigate their dissolution behaviour. X-ray, chemical and thermal analysis methods were used to characterise the products formed at various temperatures. The products obtained by heating two moles of $\text{K}_2\text{S}_2\text{O}_8$ with one mole each of CeO_2 , PuO_2 , $(\text{U,Ce})\text{O}_2$ and $(\text{U,Pu})\text{O}_2$ at 400 °C were identified as $\text{K}_4\text{Ce}(\text{SO}_4)_4$, $\text{K}_4\text{Pu}(\text{SO}_4)_4$, $\text{K}_4(\text{U,Ce})(\text{SO}_4)_4$ and $\text{K}_4(\text{U,Pu})(\text{SO}_4)_4$, respectively. $\text{K}_4\text{Ce}(\text{SO}_4)_4$ further decomposed to form $\text{K}_4\text{Ce}(\text{SO}_4)_{3.5}$ at 600 °C and mixture of K_2SO_4 and CeO_2 at 950 °C. Thus the products formed during the reaction of $2\text{K}_2\text{S}_2\text{O}_8 + \text{CeO}_2$ show that cerium undergoes changes in oxidation state from +4 to +3 and again to +4. XRD data of $\text{K}_4\text{Ce}(\text{SO}_4)_4$ and $\text{K}_4\text{Ce}(\text{SO}_4)_{3.5}$ were indexed on triclinic and monoclinic system, respectively. $\text{PuO}_2 + 2\text{K}_2\text{S}_2\text{O}_8$ reacts at 400 °C to form $\text{K}_4\text{Pu}(\text{SO}_4)_4$ which was stable upto 750 °C and further decomposes to form $\text{K}_2\text{SO}_4 + \text{PuO}_2$ at 1000 °C. The products formed at 400 °C during the reactions of the oxides and mixed oxides were found to be readily soluble in 1–2 M HNO_3 .

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1. Introduction

$(\text{U,Pu})\text{O}_2$ and $(\text{U,Pu})\text{C}$ are the mixed oxide and carbide fuels for the advance fast breeder reactors. Dissolution of the spent nuclear fuel materials in a suitable medium is an essential requirement for the chemical quality control of nuclear fuels as well as for reprocessing and refabrication of the spent fuel. Sintered UO_2 is readily soluble in nitric acid medium. However, it is difficult to dissolve sintered PuO_2 . A small amount of HF in concentrated nitric acid is required to dissolve sin-

tered PuO_2 [1]. The presence of fluoride ions enhances the corrosion of the dissolver vessel, usually made of stainless steel [2]. Since UO_2 and PuO_2 form solid solutions in the full range of 0–100%, the dissolution of mixed oxide is a difficult task.

Due to these problems in aqueous process, molten salt and other non-aqueous processes have been attempted. Earlier studies of the solid state reactions of fuel oxides with $(\text{NH}_4)_2\text{SO}_4$ were helpful for identifying various reaction products formed during the reactions and for knowing the temperature and minimum proportion of the salt required to dissolve these fuel oxides [3,4]. The relatively low melting point of alkali metal bisulphates and alkali metal pyrosulphates suggested that these compounds may be useful as reactive molten solvent. Brambilla [5] considered alkaline sulphate

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eutectic mixtures, melting at much lower temperatures than those of pure components, as a means for dissolving irradiated fuel elements such as UO_2 and $\text{UO}_2\text{-PuO}_2$. The different methods have been described for the dissolution of PuO_2 and mixed oxides of $\text{UO}_2\text{-PuO}_2$ using various fusion agents such as $\text{Na}_2\text{O}_2\text{-NaOH}$ [6], $\text{Na}_2\text{S}_2\text{O}_7\text{-K}_2\text{S}_2\text{O}_7$ [7] etc. Fusion of PuO_2 , $\text{UO}_2\text{-PuO}_2$ and $\text{PuO}_2\text{-ThO}_2$ with ammonium bisulphate at 400 °C has been developed for the dissolution of refractory materials in H_2SO_4 to produce a solution for analysis by electrometric method [8].

