

Fabrication of (Th,U)O₂ pellets containing 3 mol% of uranium by gel pelletisation technique

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Received 6 May 2003; accepted 28 November 2003

Abstract

Internal gelation process has been developed to prepare high density ThO₂–3%UO₂ pellets. The study indicated that by carefully controlling the feed composition and the heat treatment scheme, soft mixed oxide microspheres could be obtained which are amenable for pelletisation at relatively low compaction pressures (200–250 MPa). The green pellets could be sintered in air up to 97% of TD at 1350 °C. The fractured and polished surface of the pellets showed a smooth surface without any berry structure. The shrinkage behaviour of these pellets was also studied in Ar + 8% H₂ atmosphere using a dilatometer. These studies revealed that the densification starts at a low temperature of 1100 °C. The SEM studies indicated uniform microstructure in the pellets with 3–5 μm grain size with uniform pores (~1 μm) distributed homogeneously in the pellet.

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PACS: 81.20.Fw; 28.41.Bm; 82.70.Gg; 81.20.Ev

1. Introduction

Thorium is an important fuel component in the nuclear power program for fabrication of thorium-based fuels, however there are radiation exposure problems due to the presence of ²³²U. Sol–gel process uses liquids or free flowing spherical solids which are amenable for automation and remote handling. Hence, this process is ideally suited for the manufacture of such fuel. Accordingly, the present investigation was aimed to develop a process flow sheet for obtaining dense (Th,U)O₂ pellets via sol–gel microsphere pelletisation (SGMP) technique. The process employs free flowing, dust free, sol–gel derived microspheres as starting feed material for fabrication of pellets, instead of powders. That is to say, it

combines the front end of sol–gel process with the back end of conventional pelletisation flow sheet. The SGMP technique provides the microspheres with better flow properties, which help in achieving consistent die fill, without dust generating steps. Several investigations have been made on the development of gel pelletisation technique for the preparation of ThO₂ and (Th,U)O₂ pellets [1–4]. For obtaining good quality pellets from microspheres, some physical parameters are to be optimised. Microspheres should have low crushing strength, reasonably high tap density and surface area. The objective of this work is to find out heat treatment condition to obtain microspheres, which are soft but have high tap densities for a good and consistent die fill. Ganguly et al. [3] first obtained the high density ThO₂ pellets from the soft microspheres which were prepared by adding carbon black to the original sol followed by calcination of the resultant gel microspheres in air at 700 °C to get porous microspheres suitable for pelletisation. Yamagishi and Takahashi [1] also prepared soft microspheres by exchanging water in their gel structure with

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isopropyl alcohol sufficiently and thereafter evaporating it. Suryanarayana et al. [5] obtained such uranium gel microspheres, by controlling the feed broth composition and heat treatment scheme, without resorting to addition of carbon. They reported that by the use of high metal ion concentration in the feed broth yielded soft microspheres having average crush strength value <3 N/particle. They further reported that the gel network consisting of large size crystallites (>5000 Å) is responsible for the desired softness and porosity. The present investigation was directed towards standardization of feed broth composition and heat treatment scheme for obtaining soft (Th,U) O_2 microspheres by internal gelation process with optimum tap density, crush strength and surface area for the fabrication of good quality pellets.

2. Experimental

The flow sheet for the preparation of (Th,U) O_2 pellets in the present study is shown in Fig. 1. The principal steps involved for the preparation of SGMP pellets are: preparation of feed solution, gelation, washing of the gel microspheres, heat treatment of these microspheres, pelletisation and sintering to obtain high density pellets.

