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Preparation and characterization of uranyl oxalate powders

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Abstract

Uranyl oxalate powders are prepared by adding 0.5 M oxalic acid solution to the uranyl nitrate (UNH) solutions purified with TBP extraction from dissolution of the Canada originated U_3O_8 commercial concentrate. Uranyl oxalate powders are identified by chemical analysis, TGA/DTG analysis, IR analysis and by single-crystal X-ray diffraction. The effects of the precipitation conditions on the powder properties are determined. A broad particle size distribution is obtained for all precipitation variants. These powders including very fine particles are difficult to filter and are not free flowing. The reactor and mixing type have a considerable effect on the powder properties of the uranyl oxalate powders. It was possible to ameliorate the filtration and the flowability to a certain degree using a conical air agitated reactor. The flowability of these powders is 0.4 g/s with a specific surface area 6.64 m^2/g and an average particle size of 11 μm.

1. Introduction

Nuclear fuel manufacturing involves the fabrication of high density UO_2 with controlled microstructure. The pellet quality is obviously dependent, besides the pellet manufacturing process, on the characteristics of the UO_2 powder used and these characteristics are influenced closely with the chemical form and the preparation conditions of the powders from different conversion processes. It is well known that UO_2 nuclear fuel powders can be obtained from calcination and subsequent reduction of different volatile compounds of uranium such as ammonium diuranate, ammonium uranyl carbonate, uranyl nitrate, oxalate, acetate, formate and uranium (IV) oxalate, acetate, formate etc. Industrial manufacturing processes are based either on wet conversion, where intermediate products are precipitated from aqueous solutions or on dry conversion, where UF_6 is directly processed into UO_2 powder. The latter process can only start with the feed material UF_6 whereas the wet conversion processes can start either with UF_6 or UNH. The wet processes are usually designated by the uranium compounds which constitute the precipitate: e.g. ammonium diuranate (ADU), ammonium uranyl carbonate (AUC). The characteristics of UO_2 powders from these processes are well known [1–10]. A number of papers has been published on the characteristics of UO_2 powders manufactured from different conversion processes. This paper deals with the influence of uranyl oxalate production conditions on the powder properties and characterization of the uranyl oxalate obtained.

2. Experimental

2.1. Precipitation conditions

Canada originated U_3O_8 commercial concentrate is used as the initial material. Uranyl nitrate solutions are prepared by dissolving U_3O_8 in 6 M HNO_3. These solutions are purified by TBP extraction. Uranyl oxalate precipitates are obtained with the addition of 0.5 M oxalic acid solution into these pure uranyl nitrate solutions and the effect of precipitation conditions on the powder properties is investigated. The conditions varied during the precipitation are: oxalate/uranium ratio of the precipitation solution, uranium concentration of the UNH solution, precipitation temperature, oxalic acid concentration, addition rate of oxalic acid solution and

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mixing rate. Considering the effects of the precipitation parameters on the powder properties, a final precipitation is realized in a precipitation equipment consisting of a conical glass precipitation vessel (500 ml) equipped with an air inlet from bottom and three necks on the top for insertion of the thermocouple and the precipitation reactives, a temperature controller, a titroprocessor, two dosimats and a hot-plate. 50 ml uranyl nitrate solution (100 g/l) is put into the precipitation vessel and precipitated with the addition of 0.5 M oxalic acid until the oxalate/uranium ratio = 1.5 is reached maintaining the temperature at 50°C. Following this precipitation, both uranyl nitrate and oxalic acid are added drop by drop at the same time in the system conserving their proportion and amounts. The agitation is made by air from the bottom of the precipitation vessel during 180 min.

2.2. Identification and characterization

The methods of analysis which are used to determine the chemical composition of uranyl oxalate powders are listed below:

Uranium contents: potentiometric titration (Metrohm titroprocessor 686); $C_2O_4^{=}$: titration with EDTA; H_2O: thermogravimetrically.

Uranyl oxalate samples are identified and characterized by TGA/DTG analysis using a Shimadzu thermal analyzer, by IR analysis using a Perkin–Elmer model IR spectrometer and by single-crystal X-ray diffraction analysis using a Perkin–Elmer model diffractometer.

