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Recovery of uranium from fluoride matrix by solid state reaction routes

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Abstract

A simple method is developed for the separation and recovery of uranium in a CaF_2 and MgF_2 matrix, employing a solid state reaction route, heating the uranium slag-composition mixture with $(NH_4)_2SO_4$. Reactions of a synthetic slag-composition mixture with $(NH_4)_2SO_4$ above 350 °C formed sulfate compounds of uranium, calcium and magnesium. The sulfates of uranium were separated by dissolving in dilute acid. Reactions were monitored by TG-DTA analysis. Products formed at different temperatures were characterised by X-ray powder diffraction. Quantitative analysis of the products was achieved using redox titrimetry. By this method about 95% of the uranium present could be recovered from synthetic mixtures.

1. Introduction

Nuclear fuel cycle operations generate a variety of process waste streams. Waste management has become the centre of a wide interest in exploiting undeveloped energy sources and environmental control. Radioactive waste management with a proper technical and administrative plan is essential and advanced research in this field is being taken up in many countries. The uranium recovery processing option can be considered with respect to equipment requirements, preparatory processing and material accountability. Due to the high cost factor involved in the recovery process, various methods have been developed to recover uranium from waste and its low-grade sources [1–3].

The production of uranium metal by calciothermic reduction generates slag that contains mainly CaF_2 and about 2–5% of uranium in the form of unreacted uranium fluoride and some unrecovered uranium metal [4]. Magnesiothermic reduction of uranium fluoride similarly generates slag, which also contains uranium metal, and fluorides of uranium and magnesium [4]. These slags can be processed for recovery of uranium. As reported in the literature, uranium is recovered by first dissolving the slag, by refluxing it in $HNO_3 + Al(NO_3)_3$ solution, and subsequently extracting it by solvent extraction or ion exchange methods [5]. Another aqueous method, using urea and nitric acid, has also been developed in our laboratory [6]. Dry size reduction and wet operations are the standard processes followed for the recovery of uranium from its ore [4]. These aqueous methods generate large volumes of waste and are time-consuming. Earlier studies have shown that oxides and fluorides of uranium and plutonium react with $(NH_4)_2SO_4$ in the solid state, at 250 °C and above, to form their sulfate compounds [7–9], which are easily soluble in mineral acids. In this paper, a simple method is described for the recovery of uranium from a fluoride matrix by solid state reactions of slag materials with $(NH_4)_2SO_4$, followed by dissolution in dilute sulfuric or nitric acid.

2. Experimental

Synthetic mixtures, representative of slags with different combinations and ratios of UO_2 and UF_4 in

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CaF_2/MgF_2 were prepared by mechanical mixing with Analar grade $(NH_4)_2SO_4$, using a pestle and mortar. UO_2 was prepared by equilibrating U_3O_8 (nuclear grade) in an atmosphere of Ar + 7% H_2 at 800 °C for 4–5 h. UF_4 was prepared by fluorinating UO_2 with HF at 500 °C. CaF_2 and MgF_2 were procured from Aldrich (purity 99.9%). The mixtures were heated at the required temperature in a furnace in flowing air. Solid state reactions were carried out with a batch of samples, each about 5 g of the synthetic mixture. Thermograms of the reactants were taken on a ULVAC Thermoanalyzer, recording both thermogravimetric (TG) and differential thermal analysis (DTA) curves simultaneously, and at a heating rate of 10 °C/min. For DTA, sintered alumina was used as the reference material. The absorption spectra of the samples, dissolved in 1 M H_2SO_4, were recorded in the visible region on a Beckman DU7 spectrophotometer. Chemical analyses of the products, for uranium, were carried out by redox titrimetry following the Davis and Gray method [10]. X-ray diffraction (XRD) patterns were recorded on a STOE X-ray diffractometer using graphite monochromatised CuKα radiation ($\lambda = 0.15406$ nm) to identify the nature of the products formed at different temperatures.