In our earlier studies we have carried the reactions of UO_2 , ThO_2 and $(\text{U,Th})\text{O}_2$ with $\text{K}_2\text{S}_2\text{O}_8$, KHSO_4 and $\text{K}_2\text{S}_2\text{O}_7$ with a view to investigate the formation of products at different temperatures and to examine their dissolution behaviour [9]. In continuation with the earlier work, solid state reactions of PuO_2 and $(\text{U,Pu})\text{O}_2$ were carried out with $\text{K}_2\text{S}_2\text{O}_8$ at different temperatures to characterise the products formed and to study their solubilities in dilute acids. As cerium is the chemical and structural homologue of plutonium and also one of the major fission products, the reactions of CeO_2 and $(\text{U,Ce})\text{O}_2$ with $\text{K}_2\text{S}_2\text{O}_8$ were also studied. For comparative studies, reactions of CeO_2 and PuO_2 were also carried out with other potassium salts, i.e., KHSO_4 and $\text{K}_2\text{S}_2\text{O}_7$.

2. Experimental

2.1. Sample preparation

CeO_2 and PuO_2 were obtained by the decomposition of the oxalate of cerium and plutonium, respectively, at 800 °C. Mixed oxides of composition $(\text{U}_x\text{Ce}_{1-x})\text{O}_2$ with $x = 0.85$ and 0.90 and $(\text{U}_y\text{Pu}_{1-y})\text{O}_2$ with $y = 0.50$ and 0.90 were prepared by coprecipitating hydroxides of $(\text{U} + \text{Ce})$ and $(\text{U} + \text{Pu})$ by adding ammonia solution to the respective nitrate solutions, mixed in the required proportions. The hydroxides were filtered, dried and heated in $\text{Ar} + 7\%\text{H}_2$ at 800 °C for 4–5 h. Cerium oxide and plutonium oxide were mixed separately with $\text{K}_2\text{S}_2\text{O}_8$, KHSO_4 and $\text{K}_2\text{S}_2\text{O}_7$ (all available in G.R. grade) in atom ratio of Ce or Pu to K of 1:4. $(\text{U}_x\text{Ce}_{1-x})\text{O}_2$ and $(\text{U}_x\text{Pu}_{1-x})\text{O}_2$ were also mixed with all three potassium salts maintaining the atom ratio of $(\text{U} + \text{Ce})$ or $(\text{U} + \text{Pu})$ to K of 1:4. The reaction mixtures were well ground using agate pestle and mortar and heated in platinum boats in a furnace in air atmosphere at 400, 600 and 900 °C.

2.2. Instrumental analysis

Thermograms of reaction mixtures of all the potassium salts with CeO_2 and $(\text{U,Ce})\text{O}_2$ were recorded on

an SETARAM thermoanalyzer, recording both Thermogravimetric (TG) and Differential Thermal Analysis (DTA) curves simultaneously. The samples were heated in alumina cups at the heating rate of 10 °C/min in a flowing stream of air. Preheated alumina was used as the reference material for DTA measurements. The radioactive samples of reaction mixtures of PuO_2 and $(\text{U,Pu})\text{O}_2$ with 2 moles of $\text{K}_2\text{S}_2\text{O}_8$ salt were recorded on a Mettler Thermoanalyzer enclosed in the glove box for handling radioactive samples. A stream of dry air was used as cover gas.

X-ray powder diffraction patterns of the heated products were recorded on a Diano X-ray diffractometer using monochromatised $\text{CuK}\alpha$ radiation ($\lambda = 0.15406$ nm).