2.1. Preparation of thorium nitrate solution

Thorium nitrate solution was prepared by dissolving thorium nitrate crystals (Nuclear grade) in distilled

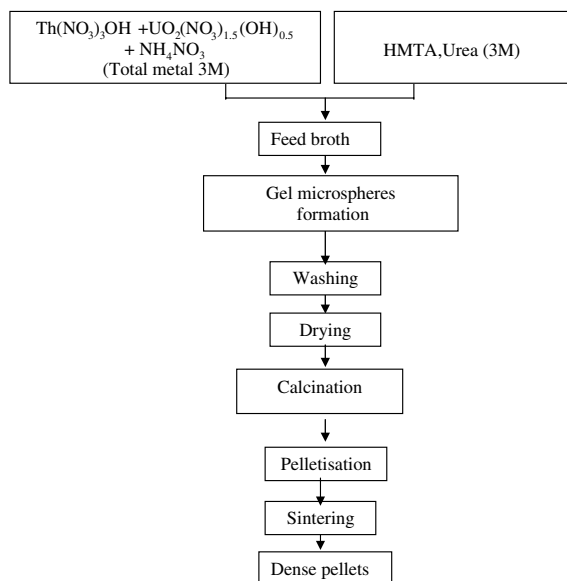


Fig. 1. Flow sheet for the preparation of (Th,U) O_2 pellets by internal gelation.

water. Nitrate content was estimated by titrimetry. The required amount of ammonium hydroxide solution was added to partially neutralize the thorium nitrate solution such that the ratio $[NH_4^+]/\{[NH_4^+]+[Th^{4+}]\} = 0.5$ in the final solution. The solution obtained was concentrated by slow heating to yield 3 M thorium nitrate solution. The thorium content was determined by gravimetric analysis for which an aliquot of the sample solution containing 200–300 mg of thorium was taken in a pre-weighed silica crucible. The sample was first heated gradually to 200 °C and then at 750 °C in air until a constant weight was obtained. The constant weight of the sample was taken as the weight of ThO_2 . Alternatively, thorium was estimated also by complexometric titration using EDTA. For this an aliquot of the sample containing ~50 mg of the thorium was taken in a conical flask. The pH of the aliquot was adjusted between 2 and 3. A few drops of Erichrome Black T was added as indicator and was titrated against standard EDTA solution, till the colour changes from pink to yellow.

2.2. Preparation of gel microspheres

2.2.1. Gelation

The assembly used for the preparation of gel microspheres is shown in Fig. 2. The equipment mainly consists of a feed tank, gelation column, conveyor belt and wash tank. For the preparation of feed broth, thorium nitrate solution was first mixed with uranyl nitrate solution followed by hexamethylenetetramine (HMTA, 3 M) and urea (3 M) solution in the required proportion. This feed solution was then converted into droplets by forcing the solution through a 1 mm ID SS capillary. For obtaining the droplets of uniform size, the capillary was vibrated at suitable frequency by an electromagnetic vibrator. These droplets were contacted with hot (90 °C) silicone oil fluid (100 cP) in the glass gelation column to obtain solid gel particles. The gel particles were separated from oil by collecting them on a conveyor belt. The gel particles were then washed with carbon tetrachloride (CCl_4) to remove the adherent oil followed by ammonium hydroxide (3 M) to remove HMTA, urea, ammonium nitrate, methylol urea etc. Several batches of 500 ml broth volumes were prepared. The compositions of the feed broth were selected from the gelation field diagram constructed by Kumar et al. [6]. The metal ion concentration ([M]) of the feed broth was varied from 1.0 to 1.3 M with a step of 0.05 M. For each metal ion concentration the [HMTA, Urea]/[M] ratio (R) was varied in the range from 1.1 to 1.5. In all the experiments the molar ratio of [U]/[Th + U] was maintained at 0.03. Also all the experimental conditions like feed broth flow rate, frequency of jet breakup, gelation temperature, drying conditions were kept fixed at 30 ml/min, 90 Hz, 90 °C and static bed drying in air circulating oven at 100 °C respectively. The wet gel microspheres were charac-

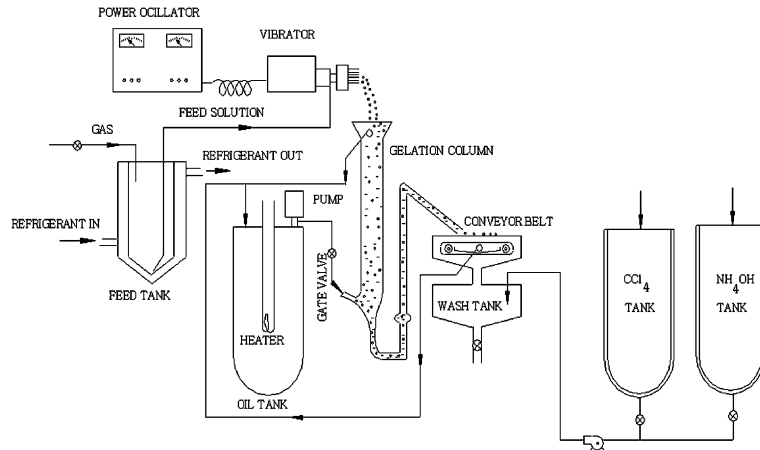


Fig. 2. Gelation assembly used for the preparation of (Th,U) O_2 microspheres.