3. Results and discussion

3.1. Calcium fluoride matrix

The thermogravimetric pattern of a mixture of CaF_2 and $(NH_4)_2SO_4$ in a 1:1.1 molar proportion, Fig. 1, showed that the decomposition and reaction of $(NH_4)_2SO_4$ with CaF_2 proceeded in three stages between 250 and 400 °C. The mass loss and XRD pattern showed the final reaction product to be $CaSO_4$, represented by the Eq. (1). No stable intermediate product could be isolated during this reaction.

$$CaF_2 + (NH_4)_2SO_4 \xrightarrow{400\ °C} CaSO_4 + 2NH_4F. \quad (1)$$

The thermogram for the reaction mixtures of $CaF_2 + UO_2$ (1:1) and $CaF_2 + UF_4$ (1:1) with 4 molar ratios of $(NH_4)_2SO_4$, Figs. 2 and 3, respectively, gave three steps in mass loss between 200 and 500 °C. These three steps are clearly distinguished by their endothermic DTA peaks. Solid state reactions of $CaF_2 + UO_2$, $CaF_2 + UF_4$ and $CaF_2 + UO_2 + UF_4$ taken with different molar proportions of $(NH_4)_2SO_4$, were carried out for 2–3 h in three temperature steps in a furnace. The reaction mixtures were heated isothermally at 350, 425 and 525 °C for 2 h to obtain constant mass. The various products formed, identified by their mass loss and XRD patterns recorded at room temperature, are given in Table 1. For the mixture of $UO_2 + UF_4 + CaF_2 + (NH_4)_2SO_4$, the observed products formed at 350, 425 and 525 °C can be represented by the sequence, given in Eqs. (2)–(4):

$$\begin{aligned} &UO_2 + UF_4 + 2CaF_2 + 8(NH_4)_2SO_4 \\ &\xrightarrow{350\ °C} 2(NH_4)_2U(SO_4)_3 + 2CaSO_4 + 8NH_4F \\ &\quad + 4NH_3\uparrow + 2H_2O\uparrow, \end{aligned} \quad (2)$$

$$(NH_4)_2U(SO_4)_3 \xrightarrow{425\,°C} U(SO_4)_2 + 2NH_3\uparrow + H_2O\uparrow + SO_3\uparrow, \quad (3)$$

$$2U(SO_4)_2 \xrightarrow[O_2]{525\ °C} 2UO_2SO_4 + 2SO_3\uparrow. \quad (4)$$

The products were further identified from their XRD patterns, Fig. 4. The XRD patterns correspond to the formation of $(NH_4)_2U(SO_4)_3 + CaSO_4$ at 350 °C,

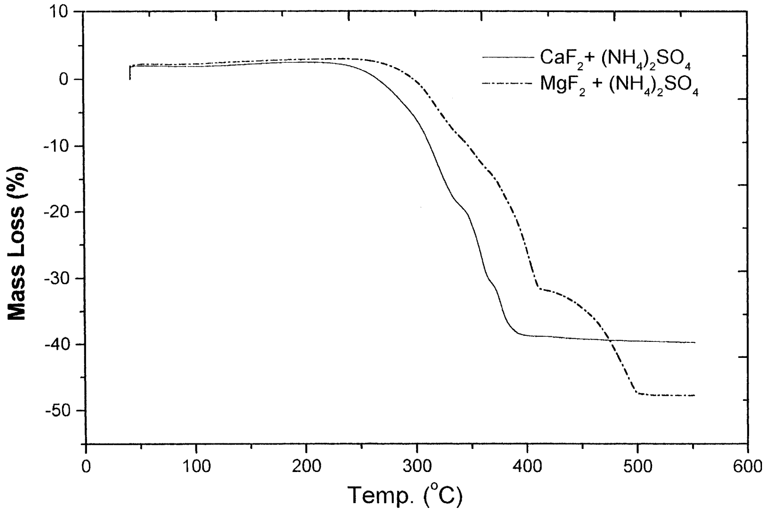

Fig. 1. TG patterns of: CaF_2/MgF_2 with $(NH_4)_2SO_4$.

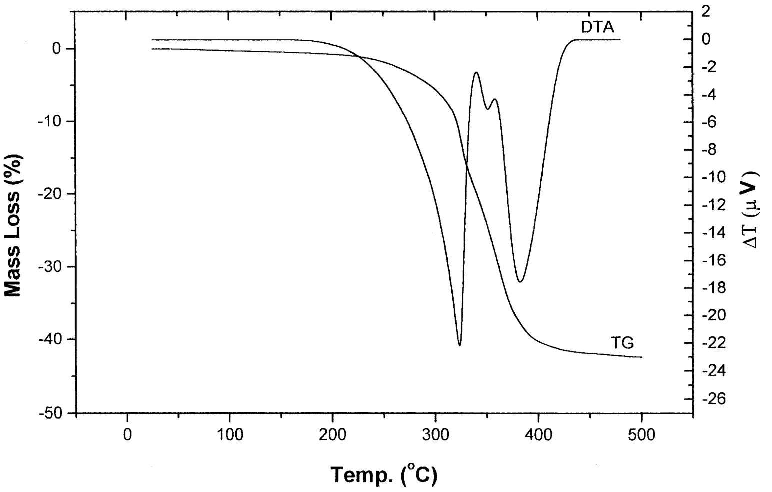

Fig. 2. TG and DTA pattern of: $UO_2 + CaF_2$ with $(NH_4)_2SO_4$.