2.3. Chemical analysis

All the heated products formed at different temperatures were treated with 1–2 M H_2SO_4 or HNO_3 . The products containing Ce, formed at different temperatures were analysed for Ce(III) and Ce(IV) contents by determining total cerium and cerium (IV) in the solution using redox titrimetric method [4]. Total cerium content was determined by oxidising cerium in the weighed aliquot of the solution, to Ce(IV) using AgO . The excess of AgO was destroyed using sulphamic acid. Ce(IV) in the solution was then reduced to Ce(III) using known excess of Fe(II) solution. Excess of Fe(II) was then determined using standard $\text{K}_2\text{Cr}_2\text{O}_7$ solution with potentiometric endpoint. For determining the amount of Ce(IV) only, weighed amount of sample was dissolved in H_2SO_4 and Ce(IV) present in the solution was reduced with known excess of standard Fe(II) which was determined using standard dichromate solution with potentiometric end point detection.

For plutonium content, weighed aliquots of the reaction products were dissolved in 2 M HNO_3 and Pu in the resulting solutions were determined using α liquid scintillation counting technique. Proper dilutions were given to the resulting solution so as to minimize the counting error. Known volume of the diluted solution was taken in 5 ml of dioxan based liquid scintillator taken in a scintillation vial. The composition of the scintillator used was

- (i) 2,5-diphenyl oxazole (PPO): 0.7%;
- (ii) 1,4-di[2-(4-methyl-5-phenyloxazolyl)]-benzene (POPOP): 0.03%;
- (iii) naphthalene: 10%;
- (iv) tri-*n*-octyl phosphine oxide (TOPO): 2%

in double distilled dioxan as a base solvent. Using specific radioactivity of plutonium; i.e., 1.5×10^5 dpm/ μg (reactor grade Pu), the amount of Pu was calculated.

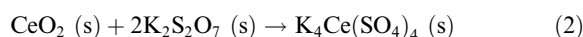
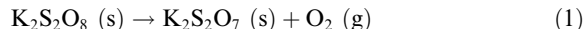
Total uranium content in the dissolved products of the mixed oxides was determined by redox titrimetry using Davies and Gray method [10].

3. Results and discussion

3.1. Reaction of CeO_2 with $\text{K}_2\text{S}_2\text{O}_8$

Thermogram of reaction mixture of CeO_2 with 2 moles of $\text{K}_2\text{S}_2\text{O}_8$ is shown in Fig. 1. TG curve of the mixture showed mass loss between 200–260, 500–720 and 780–990 °C. The DTA curve showed a sharp exothermic peak at 225 °C and two endothermic peaks at 315 and 410 °C. All the three peaks were also observed during the reactions of UO_2 and ThO_2 with $\text{K}_2\text{S}_2\text{O}_8$ [9]. The exothermic peak is due to the liberation of molecular oxygen during the conversion of $\text{K}_2\text{S}_2\text{O}_8$ to $\text{K}_2\text{S}_2\text{O}_7$ and the other two peaks at 315 and 410 °C are due to the phase transformation and melting of $\text{K}_2\text{S}_2\text{O}_7$, respectively. In addition four endothermic peaks were observed at 590, 735, 830 and 860 °C.

Isothermal heating of the reaction mixture of CeO_2 with 2 moles of $\text{K}_2\text{S}_2\text{O}_8$ at 400 °C in furnace formed $\text{K}_4\text{Ce}(\text{SO}_4)_4$ which is iso-structural with $\text{K}_4\text{U}(\text{SO}_4)_4$ and $\text{K}_4\text{Th}(\text{SO}_4)_4$. Formation of the product during the reaction is shown below:



Further isothermal heating of the reaction mixture at 600 °C for 6 h and at 950 °C for 20–22 h in the furnace led to the formation of the stable products $\text{K}_4\text{Ce}(\text{SO}_4)_{3.5}$ and the mixture of $\text{K}_2\text{SO}_4 + \text{CeO}_2$, respectively. In DTA curve of reaction mixture, the second and third endothermic DTA peaks at 590 and 735 °C were due to the

