



Preparation of homogeneous $(\text{Th}_{0.8}\text{U}_{0.2})\text{O}_2$ powders by mechanical blending of $\text{Th}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{U}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$ powders

Y. Altaş *, M. Eral, H. Tel

Institute of Nuclear Sciences, Ege University, 35100 Bornova-İzmir, Turkey

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Abstract

Thorium oxalate and uranium (IV) oxalate powders were prepared and characterized by chemical, TGA/DTG, IR and X-ray diffraction analysis. $\text{Th}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{U}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$ powders (80% Th and 20% U) were mechanically mixed in a diagonal rotating drum for 3 h. Mechanically mixed oxalates were decomposed at 623 K, calcined at 1173 K for 24 h in air and reduced for 2 h at 923 K in hydrogen atmosphere. The powders were compacted into pellets and sintered in flowing CO_2 at 1373 K for 1 h. The XRD pattern of $(\text{Th}_{0.8}\text{U}_{0.2})\text{O}_2$ obtained showed that a complete solid solution was formed. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Thorium is estimated to be about three times more abundant in the earth's crust than uranium. The abundance and long-term availability of thorium is a decisive argument in favour of the thorium fuel cycle. A combined application of both uranium and thorium fuel cycles is expected to guarantee a long-term fuel supply at tolerable and fairly stable prices. In this respect, the demonstration of thorium fuel cycles is a promising route for many countries. It is especially of interest to countries that have considerable thorium resources.

$(\text{Th}, \text{U})\text{O}_2$ mixed-oxide fuels have been studied for many years. There are principally two kinds of methods for manufacturing $(\text{Th}, \text{U})\text{O}_2$ mixed-oxide fuel [1]. ThO_2 and UO_2 powders are mixed by mechanical blending in one method and co-precipitated from a liquid solution in another. The nuclear criticality mass is larger in the former method than in the latter one which involves a liquid solution. The former method is much applicable to an industrial production. But the mixed-oxide fuel fabricated by this method does not necessarily form the

complete solid solution. ThO_2 and UO_2 powders having quite different bulk densities and morphological characteristics and because of the dominance of adhesive forces in the fine ceramic powders, the mechanical blending is not effective in producing a high degree of microhomogeneity. In this case, the formation of the solid solution can be performed only with extensive co-milling and with reaction at high temperature [2]. Many authors stressed that the key step in the development of thorium–uranium fuel is the preparation of a homogeneous oxide mixture preparation [3,4].

In this study, taking into consideration the difficulties involved in the preparation of the solid solution from the mechanically mixed-oxides, thorium and uranium which are principal constituents were mechanically mixed as their oxalates instead of oxides. For this purpose, the preparation conditions of thorium oxalate and uranium (IV) oxalate were investigated and they were precipitated individually. The structures of these powders were determined by chemical analysis, XRD, IR and thermogravimetrically. The oxalate powders were mechanically mixed at a ratio of 80% Th and 20% U, decomposed at 623 K, calcined at 1173 K for 24 h and reduced at 923 K in a hydrogen atmosphere during 2 h. The powders were compacted into pellets and the pellets were sintered in flowing CO_2 at 1373 K for 1 h. X-ray

* Corresponding author.

E-mail address: altasy@bornova.ege.edu.tr (Y. Altaş).

diffraction of these powders was taken which resulted in a complete solid solution formation was achieved.

2. Experimental

2.1. Preparation

The initial materials, ammonium diuranate (ADU) and commercial thorium nitrate salts were provided by Çekmece Nuclear Research and Training Center of Turkish Atomic Energy Authority. ADU has been produced at Çekmece Nuclear Fuel Pilot Plant by the purification of Salihli–Köprübaşı Pilot Plant originated yellow cake.

