

## **EFFECTS OF WASHING CONDITIONS ON THE THERMAL DECOMPOSITION BEHAVIOUR OF GELLED $\text{UO}_3$ MICROSPHERES**

*A. F. Bishay, A. S. Abdel Halim, F. H. Hammad  
and A. M. Elaslaby*

ATOMIC ENERGY AUTHORITY, NUCLEAR RESEARCH CENTRE,  
METALLURGY DEPARTMENT, CAIRO, EGYPT

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DTA, TG and DTG curves obtained in various atmospheres using different heating rates were used together with X-ray examinations to study the thermal decomposition mechanisms of two types of gelled  $\text{UO}_3$  microspheres: ammonia-washed (UN) and hot water-washed (UH) microspheres.

The kinetics of the thermal decompositions were studied. The specific reaction rate constant  $k_r$  for the decomposition of  $\text{UO}_3$  to  $\text{U}_3\text{O}_8$  could be expressed in terms of the activation energy and the pre-exponential factor by the expressions:

$$K_r(\text{s}^{-1}) = 1.277 \times 10^{18} \exp \frac{-295.4}{RT} \text{ for the UN spheres,}$$

$$K_r(\text{s}^{-1}) = 8.406 \times 10^{19} \exp \frac{-263.2}{RT} \text{ for the UH spheres.}$$

Dense  $\text{UO}_2$  microspheres for reactor fuels are prepared by wet chemical processes. There are several wet chemical methods that differ considerably from each other. They are generally known as "sol-gel" processes [1, 2].

They have in common the fact that a solution of uranium (uranyl nitrate) is dispersed into droplets and thereafter solidified by chemical precipitation on reaction. These gel particles are processed into the required ceramic microspheres, mainly by thermal treatment.

To achieve good spherical kernels with high density, the precipitation must always be gel-like instead of crystalline, since only a gel structure keeps the particles spherical during drying (via uniform shrinkage) whereas a crystalline precipitate results in imperfect spherical kernels.

The wet chemical processes are commonly classified into external [3] and internal [4] gelation, according to the mode of precipitation.

The aim of the present investigation was to study the effects of washing on the dissociation mechanism of gelled microspheres and to study some related kinetic parameters.

### Experimental technique

The  $\text{UO}_3$  microspheres were prepared by using the hydrolysis process (H-process) [4]. This process is based on the homogeneous hydrolysis of a concentrated  $(\text{UO}_2(\text{NO}_3)_2\text{-urea})$  solution after the addition of hexamethylenetetramine (HMTA). A concentrated uranyl nitrate solution (350 g U/l) is stabilized by urea, which forms the complex  $[\text{UO}_2(\text{NH}_2\text{CONH}_2)_2]^{2+}$ ; the urea to uranium ratio is 2:1. This starting solution is mixed with solid HMTA at temperatures  $\leq 10^\circ$  until a pH of 5.5 is reached.

This metastable solution is dispersed into droplets from a vibrating nozzle into hot silicone oil ( $90\text{--}95^\circ$ ). The droplets solidify in a few seconds and form spherical particles. The obtained  $\text{UO}_3$  kernels are dark-yellow and translucent. The kernels are washed first with carbon tetrachloride to remove the silicone oil from the surface, and then with either hot water or ammonia to remove ammonium nitrate, excess HMTA, and urea. The resulting gel particles are divided into two portions. The first portion is washed with hot water (10 min at  $95^\circ$ ) and then five times, for 15 min each, with 3% ammonia solution at room temperature: type UH. The second portion is washed 5 times for 15 min each, with 3% ammonia solution at room temperature: type UN. The hot water-washed kernels (type UH) are yellow and opaque, while those washed with ammonia solution (type UN) are orange and glossy. The washed particles are dried at  $70^\circ$  in air for 17 h.

X-ray examination was carried out to determine the intermediate phases formed on thermal decomposition. To confirm these findings, thermal analysis was performed under various atmospheres.

Thermogravimetric curves obtained at different heating rates were utilized to calculate the activation energy, using the technique recommended by Carroll and Manche [5], since the order of reaction  $n$  does not appear in that method, as this parameter has only theoretical significance if  $n = 0, 1/2, 1/3, 2/3$  or 1.

In this method,  $-dw/dt = Kf(W)$ , where  $W$  is the weight of the reactive portion of the sample and  $K$  is the rate constant related to temperature by the Arrhenius equation,  $K = Z \exp(-E/RT)$ . If the heating rate  $\Phi = dT/dt$ , then

$$\frac{-dW}{dT} = \frac{Z}{\Phi} \exp(E/RT)f(W)$$

$$\ln \left[ \Phi \left( -\frac{dW}{dT} \right) \right] = \ln [Zf(W) - E/RT]$$

A plot of  $\ln [\Phi - (dW/dT)]$  vs.  $1/T$  for a given value of  $W$ , obtained at different heating rates, will lead to a value of  $E$ .