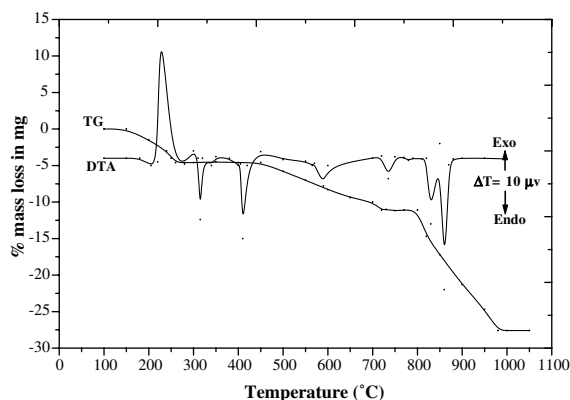
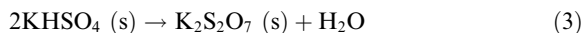


Fig. 1. TG and DTA curves of $\text{CeO}_2 + 2\text{K}_2\text{S}_2\text{O}_8$.

decomposition of $\text{K}_4\text{Ce}(\text{SO}_4)_4$ forming $\text{K}_4\text{Ce}(\text{SO}_4)_{3.5}$, and the peaks at 830 and 860 °C are due to the phase change and melting of $\text{K}_4\text{Ce}(\text{SO}_4)_{3.5}$, respectively. When the compound was cooled after the melting temperature, DTA curve showed a sharp exothermic peak at 835 °C due to the solidification of the compound. As the phase change and melting temperatures are in narrow range we could not isolate the peak due to phase change in the DTA curve during the cooling cycle of the compound. Similar DTA peaks were observed by Bonder et al. [11], during the thermal decomposition of $\text{K}_4\text{Ce}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$. The mass loss observed during heating at different stages were in agreement with the expected mass loss for the formation of the products as given in Table 1. The formation of all the products at different temperatures was also confirmed by the X-ray diffraction (XRD) patterns. XRD data of $\text{K}_4\text{Ce}(\text{SO}_4)_4$ was indexed on triclinic system. The cell parameters were refined by the least squares method using a computer program [12] and are given in Table 2. The indexed X-ray powder data of $\text{K}_4\text{Ce}(\text{SO}_4)_4$ is given in Table 3. It was observed that $\text{K}_4\text{Ce}(\text{SO}_4)_4$ was unstable and picks up the moisture when stored in air, forming $\text{K}_4\text{Ce}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ whose XRD data was comparable with the reported one [13]. The single crystal study of $\text{K}_4\text{Ce}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ has shown that the compound belongs to the monoclinic system with cell parameters included in Table 2 [14]. XRD data of $\text{K}_4\text{Ce}(\text{SO}_4)_{3.5}$, 600 °C heated product was indexed on monoclinic system with the cell parameters given in Table 2 and the XRD data of the compound is given in Table 4.

All the intermediate products of CeO_2 with 2 moles of $\text{K}_2\text{S}_2\text{O}_8$ formed at different temperatures were analysed for cerium content by redox titrimetry using chemical analysis method. The analysis results confirmed the presence of cerium in +4 state in $\text{K}_4\text{Ce}(\text{SO}_4)_4$, i.e., 400 °C heated product; whereas, $\text{K}_4\text{Ce}(\text{SO}_4)_{3.5}$ (600 °C heated product) contains cerium only in +3 oxidation state which again changes to +4 in the end product CeO_2 formed at 950 °C. Thus, cerium undergoes two successive changes of oxidation states, $\text{Ce}(\text{IV}) \rightarrow \text{Ce}(\text{III}) \rightarrow \text{Ce}(\text{IV})$, as was observed during the reaction of CeO_2 with ammonium sulphate [2].

Similar to $\text{K}_2\text{S}_2\text{O}_8$, KHSO_4 also first decomposes to $\text{K}_2\text{S}_2\text{O}_7$ as shown in Eq. (3) and then reacts with CeO_2 as given in Eq. (2).



The products formed at various temperatures during the reactions of cerium oxide with 4 moles of KHSO_4 and 2 moles of $\text{K}_2\text{S}_2\text{O}_7$ were found to be same as those formed during the reactions of CeO_2 with $2\text{K}_2\text{S}_2\text{O}_8$. The products formed during the reaction of KHSO_4 with CeO_2 are included in Table 1.