The flow sheet of the process applied is given in Fig. 1. In our previous study [5], dissolution of ADU with sulfuric acid, reduction of the uranyl ion with zinc and precipitation of $\text{UO}_2 \cdot 2\text{H}_2\text{O}$ with NH_4OH were investigated for the preparation of the U(IV) nitrate solutions. The optimum parameters determined in the former study, such as acid concentration, the amount of zinc and reduction time were also used in the present study. The $[\text{UO}_2(\text{SO}_4)_3]^{4-}$ solution which contains 107 gU/l was prepared by dissolving ADU with 2 M H_2SO_4 . U(VI) was reduced to U(IV) with addition of 50% stoichiometric excess of granulated zinc and the U(IV) was precipitated as the hydrated oxide by addition of 3 M ammonium hydroxide. The precipitation was carried out in a conical vessel, equipped with an argon inlet from the bottom to prevent the reoxidation of U(IV) and also to provide mixing. For the determination of pH corresponding to complete removal of Zn from the U(IV) oxide hydrate precipitate, the different precipitations were carried out at different pH values (pH = 7, 8, 9, 9.5 and 10). Following the filtration, the precipitates were washed with 10% ammonium hydroxide and Zn was determined in the solutions by atomic absorption spectrometry (Pye Unicam model SP-9) and titrimetrically. At pH > 9, the ammonium hydroxide did not precipitate zinc because of the formation of a Zn–ammonia complex. The hydrated uranium oxide was dissolved rapidly in 1 M nitric acid which contained 0.5 M sulphamic acid as a holding reductant. $\text{U}(\text{C}_2\text{O}_4)_2 \cdot n\text{H}_2\text{O}$ was precipitated from this solution by addition of 10% stoichiometric excess of 1 M $\text{H}_2\text{C}_2\text{O}_4$ at room temperature. After filtering, the precipitate was washed with water, alcohol and dried in air.

The 1 M $\text{Th}(\text{NO}_3)_4$ solution was prepared by dissolving commercial $\text{Th}(\text{NO}_3)_4$ concentrate with water and acidifying to 1 M with HNO_3 . $\text{Th}(\text{C}_2\text{O}_4)_2 \cdot n\text{H}_2\text{O}$ was precipitated from this solution by addition of 200% stoichiometric excess of 1 M $\text{H}_2\text{C}_2\text{O}_4$ at 10°C. After filtering, the precipitate was washed with water, alcohol and dried in air.

$\text{Th}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{U}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$ powders were mechanically mixed in a diagonal rotating drum for 3 h in a ratio of 80% Th and 20% U. Mechanically mixed oxalates were decomposed at 623 K, calcined at 1173 K for 24 h in air and reduced for 2 h at 923 K in hydrogen atmosphere. The powders were compacted into pellets in a double acting hydraulic press at 300 MPa and the pellets were sintered in flowing CO_2 at 1373 K for 1 h. An XRD pattern was taken from the $(\text{Th}_{0.8}\text{U}_{0.2})\text{O}_2$ obtained.

2.2. Identification and characterization

The methods of analysis used to determine the chemical composition of both thorium oxalate and uranium (IV) oxalate powders are listed below: Uranium content: potentiometric titration (Metrohm Titroprocessor 686); thorium content: EDTA titration; $\text{C}_2\text{O}_4^{2-}$: titration with KMnO_4 ; H_2O : thermogravimetry.

Thorium oxalate and uranium (IV) oxalate samples were characterized by TGA/DTG analysis using a Shimadzu thermal analyzer, by IR analysis using a Perkin–Elmer model IR spectrometer and by X-ray diffraction analysis using a Perkin–Elmer model diffractometer.

In order to investigate powder properties, the specific surface area was measured by the BET method using a high speed surface area analyzer (Micrometrics 2200 model). The average particle size was measured with a Fisher 95 sub-sieve sizer. The distribution of the particle size was determined spectrophotometrically by the sedimentation method based on Stokes' law.

The flowability was measured by a stainless steel funnel (TS4483 Turkish Standards) with an inlet diameter of 3.2 mm and an opening angle of 60°.

The bulk and the tap densities of thorium oxalate and uranium (IV) oxalate were measured.

3. Results and discussion

Sulfuric acid is a suitable medium for the reduction of uranyl ions. U(IV) sulphate is rather stable towards oxidation due to the strong complex formation between U^{4+} and SO_4^{2-} . Direct reduction of U(VI) in a nitric acid–hydrazine medium is impractical because the reaction between zinc and nitrate rapidly consumes the hydrazine and the removal of zinc ions from the U(IV) nitrate solutions is also required. Electrolytic or photochemical reduction of uranyl ions is also possible, but the reduction is not fast and complete. The metals most commonly used for the uranyl ion reduction are usually amalgamated for more rapid reduction, but mercury ions would be difficult to remove from the product U(IV) solution. Zinc is an inexpensive and effective reductant in the absence of mercury. This metal has the additional advantage that its amphoteric property