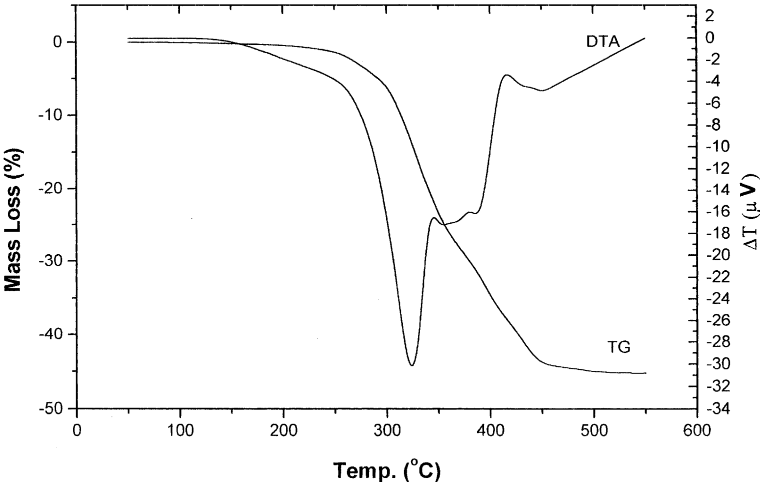

Fig. 3. TG and DTA pattern of: $UF_4 + CaF_2$ with $(NH_4)_2SO_4$.

Table 1
Products identified by mass loss and XRD during solid state reaction of $(NH_4)_2SO_4$ with UO_2/UF_4 in CaF_2 matrix at different temperatures

Reactants	Molar proportion	Temp. (°C)	Products	Mass loss (%)	
				Observed	Expected
$(NH_4)_2SO_4 + CaF_2$	1:1	400	$CaSO_4$	35.5	35.2
$(NH_4)_2SO_4 + UO_2 + CaF_2$	4:1:1	350	$CaSO_4 + (NH_4)_2U(SO_4)_3$	19.2	20.3
		425	$CaSO_4 + U(SO_4)_2$	34.5	35.4
		525	$CaSO_4 + UO_2SO_4$	42.4	42.7
$(NH_4)_2SO_4 + UF_4 + CaF_2$	4:1:1	350	$CaSO_4 + (NH_4)_2U(SO_4)_3$	23.2	24.1
		425	$CaSO_4 + U(SO_4)_2$	37.5	38.5
		525	$CaSO_4 + UO_2SO_4$	45.1	45.4