Table 1
Reaction products of CeO₂, PuO₂, (U_{0.85}Ce_{0.15})O₂, and (U_{0.9}Pu_{0.1})O₂ with KHSO₄ and K₂S₂O₈

Reactants	Reactant ratios	Temperature range (°C)	Mass loss (%)		Products identified ^a	Product ratios
			Observed	Calculated		
CeO ₂ + KHSO ₄	1:4	200–355	5.12	5.00	K ₄ Ce(SO ₄) ₄	1
		500–720	11.81	11.72	K ₄ Ce(SO ₄) _{3.5}	1
		780–980	27.48	27.35	K ₂ SO ₄ + CeO ₂	2:1
CeO ₂ + K ₂ S ₂ O ₈	1:2	200–260	4.59	4.47	K ₄ Ce(SO ₄) ₄	1
		500–720	11.18	11.21	K ₄ Ce(SO ₄) _{3.5}	1
		800–1000	27.06	26.94	K ₂ SO ₄ + CeO ₂	2:1
PuO ₂ + KHSO ₄	1:4	200–225	4.39	4.38	K ₄ Pu(SO ₄) ₄	1
		750–1000	23.98	24.06	K ₂ SO ₄ + PuO ₂	2:1
PuO ₂ + K ₂ S ₂ O ₈	1:2	200–220	3.98	3.91	K ₄ Pu(SO ₄) ₄	1
		750–1000	23.45	23.66	K ₂ SO ₄ + PuO ₂	2:1
(U _{0.85} Ce _{0.15})O ₂ + K ₂ S ₂ O ₈	1:2	200–280	3.82	4.02	K ₄ (U,Ce)(SO ₄) ₄	1
		400–620	11.49	11.72	K ₄ UO ₂ (SO ₄) ₃ + K ₄ Ce(SO ₄) _{3.5}	0.85:0.15
		750–1000	26.27	26.33	K ₂ U ₂ O ₇ + CeO ₂ + K ₂ SO ₄	0.425:0.15:1.57
(U _{0.9} Pu _{0.1})O ₂ + K ₂ S ₂ O ₈	1:2	200–480	4.01	3.95	K ₄ (U,Pu)(SO ₄) ₄	1
		500–850	10.87	11.01	K ₄ UO ₂ (SO ₄) ₃ + K ₄ Pu(SO ₄) ₄	0.9:0.1
		860–1000	26.19	26.35	K ₂ U ₂ O ₇ + PuO ₂ + K ₂ SO ₄	0.45:0.1:1.55

^a Products identified by XRD and/or thermogravimetry.

Table 2
Cell parameters of K₄Ce(SO₄)₄, K₄Ce(SO₄)₄·2H₂O, K₄Ce(SO₄)_{3.5} and K₄Pu(SO₄)₄·2H₂O

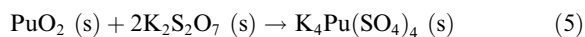
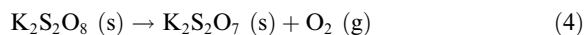
Cell parameters	K ₄ Ce(SO ₄) ₄	K ₄ Ce(SO ₄) ₄ ·2H ₂ O ^a	K ₄ Ce(SO ₄) _{3.5}	K ₄ Pu(SO ₄) ₄ ·2H ₂ O ^a
<i>a</i> (nm)	1.8046(7)	1.2412(1)	0.8709(6)	1.24175(7)
<i>b</i> (nm)	0.9771(5)	1.1166(1)	0.7051(3)	1.11583(7)
<i>c</i> (nm)	1.3817(7)	1.3571(1)	1.7009(10)	1.35530(9)
α (°)	134.80(2)	–	–	–
β (°)	108.74(5)	111.77(1)	101.08(4)	111.82(1)
γ (°)	77.65(5)	–	–	–
<i>V</i> (nm ³)	1.6368	1.7467	1.0250	1.7327
<i>Z</i>	4	4	4	4
$\rho_{\text{calc.}}$ (g cm ⁻³)	2.76	2.72	4.10	3.13

^a Reported in the literature [14,15].