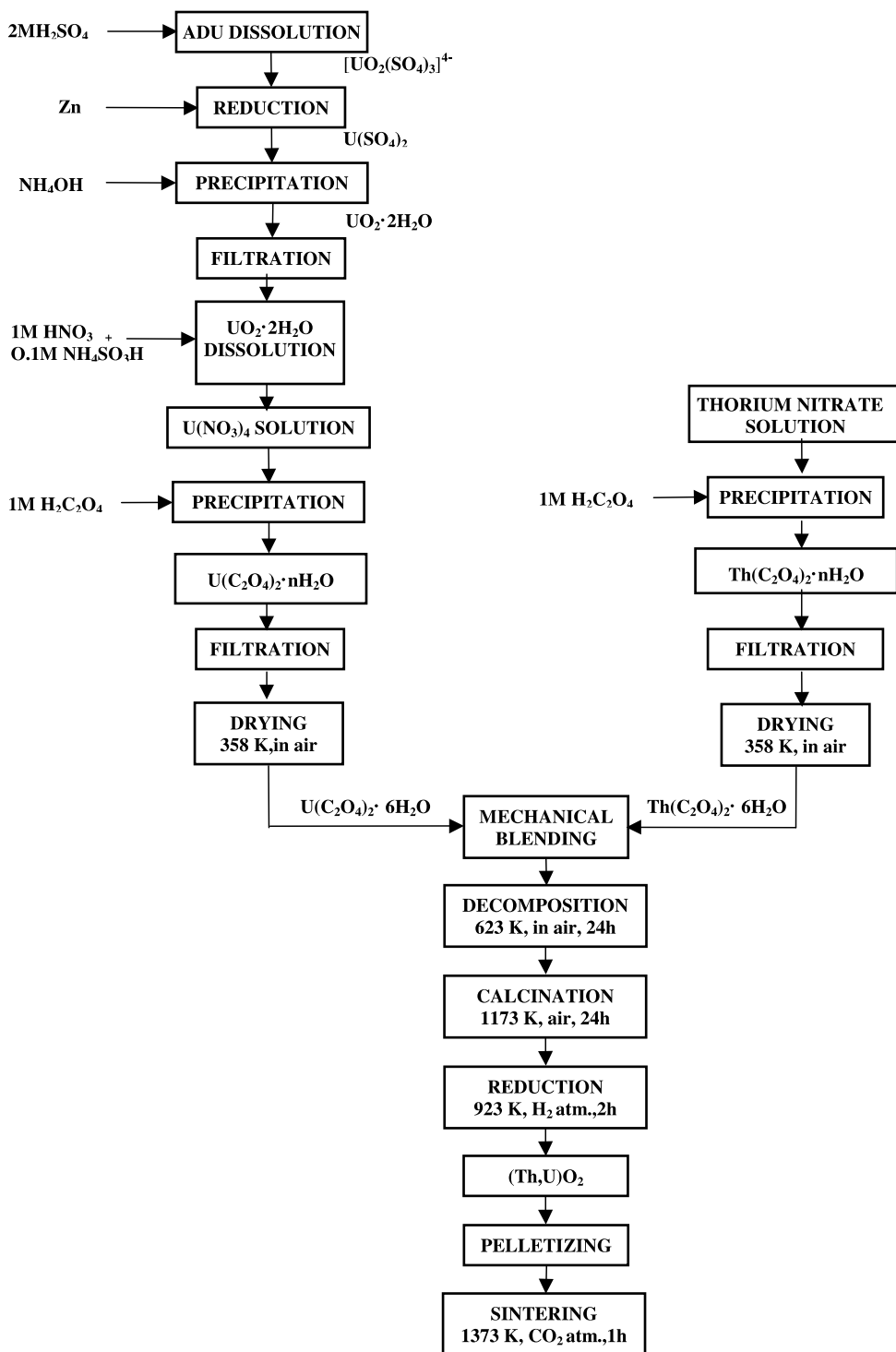


Fig. 1. The flow sheet of the process.

permits it to be readily separated from the U(IV) oxide hydrate. For the reduction of uranyl ions in a sulfuric acid medium (1.5 M), a 50% excess of a stoichiometric

amount of zinc and 1 h reduction time were determined as optimum conditions. It was observed that high sulfuric acid concentrations (>3 M) increase the rate of air

oxidation, and too low sulfuric acid concentrations (<1 M) result in incomplete reduction.