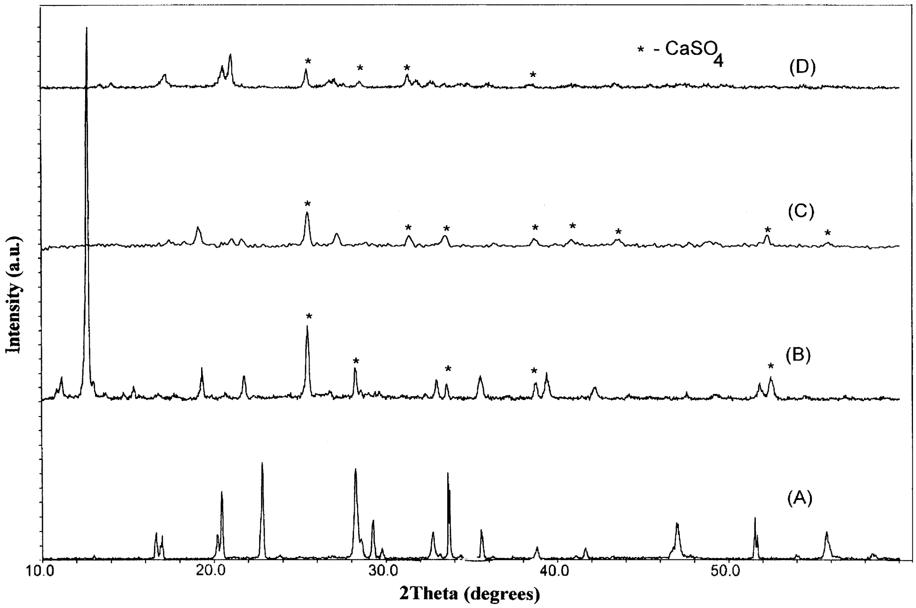

Fig. 4. XRD pattern of: $UO_2 + UF_4 + CaF_2$ with $(NH_4)_2SO_4$. (A) Unreacted $UO_2 + UF_4 + CaF_2$ with $(NH_4)_2SO_4$, (B) $(NH_4)_2U(SO_4)_3 + CaSO_4$ (*) at 350 °C, (C) $U(SO_4)_2 + CaSO_4$ (*) at 425 °C, (D) UO_2SO_4 and $CaSO_4$ (*) at 525 °C.

$U(SO_4)_2 + CaSO_4$ at 425 °C, and $UO_2SO_4 + CaSO_4$ at 525 °C [7,11]. The reactions at 350 °C proceed with evolution of NH_4F, confirmed from the XRD pattern of the condensate collected in the cooler zone of the reaction tube. The XRD pattern of the product formed at 425 °C was recorded in a dry atmosphere immediately after removing the samples from the furnace. On storage overnight in an open atmosphere, $U(SO_4)_2$ gets converted to $U(SO_4)_2 \cdot 4H_2O$ due to its hygroscopic nature. This observation was confirmed by comparing the XRD data, of the stored sample with that of the $U(SO_4)_2 \cdot 4H_2O$ [11]. The formation of $U(SO_4)_2$ was further established from the similarity of its XRD pattern, with that of, anhydrous compound of $U(SO_4)_2 \cdot 4H_2O$ prepared after dehydrating it at 250 °C. In Eqs. (3) and (4), SO_3 formation is thermodynamically more preferred to SO_2 formation ($2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$, Δ_rG^o (700–800 K) = −(65.9–47.2) kJ mol^{-1}) [12].

UV–visible spectra of $(NH_4)_2U(SO_4)_3$, $U(SO_4)_2$ and UO_2SO_4 were recorded after dissolving the compounds in 1 M H_2SO_4. The peaks observed at 652, 548, 494, 482 and 430 nm for the solutions of $(NH_4)_2U(SO_4)_3$ and $U(SO_4)_2$ are characteristics of +4 oxidation state of uranium. The characteristic peak obtained at 421 nm for UO_2SO_4 solution inferred the presence of uranium in +6 oxidation state in UO_2SO_4 [13].

When heated in air, $(NH_4)_2SO_4$ decomposes above 250 °C, forming NH_4HSO_4, and is accompanied by an endothermic DTA peak at 330 °C [14]. Further decomposition occurs at 410 °C, at a faster rate, forming sulfuric acid, which is very reactive at this temperature and reacts with metal oxides and fluorides, forming the corresponding sulfates. The decomposition of $(NH_4)_2SO_4$ can be shown as:

$$(NH_4)_2SO_4 \xrightarrow{250\text{–}350\,°C} NH_4HSO_4 + NH_3\uparrow, \qquad (5)$$

$$NH_4HSO_4 \xrightarrow{350\text{–}450\,°C} NH_3\uparrow + H_2SO_4. \qquad (6)$$

With mixtures of UO_2/UF_4 having 3 molar ratios of $(NH_4)_2SO_4$, the reaction was not complete. For the mixtures having 5 or more molar ratios of $(NH_4)_2SO_4$, the TG curve showed an additional mass loss step indicating the loss of unreacted $(NH_4)_2SO_4$. About 10% excess $(NH_4)_2SO_4$ was always added, more than necessary as per Eq. (2) for complete reaction. Unreacted $(NH_4)_2SO_4$ decomposes in two steps in the range 25–325 °C and 325–550 °C, respectively; each accompanied by an endothermic DTA peak [15] as follows:

$$(NH_4)_2SO_4 \xrightarrow{25\text{–}325\,°C} 2NH_3\uparrow + H_2O\uparrow + SO_3\uparrow, \qquad (7)$$

$$2NH_3 + 3SO_3 \xrightarrow{325\text{–}550\,°C} 3SO_2\uparrow + N_2\uparrow + 3H_2O\uparrow. \qquad (8)$$

These Eqs. (5)–(8) explain that solid state reactions of $(NH_4)_2SO_4$ with UO_2 or UF_4 in the fluoride matrix take place by reaction with sulfuric acid around 350 °C, and that the excess $(NH_4)_2SO_4$ decomposes to gaseous products. In Eq. (8) N_2 is formed as, this reaction is thermodynamically stable [Δ_rG^o (600–900 K) = −(546–652) kJ mol^{-1}] [12].