terized with respect to physical appearance and leaching behaviour during ammonia washing.

2.2.2. Ammonia washing

The degreased gel microspheres after CCl_4 wash were subjected to 3 M NH_4OH washing. During this step, the residual chemicals and unwanted reaction products are leached out and hydrolysis reaction is completed. The gel microspheres were loaded in a glass column of 7.5 cm \varnothing and 15 cm height. The NH_4OH solution was passed through the column at the rate of 3 bed volumes (3000 ml/h). Among the chemicals being leached out from the gel microspheres, NO_3^- has been reported as the slowest diffusing species [7]. In order to monitor the progress of ammonia washing, the wash effluent was continuously monitored for the decrease in its nitrate content as a function of time. Ionic conductivity of the effluent was used for measuring the nitrate content. The fresh wash solution (3 M NH_4OH) showed an ionic conductivity of 2.5–3 mS. The gel microspheres were washed till the conductivity of the effluent dropped below 4 mS which corresponds to a nitrate concentration of <0.5 mg/ml.

2.2.3. Heat treatment studies

The wet gel particles after the ammonia washing step were dried in an air oven at 100 $^{\circ}C$ for 6 h followed by heating at 250 $^{\circ}C$ for 3 h. The dried microspheres were further heat-treated to 300–700 $^{\circ}C$ for 4 h in air atmosphere. The heat treated product was characterized by measuring tap density, crush strength and specific surface area. These microspheres were utilized for fabrication of pellets.

2.2.4. Pelletisation of microspheres

The microspheres were pelletised in a single acting manual press at 150–350 MPa pressure, using 4% stearic acid in acetone as die lubricant, to obtain green pellets of

2.0 cm \varnothing and about 1.5 cm length. The density of these pellets was determined by geometrical method. These pellets were subjected to acetone dip test to rule out the defective ones.

2.2.5. Sintering of (Th,U) O_2 pellets

Sintering behaviour of (Th,U) O_2 pellets was studied in an air furnace at temperatures ranging from 900 to 1600 $^{\circ}C$. For this, pellets were loaded in a super canthal furnace and heated at the rate of 5 $^{\circ}C/min$ to 900 $^{\circ}C$, soaked there for 4 h and finally reduced in Ar + 8% H_2 atmosphere at 800 $^{\circ}C$. The density of these pellets was determined using both geometrical method and liquid displacement method. The above experiment was repeated by using different sets of green pellets at different temperatures up to 1600 $^{\circ}C$ with a step of 100 $^{\circ}C$. However, sintering behaviour in reducing atmosphere was studied by dilatometer. The shrinkage was measured in axial direction using a push rod type dilatometer (Netzsch 402 E/7). The sample supporter, measuring unit and displaceable furnace were arranged for horizontal mounting apparatus. The length change measurements were made by a linear voltage differential transformer (LVDT), which was maintained at a constant temperature by means of water circulation from a constant temperature bath. The accuracy of the measurement of change in length was within $\pm 0.1 \mu m$. The temperature was measured using a calibrated thermocouple, which was placed just above the sample. The rate of heating of the samples was 8 $^{\circ}C/min$ for the dilatometric experiments.

2.2.6. Microstructural examination of sintered pellets

The sintered (Th,U) O_2 pellets were sectioned using a diamond blade cutter and then they were ground with three different grades of abrasive papers to obtain a flat surface. These pellets were then polished to get $\sim 1 \mu m$

finish. These polished pellets were etched thermally [8] in vacuum at 1350 °C for 3–5 h. These were then silver coated for carrying out microstructural examination using a Geol T-330A Scanning Electron Microscope.