3.2. Reaction of PuO₂ with K₂S₂O₈

TG and DTA curves of reaction mixtures of PuO₂ with 2 moles of K₂S₂O₈ recorded up to 1000 °C in air, are shown in Fig. 2. TG curve showed mass loss between two steps, 200–220 and 750–1000 °C. As observed in the thermogram of CeO₂ + 2 moles of K₂S₂O₈, DTA curve of PuO₂ + 2 moles of K₂S₂O₈ also showed a sharp exothermic peak at 250 °C and two endothermic peaks at 315 and 410 °C due to the liberation of molecular oxygen during the conversion of K₂S₂O₈ to K₂S₂O₇, phase transformation and melting of K₂S₂O₇, respectively. Reaction of PuO₂ with 2 moles of K₂S₂O₈ at 400 °C

led to the formation of K₄Pu(SO₄)₄ according to Eqs. (4) and (5) given below:



K₄Pu(SO₄)₄ was found to be unstable in air and got converted to stable hydrate K₄Pu(SO₄)₄·2H₂O, which is isomorphous with K₄Ce(SO₄)₄·2H₂O [14]. The crystal structure of K₄Pu(SO₄)₄·2H₂O has been investigated and the compound was indexed on monoclinic cell with *a* = 1.2417(7) nm, *b* = 1.1158(7) nm, *c* = 1.3553(9) nm and β = 111.82°(1) [15]. K₄Pu(SO₄)₄ decomposition

Table 3
XRD data of $K_4Ce(SO_4)_4$, $\lambda = 0.15406$ nm

<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{obs} (nm)	<i>d</i> _{cal} (nm)	<i>I</i> / <i>I</i> ₀
-1	0	1	0.9361	0.9338	100
1	0	1	0.7513	0.7552	76
-1	-1	2	0.6905	0.6894	60
1	1	0	0.6371	0.6382	74
-2	-1	2	0.6241	0.6254	8
2	-1	0	0.5434	0.5432	48
-1	-2	1	0.4325	0.4319	8
-4	-1	2	0.4255	0.4257	15
-3	-2	3	0.3978	0.3980	10
-5	-1	2	0.3531	0.3529	8
1	-2	0	0.3408	0.3409	52
2	-2	3	0.3368	0.3365	88
3	0	2	0.3276	0.3273	15
-4	-2	4	0.3128	0.3127	5
-1	-3	2	0.3091	0.3091	60
1	-3	3	0.3006	0.3005	70
0	-3	4	0.2960	0.2961	60
3	-1	3	0.2946	0.2948	75
-4	1	2	0.2710	0.2710	50
-3	2	1	0.2532	0.2533	4
4	2	1	0.2206	0.2206	5
-1	2	2	0.2194	0.2194	5
-1	1	4	0.1916	0.1916	35
0	0	5	0.1901	0.1901	40
7	2	1	0.1742	0.1742	28
-11	-1	2	0.1634	0.1634	5

Table 4
XRD data of $K_4Ce(SO_4)_{3.5}$, $\lambda = 0.15406$ nm

<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{obs} (nm)	<i>d</i> _{cal} (nm)	<i>I</i> / <i>I</i> ₀
-1	0	1	0.8245	0.8280	43
1	0	1	0.7065	0.7076	43
0	1	1	0.6500	0.6495	100
0	1	2	0.5386	0.5386	34
-2	0	1	0.4338	0.4345	38
-1	1	3	0.4150	0.4151	35
-2	0	3	0.3766	0.3756	42
1	2	1	0.3157	0.3156	66
-1	1	5	0.3010	0.3014	40
-1	2	3	0.2907	0.2907	34
2	0	4	0.2734	0.2735	38
2	1	4	0.2549	0.2550	30
0	2	5	0.2425	0.2424	29
0	3	0	0.2349	0.2350	32
2	2	4	0.2162	0.2161	30
3	2	2	0.2067	0.2066	28
0	3	5	0.1922	0.1922	34
-2	2	8	0.1763	0.1763	30

starts at about 750 °C and is complete at 1000 °C, forming a mixture of PuO_2 and K_2SO_4 [14]. This mass loss due to sulphate decomposition is accompanied with