The UO_2SO_4formed at 525 °C has uranium in +6 oxidation state and has better solubility in acids than the sulfates formed at lower temperatures, where uranium is in +4 oxidation sate. Uranium was separated from other reaction product $CaSO_4$, formed at the end of the reaction by dissolving UO_2SO_4 in warm 1 M HNO_3 or 1 M H_2SO_4. The solution was cooled to room temperature to precipitate out the $CaSO_4$ that has gone into solution. Finally, the separation of uranium from the CaF_2 matrix after solid state reactions was confirmed by recording the X-ray fluorescence (XRF) spectra of the residue and filtrate. The XRF spectrum of $CaSO_4$ residue did not show the L X-ray lines of uranium and the spectrum of the filtrate did not show any K X ray lines of calcium. Chemical analysis of the filtrate, by redox titrimetry, showed that about 95% of uranium could be recovered by this method. The yellowish filtrate was precipitated as ammonium diuranate (ADU) with ammonia, which exists mainly as hydrated uranyl hydroxide containing NH_4^+ solution. ADU was heated at 800 °C to give U_3O_8. Thus, in this process the amount of waste generated is small and suitable for easy and safe disposal.

3.2. Magnesium fluoride matrix

Magnesium is conventionally used for the reduction of uranium oxide/fluoride to its metal. Magnesium has similar chemical properties to that of calcium. It is much cheaper than calcium; can be easily purified to meet stringent nuclear specifications; and its consumption is less than that of calcium.

The thermogravimetric pattern of the mixture of MgF_2 and $(NH_4)_2SO_4$ in 1:1.5 molar proportion is shown in Fig. 1. The mass loss and XRD data [11] showed that $(NH_4)_2SO_4$ reacts with MgF_2, as per the Eqs. (9) and (10) given below:

$$2\mathrm{MgF_2}+3(\mathrm{NH_4})_2\mathrm{SO_4}\xrightarrow{400\,^{\circ}\mathrm{C}}(\mathrm{NH_4})_2\mathrm{Mg_2(SO_4)_3}+4\mathrm{NH_4F}, \tag{9}$$

$$(\mathrm{NH_4})_2\mathrm{Mg_2(SO_4)_3}\xrightarrow{450\text{–}500\,^{\circ}\mathrm{C}}2\mathrm{MgSO_4}+2\mathrm{NH_3}\uparrow+\mathrm{SO_3}\uparrow+\mathrm{H_2O}\uparrow. \tag{10}$$

MgF_2 forms a stable intermediate compound $(NH_4)_2Mg_2(SO_4)_3$ with $(NH_4)_2SO_4$. Formation of $MgSO_4$ takes place at a higher temperature than that required for the formation of $CaSO_4$, Eq. (1). This is due to the fact that, magnesium is less efficient reducing agent than calcium. The TG-DTA pattern for a synthetic mixture of MgF_2 and UO_2 (or UF_4) with $(NH_4)_2SO_4$ also showed that the reactions take place in three steps in the temperature range of 250–550 °C. As seen in Fig. 5, the reactions of MgF_2 and UO_2 with $(NH_4)_2SO_4$ take place comparatively at higher temperature than the reactions in the CaF_2 matrix. Accordingly, reaction mixtures were heated in three steps in a furnace at 350, 450 and 550 °C for about 3 h at each step. Their products were identified from mass loss and their XRD patterns, recorded at room temperature. The XRD patterns, Fig. 6, correspond to the formation of $(NH_4)_2U(SO_4)_3 + (NH_4)_2Mg_2(SO_4)_3$ at 350 °C, $U(SO_4)_2 + MgSO_4$ at 450 °C, and $UO_2SO_4 + MgSO_4$ at 550 °C [7,11]. As in the case for the reactions with the CaF_2 matrix, the XRD patterns of the products formed at 450 °C was recorded in the dry atmosphere and immediately after removing the sample from the furnace. Since the formation of crystalline $MgSO_4$ takes place at a much slower rate and at higher temperature than CaF_2 (Fig. 1), the XRD lines due to $MgSO_4$ phase in the products formed at 450 °C, were quite week. The oxidation state of uranium as +4 in $(NH_4)_2U(SO_4)_3$ and $U(SO_4)_2$ and +6 in UO_2SO_4, was confirmed from the