## Results and discussion

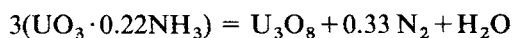
The DTA curves obtained are similar to those published earlier [6, 7]. The results show certain stages of decomposition, each involving a loss in weight. The water loss starts at 95°, due to the removal of the adsorbed water. Below this temperature, no weight change is observed. The peaks at 260° and 280° for the UN and UH samples, respectively, correspond to the removal of coordinated water molecules. Both peaks occurred at higher temperatures in the presence of humid air. This is in good agreement with the results published earlier [6]. Ippolitova et al. [8] found that the dehydration starts at 20° and proceeds up to 200°. Szabó [9] observed it to proceed up to 220°, while Stuart [10] found it to proceed up to 275° in an inert gas.

It was found that dry air shifts the reaction towards higher temperatures for the UN spheres. Washing with hot water (UN spheres) shifts the decomposition towards higher temperatures. This result is in good agreement with that of Turcanu [7]. The microspheres incorporate urea and HMTA, when the resulting gases will have to penetrate a barely permeable membrane, reducing the gas release rate. This will lead to a significant shift of the process towards higher temperatures. The contribution of the organic compounds (included in the microspheres) to the volume of eliminated volatile compounds will be particularly important, with direct influences on the porosity and on the chemical composition [11, 12]. Turcanu et al. [7] suggested a general formula  $\text{UO}_3 \cdot 0.66\text{NH}_3 \cdot 4\text{H}_2\text{O}$  for the unwashed microspheres, and stated that the water is completely eliminated at 460°.

The existence of a deflection between 310° and 360° for the UN spheres is mainly associated with the evolution of ammonia. For the UH spheres, this peak is not observed, indicating that water washing removes all the ammonia. This result is in agreement with the finding of Janov [13]. It was found that dry air shifts the deflection towards higher temperatures. Other investigators [8, 14, 15] reported that the deflection in the region 310–450° is mainly associated with the evolution of ammonia.

The peaks appearing at 570° and 580° for the UN and UH spheres, respectively, correspond to the conversion of  $\text{UO}_3$  to  $\text{U}_3\text{O}_8$ , as confirmed by X-ray measurements (ASTM card 2-0276). Whereas Dharwadkar et al. [16] stated that this decomposition starts above 545° and terminates at about 625°, El-Fekey et al. [14] found that it starts at 640°. This variation can be attributed to the smaller crystallite size of the gelled  $\text{UO}_3$  microspheres, and consequently to the higher specific surface area, which leads to a more active material. It can also be attributed to the use of different sample weights during heating, i.e. this variation is due to the effect of the thickness of the sample. The thickness of the sample has been found to have a pronounced effect on the compound formed during decomposition [17, 18]. Dharwadkar [16] mentioned that 3 g samples were used on the holder.

Price [11] described this stage as a process of self-reduction within the solid, and stated that it is not reduction of  $\text{UO}_3$  by evolved ammonia gas as proposed by Notz [15]. Stuart [10] identified this stage as a decomposition of the complex ammonia  $\text{UO}_3 \cdot x\text{NH}_3$ , formally represented by:



It was suggested that the ammonia retained by the solid prior to this stage is generally too small to account for the stoichiometry of this reaction. Price [19] and Stuart [10] also stated that gas analysis and infrared data gave no direct evidence to support this view, but thermogravimetric data indicate that the weights of completely self-reduced residues exceed the estimated weights of  $\text{U}_3\text{O}_8$  by about 1.04% and 1.08% for the UH type and UN type spheres, respectively.

#### *Calculations of some kinetic parameters*

The previous results indicate that the thermal decomposition includes dehydration, ammonia removal to form  $\text{UO}_3$ , and thermal decomposition of  $\text{UO}_3$  to  $\text{U}_3\text{O}_8$ .

The order of reaction  $n$  does not appear in this method as this parameter has only theoretical significance if  $n = 0, 1/2, 1/3, 2/3$  or 1 [20]. The activation energy values were calculated using the method mentioned above. They were found to be 191.2 and 166.5  $\text{kJ mol}^{-1}$  for the dehydration reaction for the UH type and the UN type spheres, respectively. These values were calculated for a heating rate of 30 deg/min and a temperature of 280° for the UH type spheres and 260° for the UN type spheres.