In our thermogravimetric analysis, 22.5 mg of uranyl oxalate sample is weighed and operated at the following conditions: atmosphere: air; heating rate: 10°C/min; full scale: 20 mg(±10 mg); range: 4 mV/min. For IR analysis, uranyl oxalate powder was mixed with KBr, pressed and the IR spectrum was taken between 600 and 4000 cm^{-1}. The X-ray diffraction data were obtained using Cu-K_α radiation ($\lambda = 154.18$ pm).

In order to investigate powder properties, the specific surface area is measured by the BET method using a high speed surface area analyzer 2200, the average particle size is measured with a Fisher 95 sub-sieve sizer. The distribution of the particle size is determined spectrophotometrically by the sedimentation method based on Stokes' law. For the determination of the particle size distribution, 20 mg of the uranyl oxalate sample is weighed in a 1 cm glass cuvette of the Shimadzu UV-260 spectrophotometer and 2-octanol is added. The cuvette is shaked strongly until a uniform suspension occurs. As soon as the sample is placed in the spectrophotometer, the optical density is measured at 432 μm by regular intervals. Pure 2-octanol is used as reference.

The flowability is measured by a stainless steel funnel (TS 4483 Turkish Standards) with an inlet diameter of 3.2 mm and an opening angle of 60°.

3. Results and discussion

The chemical analysis indicates that the uranyl oxalate powder includes 57.75% uranium and 21.37% oxalate. These results are in perfect agreement with the values theoretically calculated from the chemical formula of $UO_2C_2O_4{\cdot}3H_2O$. The thermal analysis results also confirm that the chemical composition of the oxalate powder is closely dependent on this formula. The DTA/DTG curves are shown in Fig. 1. The DTG curve indicates that the decomposition of uranyl oxalate occurs in three steps. It loses two molecules of water in the first step at 100°C and one molecule of water in the second step at 170°C to form the anhydrous salt. The oxalate is decomposed in the third step at 365°C. We calculated the weight loss as 34.52% by the investigation of the TGA diagram, nearly to the theoretically calculated value (34.46%).

The X-ray diffraction data are given in Table 1. These values are in good agreement with the ASTM card (14-821) [11]. Uranyl oxalate has a monoclinic structure.

Regarding to the IR spectrum of the uranyl oxalate powder, the prominent bands and their assignments are listed as follows: (3500–3000 cm^{-1})γ_{OH}; (1680–1550 cm^{-1}) $\gamma_{\mathrm{sym\ OCO}}$; (1350–1300 cm^{-1})$\gamma_{\mathrm{asym\ OCO}}$; (900 cm^{-1})$\gamma_{\mathrm{sym\ C=O}}$; (800 cm^{-1})ρ_{COO}.

The precipitation conditions and powder properties of uranyl oxalate powders are given in Table 2. As can be clearly seen, the average particle size of uranyl oxalate powders increases with the $C_2O_4^{=}$/U ratio, uranium concentration and precipitation temperature while it decreases with increasing oxalic acid concentration. The

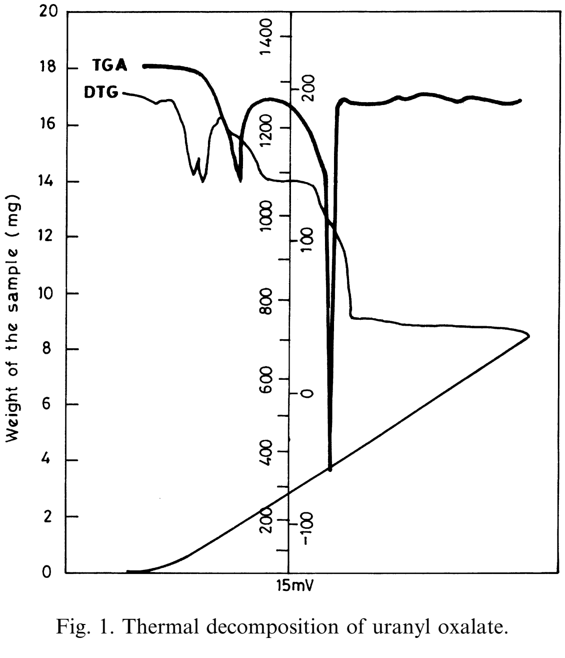

Fig. 1. Thermal decomposition of uranyl oxalate.