The precipitation of hydrated U(IV) oxide from sulfate solution must be accomplished in inert atmosphere to prevent the reoxidation of U(IV) and to eliminate Zn as Zn–ammonia complex. The ammonium hydroxide must be added at least until the pH reaches 9.

The hydrated U(IV) oxide precipitate had initially a light green color, then it gradually became dark green. When the precipitate was washed with water to remove excess base and sulfate salts, its color changed to a dark gray-green. The precipitate oxidized readily in air. After filtration and washing, the attempts to dry the precipitate either by heating it in an oven or washing it with alcohol caused 56% of the U(IV) to be oxidized. To prevent the rapid oxidation, after filtration and washing, the precipitate was dissolved rapidly without drying in 1 M nitric acid containing 0.5 M sulphamic acid as a holding reductant. In this case U(VI) concentration was <2%.

The chemical analysis indicated that the U(IV) oxalate powder contained 45.5% uranium and 33.7% oxalate. These results are in perfect agreement with the values theoretically calculated from the chemical formula of $U(C_2O_2)_2 \cdot 6H_2O$.

The TGA/DTG curves are shown in Fig. 2. From the weight loss we calculated that U(IV) oxalate powder contains six molecules of water. The DTG curve indicates that the decomposition of U(IV) oxalate occurs in three steps (115°C, 190°C and 331°C). The first and second peaks indicate the loss of moisture and two molecules of water, respectively. The third peak is related to the decomposition of four molecules of water

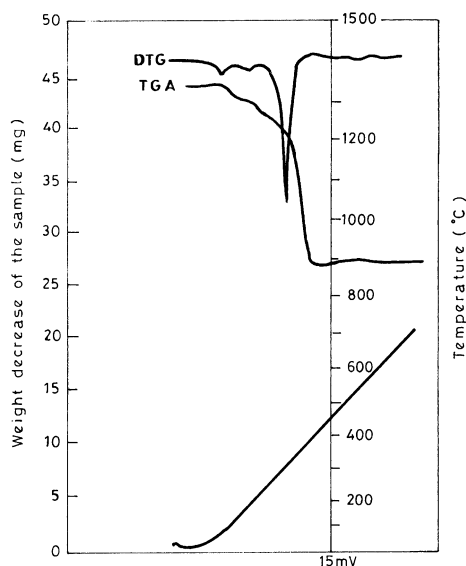


Fig. 2. Thermal analysis of U(IV) oxalate.

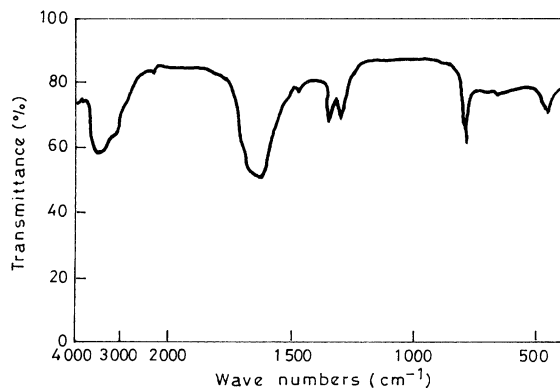


Fig. 3. IR spectrum of the U(IV) oxalate.

together with oxalate. These results are in agreement with the literature findings [6].

The IR spectrum of the uranium (IV) oxalate is given in Fig. 3. The prominent bands and their assignments are listed as follows: $(3400\text{ cm}^{-1})\nu_{O-H}$; $(1640\text{ cm}^{-1})\nu_{\text{sym}OCO}$; $(1310\text{ cm}^{-1})\nu_{\text{Asy}OCO}$ and $(800\text{ cm}^{-1})\rho_{COO}$ or π_{COO} . These results are in good agreement with the literature findings [7].

The particle size distribution of the thorium oxalate and uranium (IV) oxalate powders is given in Fig. 4. In comparison with the thorium oxalate, a narrower particle size distribution was obtained for uranium (IV) oxalate powder. As clearly seen, 10% of the thorium oxalate particles are larger than $40\text{ }\mu\text{m}$ and 15% of them are smaller than $2\text{ }\mu\text{m}$. A high percentage of the particles ($\approx 75\%$) are within the range of $2\text{--}10\text{ }\mu\text{m}$. For uranium (IV) oxalate practically no particles were observed above $40\text{ }\mu\text{m}$. Approximately 80% of the particles are within the range of $4\text{--}10\text{ }\mu\text{m}$. The mean particle size of both thorium oxalate and uranium (IV) oxalate were determined as 5 and $6\text{ }\mu\text{m}$, respectively.