3. Results

3.1. Preparation of gel microspheres

3.1.1. Physical characterization of gel microspheres

In all the experiments, uniform sized wet gel microspheres of ~2.0 mm diameter were obtained. The wet gel microspheres were pale yellow in colour with the texture varied from translucent to opaque. The translucent microspheres were hard in nature but the opaque microspheres were either hard or soft. The variation of physical characteristics of gel microspheres as a function of feed broth composition is tabulated in Table 1. It can be seen from the table that for a given metal ion concentration up to 1.3 M, with increasing HMTA + urea to metal ion concentration ratio R , the gel texture changed from opaque to translucent. For $[M] = 1.35$, experiments could not be done for $R > 1.2$.

3.1.2. Ammonia washing of the gel microspheres

Washing characteristics of the gel microspheres prepared from feed broth of different composition are given in Table 1. The total time required for complete removal of residual chemicals varied from 69 to 130 min. The removal of chemicals from the translucent gel was much slower than from the opaque gel. The leaching of thorium and uranium was observed only in the case of soft opaque gel. During the washing step in some cases, there was a transformation of translucent gel into opaque gel.

3.2. Drying

The diameter of 100 °C dried, crack free gel microspheres was around 1.6 mm. More than 95% of the product was retained on a sieve of ASTM no. 14 and passed through a sieve no. 12. This product was used for further experiments. The variation of dry gel characteristics dried at 100 °C with feed composition is given in Table 1. The gel was categorized as types A, B and C depending on the nature of 100 °C dried gel particles. The hard translucent gel microspheres (type A) cracked during drying. Type C is the gel microspheres of which

Table 1
Gel characteristics and washing behaviour of gel microspheres

Feed composition		Appearance of wet gel microspheres	Washing time (min)	Leaching of Th&U ^b	Nature of microspheres dried at 100 °C	Category of gel
[M] ^a	[HMTA, Urea]/[M] (R)					
1.1	1.55	Hard translucent	130	No	Cracked	A
	1.45	Hard translucent	120	No	Cracked	A
	1.35	Hard translucent	108	No	Cracked	A
1.15	1.5	Hard translucent	120	No	Cracked	A
	1.4	Opaque	104	No	Intact	B
	1.45	Hard translucent	120	No	Cracked	A
1.2	1.45	Hard translucent	104	No	Cracked	A
	1.4	Opaque	98	No	Intact	B
	1.35	Opaque	80	No	Intact	B
1.25	1.4 ^c	Hard translucent	79	No	Intact	A
	1.35	Opaque	78	No	Intact	B
	1.3	Opaque	75	No	Intact	B
	1.2	Opaque	75	No	Intact	B
	1.15	Opaque	69	No	Intact	B
	1.1	Soft opaque	–	Yes	Eroded	C
1.3	1.35	Hard translucent	78	No	Cracked	A
	1.3	Opaque	70	No	Intact	B
	1.2	Soft opaque	–	Yes	Eroded	C
1.35	1.2	Soft opaque	–	Yes	Eroded	C
	1.15	Soft opaque	–	Yes	Eroded	C

A = Hard translucent, B = opaque; smooth surface, C = opaque; eroded surface.

^a Metal ion concentration in mol/l, $[U]/[Th+U] = 0.03$.

^b Th and U content was not determined quantitatively. The wash solution appeared turbid when there is leaching.

^c Hard translucent gel turned opaque gel during washing.

the surface was eroded during ammonia washing. The opaque gel microspheres had smooth surface and were free from any defect (type B). It can be seen from the table that the B type gel could be obtained only for $[M] > 1.1$ M in the feed broth. Also with increase in $[M]$, the range of R that yielded the B type gel increased up to $[M] = 1.25$ M and decreased thereafter. These gel microspheres from category B were used for further experiments.