Table 1
X-ray diffraction data of the uranyl oxalate powder

d (pm)	I/I_0	*hkl*	*d* (pm)	I/I_0	*hkl*
850	85	020	325	5	102
625	80	021	318	35	112,141
523	10	110	290	20	
487	55	031,111	285	45	
463	35	002,120	283	15	
431	100	111	276	5	
405	15	022	270	10	
396	50	130	262	10	
385	55	041,102	254	30	
376	20	131,112	249	20	
350	5	131,122	244		

mixing rate and the addition rate of the oxalic acid does not have a considerable effect on the particle size. The minimum and maximum average particle size is 1.8 and 4.1 μm, respectively. The specific surface area values are between 5.16 and 9.10 m^2/g and decrease with increasing particle size. The distribution of the particle size depending on the precipitation conditions are given in Fig. 2. A broad particle size distribution was obtained for all precipitation conditions. In all cases the maximum particle size was about 30 μm. A high percentage of fine particles was observed. The percentage of the fine particles (<1 μm) was as follows: for $C_2O_4^-$/U ratios of 1.5% and 2.0%, 24% and 22%, respectively; for U concentrations of 50%, 100% and 300% gU/l, 40%, 24% and 16%, respectively; for precipitation temperatures of 10, 20 and 50°C, 26%, 24% and 4%, respectively. For oxalic acid concentrations of 0.25 and 0.50 M, 12% and 24%, respectively.

The powders obtained by all of these conditions having a broad particle size distribution and including a high percentage of 'fines' were difficult to filter and were not free flowing. The precipitation yield of the uranyl oxalate powders was about 80%. In comparison with the ADU and AUC powders, the uranyl oxalate powder seems to be disadvantageous from the point of view of poor recovery, filtration difficulty and poor flowability. It was possible to ameliorate the filtration and the

Table 2
Precipitation conditions and powder properties of uranyl oxalate

Precipitation parameters	UNH solution						
	U concentration (g/l)	Amount used (ml)	Amount of oxalic acid[a] C_2O_4/U	Precipitation temperature (°C)	Average particle size (μm)	BET surf. area (m^2/g)	Yield (%)
C_2O_4/U ratio							
	100	50	1.0	25	2.3	9.10	75.4
	100	50	1.5	25	2.4	8.92	79.8
	100	50	2.0	25	3.2	6.64	74.4
Uranium concentration (g/l)							
	50	50	1.5	25	1.8	11.60	73.9
	100	50	1.5	25	2.4	8.92	79.8
	150	50	1.5	25	–	–	78.0
	300	50	1.5	25	4.1	5.16	79.8
Precipitation temperature (°C)							
	100	50	1.5	10	1.9	11.00	82.0
	100	50	1.5	25	2.4	8.92	79.8
	100	50	1.5	50	2.8	7.63	76.5
Oxalic acid concentration (M)							
	100	50	1.5 (0.25 M)	25	3.8	5.59	74.4
	100	50	1.5 (0.50 M)	25	2.4	8.92	79.8
Addition rate of oxalic acid (ml/min)							
1	100	50	1.5	25	2.4	8.92	80.1
12	100	50	1.5	25	2.3	8.95	79.9
Mixing rate (rpm)							
60	100	50	1.5	25	2.5	8.91	79.7
300	100	50	1.5	25	2.4	8.95	79.8

[a] 0.5 M oxalic acid was used in all precipitation conditions except the one indicated.