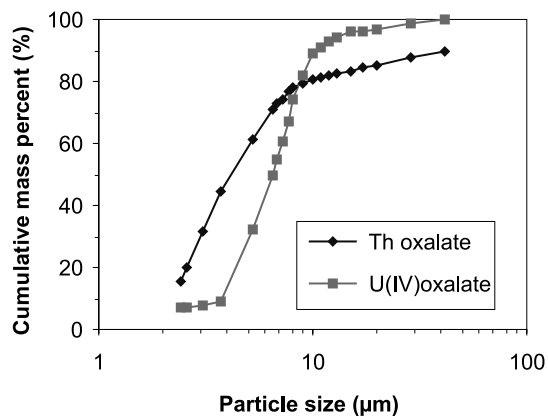


Fig. 4. Particle size distribution of Th and U(IV) oxalate powders.

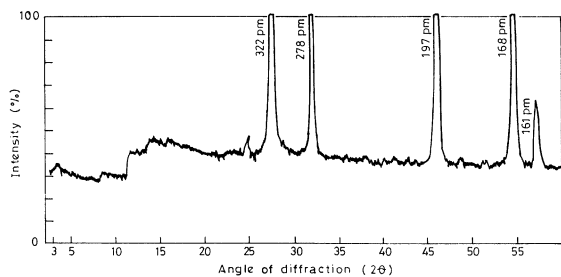


Fig. 5. XRD pattern of $(\text{Th}_{0.8}\text{U}_{0.2})\text{O}_2$ powder (via oxalate mixture method).

The flowability of both thorium and uranium (IV) oxalate powders were 0.5 g/s. The bulk densities of thorium oxalate and uranium (IV) oxalate were 0.52 and 0.45 g/cm³ and the tap densities were 0.68 and 0.61 g/cm³, respectively.

The specific surface area values of the thorium oxalate and uranium (IV) oxalate powders were 6.3 and 5.9 m²/g, respectively.

The X-ray diffraction pattern of the mixed-oxide powder is shown in Fig. 5. The data are in good agreement with the ASTM data (ASTM card number: 30–1360), and it is clearly seen that a single-phase solid solution was formed.

In comparison with conventional oxide mixture preparation techniques, where the solid solution formation is difficult due to the very different powder properties of the individual oxides, the oxalate mixture method has a considerable advantage from the point of view of homogenization and facile formation of the solid solution. The complete solid solution formation of the oxides from the conventional oxide mixture method is only possible with extensive co-milling and reaction at high temperature, while the complete solid solution formation of the oxides by the oxalate mixture method is possible by blending the oxalates in a diagonal rotating drum for only 3 h and subsequent heating at relatively low temperature (1373 K). This result may be attributed to the powder properties of the constituents. The thorium and uranium (IV) oxalates prepared in this work have similar powder properties, very close bulk and tap densities, specific surface area, mean particle size and particle size distribution. The mechanical blending of these two constituents having very close powder properties provides a good homogenization and following

the subsequent decomposition, reduction and sintering steps a complete solid solution is formed. These results are comparable with the mixed-oxides derived from the co-precipitation of the $(\text{Th}, \text{U})(\text{C}_2\text{O}_4)_2$ powders which were studied in our previous work [5]. The green densities of the pellets produced from the mixed-oxides obtained via the oxalate mixture method were found to be in the order of 40% TD. The sintered densities of the pellets were found to be 88% TD. These values are relatively high as compared to the density values of mixed-oxide obtained by co-precipitation, which were 37% and 81%, respectively.

Consequently, besides of the considerable advantages of conventional powder techniques, $(\text{Th}, \text{U})\text{O}_2$ powder prepared via mechanical blending of oxalates has also comparable results with mixed-oxide prepared by co-precipitation which is not applicable widely to an industrial production for the criticality reasons. In this study suitable powder properties, high homogeneity and the formation of a solid solution are achieved. It is necessary to investigate the optimisation of different parameters of pre-conditioning, pelletizing and sintering conditions in order to reach high densities.

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