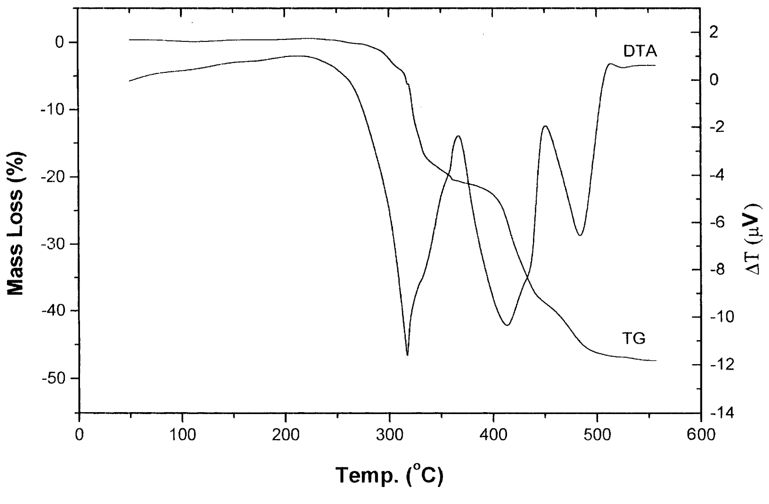

Fig. 5. TG and DTA pattern of: $UO_2 + MgF_2$ with $(NH_4)_2SO_4$.

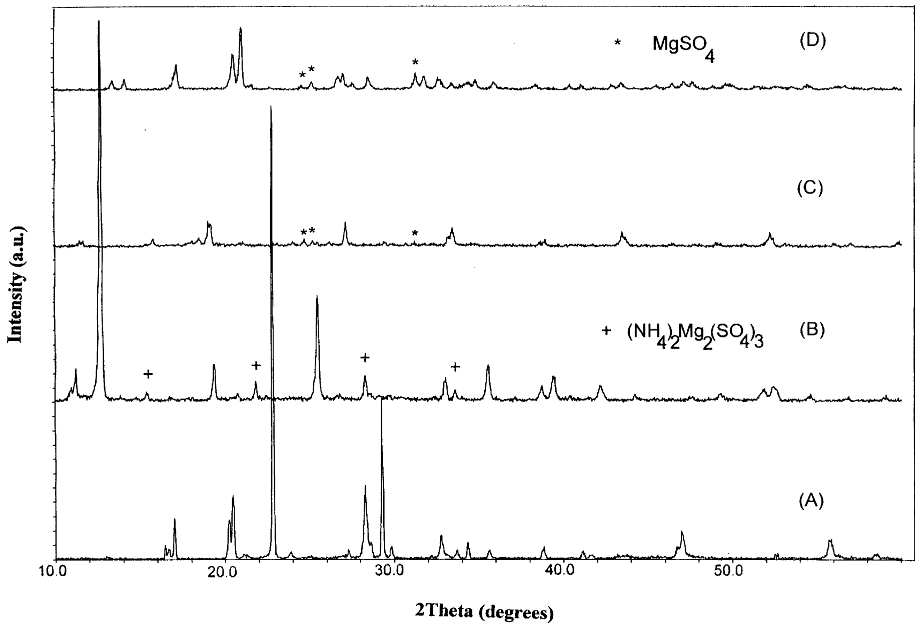

Fig. 6. XRD pattern of: $UO_2 + UF_4 + MgF_2$ with $(NH_4)_2SO_4$. (A) Unreacted $UO_2 + UF_4 + MgF_2$ with $(NH_4)_2SO_4$, (B) $(NH_4)_2U(SO_4)_3 + (NH_4)_2Mg_2(SO_4)_3$ (+) at 350 °C, (C) $U(SO_4)_2 + MgSO_4$ (*) at 450 °C, (D) UO_2SO_4 and $MgSO_4$ (*) at 550 °C.

UV–visible spectra recorded in 1 M H_2SO_4. The XRD pattern of the products formed after heating the reaction mixtures at 550 °C showed the products to be $MgSO_4$ and UO_2SO_4 [11]. The reaction products formed and identified are given in Table 2.