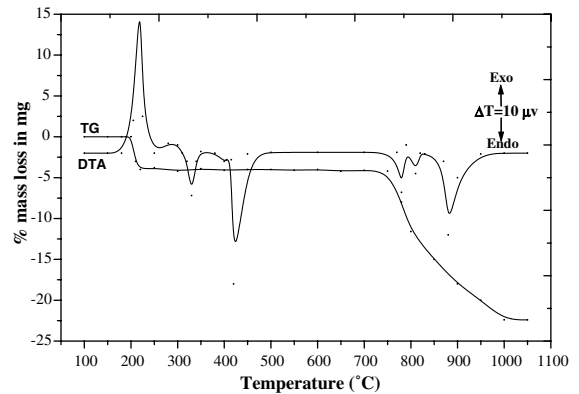


Fig. 2. TG and DTA curves of $PuO_2 + 2K_2S_2O_8$.

three endothermic DTA peaks at 780, 820 and 870 °C. The identity of the product was confirmed by heating the reaction mixture in furnace at 900 °C for 22–24 h and recording the XRD of the product. The products obtained during the reaction of PuO_2 with 2 moles of $K_2S_2O_8$ are also summarised in Table 1. As observed during the reaction of CeO_2 with the three potassium salts, the products obtained by reacting PuO_2 with $K_2S_2O_8$, $KHSO_4$ and $K_2S_2O_7$ were also identical, which was confirmed by mass loss calculations from the TG curves and XRD patterns of the products. The products obtained by heating the reaction mixtures of $PuO_2 + 4$ moles of $KHSO_4$ are included in Table 1.

3.3. Reaction of $(U,Ce)O_2$ and $(U,Pu)O_2$ with $K_2S_2O_8$

Low fired (800 °C) mixed oxides of $(U_x,Ce_{1-x})O_2$ with $x = 0.85$ and 0.90 and $(U_y,Pu_{1-y})O_2$ with $y = 0.50$ and 0.90 were reacted with 2 moles of $K_2S_2O_8$ at different temperatures and the products were characterised by XRD method. 400 °C heated product of $(U_x,Ce_{1-x})O_2 + 2$ moles of $K_2S_2O_8$ was identified as double sulphate of mixed oxides, $K_4(U,Ce)(SO_4)_4$. 600 °C heated product was found to be the mixture of $K_4UO_2(SO_4)_3$ and $K_4Ce(SO_4)_{3.5}$. Further heating at 950 °C for 18–20 h confirmed the product as mixture of $K_2U_2O_7 + CeO_2 + K_2SO_4$. The products obtained during the reaction of $(U_{0.85},Ce_{0.15})O_2$ with 2 moles of $K_2S_2O_8$ are listed in Table 1. $(U_y,Pu_{1-y})O_2$ and 2 moles of $K_2S_2O_8$ was reacted at 400 °C and the product was identified as $K_4(U,Pu)(SO_4)_4$ which decomposes around 600 °C, forming mixture of $K_4UO_2(SO_4)_3$ and $K_4Pu(SO_4)_4$. When further heated around 1000 °C, the product was identified as a mixture of $K_2U_2O_7 + PuO_2 + K_2SO_4$. The products obtained during the reaction of $(U_{0.9},Pu_{0.1})O_2$ with 2 moles of $K_2S_2O_8$ are included in Table 1.