The specific reaction rate constant  $K_r$  for dehydration can be expressed by the following expressions:

$$K_r(\text{s}^{-1}) = 2.013 \times 10^{18} \exp \frac{-166.5}{RT} \text{ for the UN spheres,}$$

and

$$K_r(\text{s}^{-1}) = 1.184 \times 10^{20} \exp \frac{-191.2}{RT} \text{ for the UH spheres.}$$

The activation energies for the decomposition of  $\text{UO}_3$  to  $\text{U}_3\text{O}_8$  were found to be 295.4 and 263.2  $\text{kJ mol}^{-1}$  for the UH and the UN type spheres, respectively. The frequency factor for the decomposition [16] was found to be  $8.406 \times 10^{19} \text{ s}^{-1}$  and  $1.277 \times 10^{18} \text{ s}^{-1}$  for the UH and UN type spheres, respectively. Using the interrelationship [21] of the frequency  $Z$  with the entropy, the latter was calculated to be 91.65 and 83.288 for the UH and UN type spheres, respectively.

The specific reaction rate constant  $K_r$  for the decomposition of  $\text{UO}_3$  to  $\text{U}_3\text{O}_8$  is expressed by

$$K_r(\text{s}^{-1}) = 1.277 \times 10^{18} \exp \frac{-295.4}{RT} \text{ for the UN type spheres,}$$

and

$$K_r(\text{s}^{-1}) = 8.406 \times 10^{19} \exp \frac{-263.2}{RT} \text{ for the UH type spheres.}$$

## Conclusions

The results can be summarized as follows:

1. The removal of adsorbed water for the UN and UH type spheres starts at  $95^\circ$ , while the loss of crystalline water starts at  $260^\circ$  for the UN type spheres and at  $280^\circ$  for the UH type spheres.
2. Ammonia removal for the UN type spheres starts at  $310^\circ$  and ends at  $360^\circ$ . For the UH type spheres, a peak for ammonia evolution does not appear, indicating that the hot water washing removes all the ammonia.
3. The presence of humid air shifts the reaction towards higher temperatures for the UH type spheres, while dry air shifts the reaction towards higher temperatures for the UN type spheres.
4. The activation energy for dehydration is  $45.697$  and  $39.776 \text{ kcal mol}^{-1}$  for the UH and UN type spheres, respectively.
5. The activation energy for the decomposition of  $\text{UO}_3$  to  $\text{U}_3\text{O}_8$  is  $295.4$  and  $263.2 \text{ kJ mol}^{-1}$  for the UH and UN type spheres, respectively.

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**Zusammenfassung** — Der Mechanismus der thermischen Zersetzung von zwei Typen von gelförmigen  $UO_3$ -Mikrokugeln, nämlich mit Ammoniak (UN) und mit heißem Wasser (UH) gewaschene Mikrokugeln, wurde in verschiedenen Atmosphären und bei unterschiedlichen Aufheizgeschwindigkeiten durch DTA, TG und DTG sowie durch Röntgendiffraktometrie untersucht. Die Kinetik der thermischen Zersetzung wurde untersucht. Die spezifische Geschwindigkeitskonstante  $K_r$  der Zersetzung von  $UO_3$  zu  $U_3O_8$  kann mit den Werten für die Aktivierungsenergie und den präexponentiellen Faktor durch folgende Ausdrücke beschrieben werden:

$$K_r(s^{-1}) = 1,277 \times 10^{18} \exp \frac{-295,4}{RT} \text{ für UN-Kugeln}$$

$$K_r(s^{-1}) = 8,406 \cdot 10^{19} \exp \frac{-263,2}{RT} \text{ für UH-Kugeln.}$$

**Резюме** — ДТА, ТГ и ДТГ кривые, измеренные в различных атмосферах и при разных скоростях нагрева, совместно с рентгенофазовым анализом, были использованы при исследовании механизма термического разложения двух типов микросферической гелеобразной трехоксида урана: промытой аммиаком и горячей водой. Изучены кинетические параметры реакции термического разложения. Удельная константа скорости ( $K_r$ ) реакции разложения  $UO_3$  до  $U_3O_8$ , выраженная через энергию активации и предэкспоненциальный множитель, представлена следующими уравнениями:

$$K_r(\text{сек}^{-1}) = 1,277 \cdot 10^{18} \exp \frac{-295,4}{RT} \text{ в случае микросфер, промытых аммиаком}$$

$$K_r(\text{сек}^{-1}) = 8,406 \cdot 10^{19} \exp \frac{-263,2}{RT} \text{ в случае микросфер, промытых горячей водой.}$$