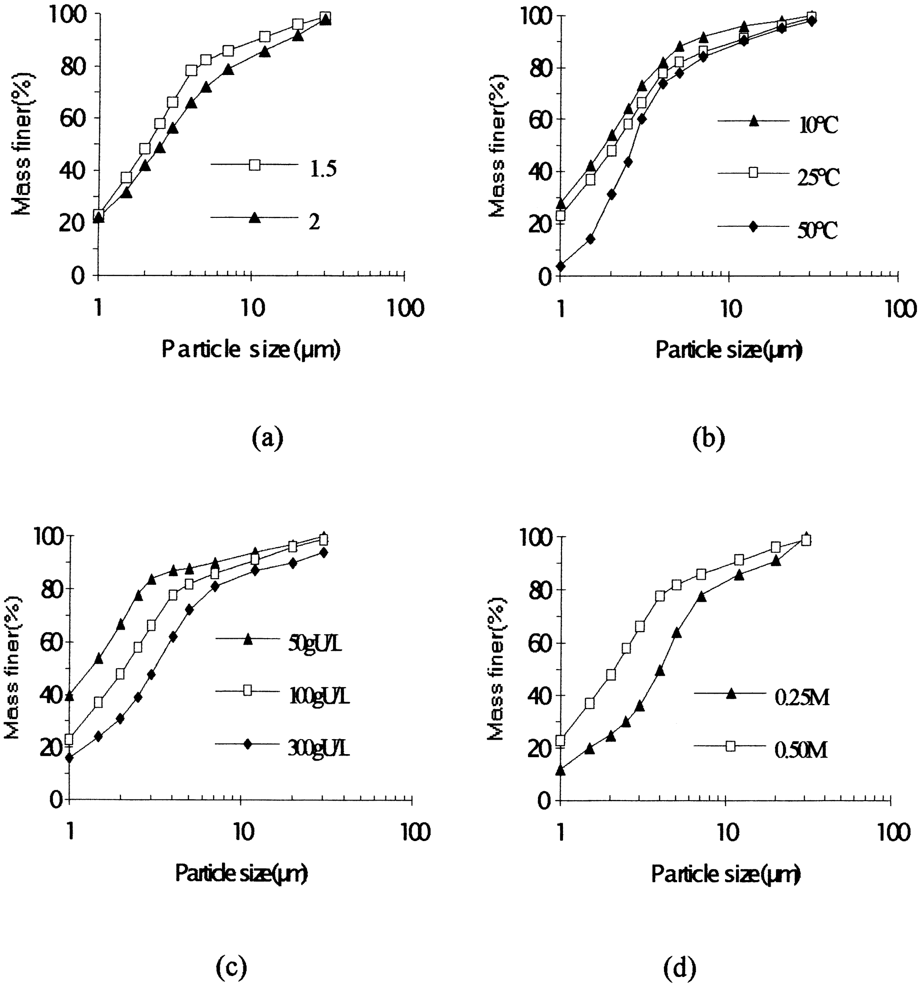

Fig. 2. Particle size distribution of uranyl oxalate powders at the different precipitation conditions: (a) C_2O_4/U ratio, (b) precipitation temperature, (c) Uranium concentration, and (d) Oxalic acid concentration.

flowability to a certain degree using a conical and air agitated reactor. The flowability of these powders was 0.4 g/s with a specific surface area 6.64 m^2/g and an average particle size of 11 μm. The particle size distribution of this powder is given in Fig. 3. In comparison with the other powders a narrower particle size distribution was obtained. The main effect of the reactor and agitation type was a reduction of the 'fines' while the size of the larger particles was less affected. It can be attributed to the air agitation and conical type of the reactor. The air agitation from the bottom, affecting the precipitation, provides a gentle sedimentation and interior circulation and under these circumstances the uranyl oxalate powder gains homogenization and flowability.

In this study, the amelioration of the uranyl oxalate powders' properties, satisfies the basic requirements needed for the production of UO_2 powders. Since the

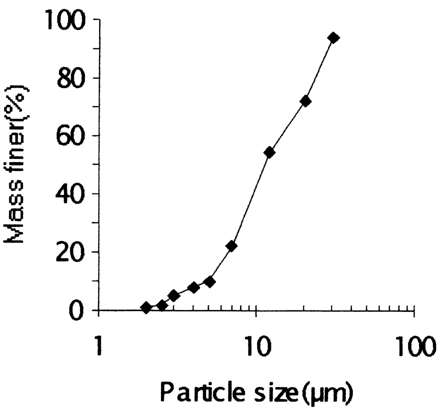

Fig. 3. Particle size distribution of uranyl oxalate powder obtained in an air-agitated reactor.

characteristics of the UO_2 powder are closely dependent, beside of the conversion process, on calcination, reduction and sintering conditions, in order to obtain of high density and good pellets, the conditions mentioned above must be investigated.

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