Table 5

Solubility data of the products formed by reacting CeO₂, PuO₂, (U_{0.85},Ce_{0.15})O₂, (U_{0.9},Ce_{0.1})O₂, (U_{0.5},Pu_{0.5})O₂ and (U_{0.9},Pu_{0.1})O₂ with 2 moles of K₂S₂O₈ salt at 400 °C

Oxides	Metal content in the dissolved products (mg)					
	U		Ce		Pu	
	Expected	Analysed	Expected	Analysed	Expected	Analysed
CeO ₂	–	–	406.9	406.1	–	–
PuO ₂	–	–	–	–	440.9	437.8
(U _{0.85} ,Ce _{0.15})O ₂	374.7	373.5	61.1	60.4	–	–
(U _{0.9} ,Ce _{0.1})O ₂	396.7	392.3	40.7	40.6	–	–
(U _{0.5} ,Pu _{0.5})O ₂	220.4	219.1	–	–	220.5	219.6
(U _{0.9} ,Pu _{0.1})O ₂	396.7	393.9	–	–	44.1	43.9

4. Dissolution studies

During the treatment of fuel materials with various salts to dissolve them in dilute acid, identification of the solid products formed is helpful to know the minimum temperature of reactions [16] and to determine the minimum amount of salt required for the completion of the reaction [17].

When CeO₂ and PuO₂ were reacted with K₂S₂O₈, KHSO₄ and K₂S₂O₇ salts in atom ratio of Ce or/and Pu to K of 1:4 at 400 and 600 °C, the products formed at both the temperatures were readily soluble in 1–2 M HNO₃ or H₂SO₄. Similarly Ce and Pu in their mixed oxide, i.e., (U,Ce)O₂ and (U,Pu)O₂ were completely dissolved in warm 2 M HNO₃ when heated with the salts of potassium at 400 and 600 °C.

In order to study the quantitative dissolution of oxides, weighted amounts of CeO₂, PuO₂, (U_{*x*},Ce_{1–*x*})O₂ with *x* = 0.85 and 0.90 and (U_{*y*},Pu_{1–*y*})O₂ with *y* = 0.90 and 0.50 were mixed separately with K₂S₂O₈ in 1:2 molar proportion and heated in the platinum boat in a furnace at 400 °C for 8–10 h. All the products were treated with warm 2 M HNO₃ and solutions were analysed for uranium, cerium and plutonium content. Uranium and cerium were analysed by chemical analysis using redox titrimetric method. Plutonium content in the products obtained by reacting plutonium oxide and (U,Pu)O₂ with K₂S₂O₈ was determined by α scintillation counter. Results of the analysis of uranium, cerium and plutonium content in the dissolved heated products of the respective oxides and mixed oxides are given in Table 5.

5. Conclusion

CeO₂, PuO₂ and mixed oxides of (U,Ce)O₂ and (U,Pu)O₂ were reacted with K₂S₂O₈, KHSO₄ and K₂S₂O₇ at different temperatures aiming to identify the various products formed at these temperatures and to study the dissolution behaviour of the products. It was observed that the three salts react with the oxides at var-

ious temperatures to form the identical products. Products formed by heating CeO₂ and PuO₂ with potassium salts at 400 °C were identified as K₄Ce(SO₄)₄ and K₄Pu(SO₄)₄, respectively. XRD data of K₄Ce(SO₄)₄ was indexed on triclinic system. Decomposition of K₄Ce(SO₄)₄ at 600 °C led to the formation K₄Ce(SO₄)_{3.5} and finally forms CeO₂ at 900 °C. So, during the reaction of CeO₂ with potassium salts, cerium undergoes two successive changes of oxidation states, Ce(IV) → Ce(III) → Ce(IV). K₄Pu(SO₄)₄, the product formed by reacting PuO₂ with potassium salts at 400 °C was stable upto 750 °C and finally decomposes to PuO₂ at 1000 °C. The products formed at 400 and 600 °C by heating low fired CeO₂, PuO₂ and their mixed oxides with potassium salts were completely soluble in 2 M HNO₃.

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