The reaction sequence for the mixture of $UF_4 + UO_2 + MgF_2$ with $(NH_4)_2SO_4$ is shown by the Eqs. (11)–(13) given below:

$$\begin{aligned} &UF_4 + UO_2 + 2MgF_2 + 9(NH_4)_2SO_4 \\ &\xrightarrow{350\,°C} 2(NH_4)_2U(SO_4)_3 + (NH_4)_2Mg_2(SO_4)_3 \\ &\quad + 8NH_4F\uparrow + 4NH_3\uparrow + 2H_2O\uparrow, \end{aligned} \tag{11}$$

$$\begin{aligned} &2(NH_4)_2U(SO_4)_3 + (NH_4)_2Mg_2(SO_4)_3 \\ &\xrightarrow{450\,°C} 2U(SO_4)_2 + 2MgSO_4 + 6NH_3\uparrow + 3H_2O\uparrow \\ &\quad + 3SO_3\uparrow, \end{aligned} \tag{12}$$

$$2U(SO_4)_2 \xrightarrow[O_2]{550\,°C} 2UO_2SO_4 + 2SO_3\uparrow\,. \tag{13}$$

The final products of UO_2SO_4 and $MgSO_4$ were treated with an alcohol–water mixture to separate off most of the $MgSO_4$ in this solvent. The residue, UO_2SO_4, was dissolved in 1 M HNO_3. Ammonia was then added, to

Table 2
Products identified by mass loss and XRD during solid state reactions of $(NH_4)_2SO_4$ with UO_2/UF_4 in MgF_2 matrix at different temperatures

Reactants	Molar proportion	Temp. (°C)	Products	Mass loss (%)	
				Observed	Expected
$(NH_4)_2SO_4 + MgF_2$	3:2	400	$(NH_4)_2Mg_2(SO_4)_3$	29.2	28.4
		500	$MgSO_4$	53.4	53.8
$(NH_4)_2SO_4 + UO_2 + MgF_2$	9:2:2	350	$(NH_4)_2Mg_2(SO_4)_3$ $+ (NH_4)_2U(SO_4)_3$	18.5	19.2
		450	$MgSO_4 + U(SO_4)_2$	40.2	40.6
		550	$MgSO_4 + UO_2SO_4$	47.3	47.5
$(NH_4)_2SO_4 + UF_4 + MgF_2$	9:2:2	350	$(NH_4)_2Mg_2(SO_4)_3$ $+ (NH_4)_2U(SO_4)_3$	21.0	21.1
		450	$MgSO_4 + U(SO_4)_2$	42.5	43.3
		550	$MgSO_4 + UO_2SO_4$	49.5	49.9

precipitate uranium as ADU, which on heating at 800 °C formed U_3O_8.

After recovering uranium from synthetic samples, the same procedure was applied for the recovery of uranium from the MgF_2 slag obtained from the Uranium Metal Plant, BARC. The XRD pattern of the slag showed it to contain MgF_2 and UO_2. Five gram, samples, of the slag were heated at 550 °C with 20% molar excess of ammonium sulfate. Following the same procedure used for the synthetic samples, uranium was separated as UO_2SO_4 from $MgSO_4$ and precipitated as ADU in ammonia solution. Finally, uranium was converted to U_3O_8 by heating ADU to 800 °C.

4. Conclusion

Solid state reactions of UO_2/UF_4 in a CaF_2 matrix with $(NH_4)_2SO_4$ form $CaSO_4 + (NH_4)_2U(SO_4)_3$ at 350 °C, $CaSO_4 + U(SO_4)_2$ at 425 °C and $CaSO_4 + UO_2SO_4$ at 525 °C. In the MgF_2 matrix containing UO_2/UF_4 with $(NH_4)_2SO_4$, solid state reactions lead to the formation of $(NH_4)_2Mg_2(SO_4)_3 + (NH_4)_2U(SO_4)_3$ at 350 °C, $MgSO_4 + U(SO_4)_2$ at 450 °C, and $MgSO_4 + UO_2SO_4$ at 550 °C. Uranium could be separated by dissolving the final products in dilute HNO_3 or H_2SO_4 and precipitating as ADU. About 95% of the uranium initially present could be recovered as U_3O_8 by heating ADU to 800 °C. The amount of waste generated is much less than that produced by other techniques and is suitable for easy and safe disposal.

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