Table 2
Variation of surface area, tap density and crush strength of the (Th,U)O₂ microspheres heated in air at 300 °C with composition

Feed composition		Surface area (m ² /g)	Tap density (g/cm ³)	Crush strength (N/particle)
[M]	R			
1.15	1.40	30.0	0.98	6.0
1.20	1.40	22.83	1.16	6.0
1.20	1.35	22.00	1.10	5.9
1.25	1.35	20.90	1.29	4.7
1.25	1.30	20.40	1.24	3.0
1.25	1.20	19.70	1.20	2.5
1.25	1.15	18.51	1.20	2.0
1.30	1.3	–	1.27	3.0

3.3. Heat treatment of microspheres

It can be seen from Table 2 that tap density of the 300 °C heated microspheres did not change much with the composition of the feed broth used for their preparation. However, the specific surface area of the microspheres decreased with the increase of metal ion concentration in the feed broth. The crush strength values for a particular metal ion concentration ($[M] = 1.25$) decreased with decrease in the R value. Table 3 gives the specific surface area, tap density and crush strength at different temperatures. The rate of decrease of specific surface area with temperature for microspheres largely changed with $[M]$. For $[M] = 1.15$ and 1.20, the surface area value at 600 °C decreased by around 50% of the value at 300 °C. However, for $[M] = 1.25$ the surface area values decreased by 75% for $R = 1.3$ and 82% for $R = 1.15$ when temperature was increased from 300 to 600 °C. The patterns of increase in average crush strength with temperature for different $[M]$ was quite different. It increased with temperature for lower $[M]$, but remained almost constant up to 500 °C for higher $[M]$. The tap density of the microspheres increased with increasing temperature. In the case of metal ion concentrations ≤ 1.2 M, the tap density could not increase beyond 1.4 g/cm³ even after calcining at 600 °C. Whereas for the metal ion concentration of 1.25

Table 3
Variation of specific surface area, tap density and crush strength of (Th,U)O₂ microspheres with temperature and composition (microspheres were heated in air atmosphere for 4 h)

Serial no.	Feed composition		Heating temperature (°C)	Specific surface area (m ² /g)	Tap density (g/cm ³)	Crush strength (N/particle)
	[M]	R				
1	1.15	1.4	300	30.0	0.98	6.0
			400	24.81	1.16	6.3
			500	19.25	1.25	7.9
			600	12.80	1.32	10.8
			700	6.80	1.54	13.1
2	1.20	1.4	300	22.83	1.16	6.0
			400	19.0	1.23	6.1
			500	16.86	1.30	7.0
			600	12.07	1.39	9.0
			700	6.20	1.48	11.3
3	1.25	1.3	300	20.40	1.24	3.0
			400	13.62	1.36	3.0
			500	9.99	1.52	3.5
			600	5.00	1.68	6.3
			700	4.23	1.80	8.0
4	1.25	1.15	300	18.51	1.20	2.0
			400	10.85	1.28	2.5
			500	5.36	1.48	2.5
			600	3.32	1.53	4.5
			700	–	1.70	6.9

M, the tap density of 1.5 g/cm^3 could be obtained at $500 \text{ }^\circ\text{C}$.

3.4. Pelletisation and sintering

The microspheres with tap densities higher than 1.3 g/cc were used for pelletisation studies. It was observed that the microspheres with high crush strength required higher compacting pressures to have a reasonably high green pellet density. The green density varied from 3.6 to 5.0 g/cm^3 depending upon the pressure of compaction and crush strength value. It was also observed that to obtain defect free pellets of green density more than 40% of TD with an l/d value ≥ 0.75 , the tap density of the microspheres required was around 1.5 g/cm^3 . Table 4 gives the dependence of green density and sintered density on compaction pressure. Figs. 3 and 4 show the variation of sintered density with temperature of sintering for the composition $[\text{Th} + \text{U}] = 1.25$, $R = 1.15$ in air and $\text{Ar} + 8\% \text{H}_2$ atmosphere, respectively. The maximum sintered density of 97% of TD could be obtained

Table 4
Dependence of green and sintered density of $(\text{Th,U})\text{O}_2$ pellets on compacting pressure

Compacting pressure (MPa)	Green density (% of TD)	Sintered density ^a (% of TD)
150	36.0	84
200	39.8	91
250	44.3	96
300	45.6	97
350 ^b	47.8	–
400 ^b	50.0	–

^a Sintered in air at $1350 \text{ }^\circ\text{C}$ for 4 h.

^b Caused lamination.

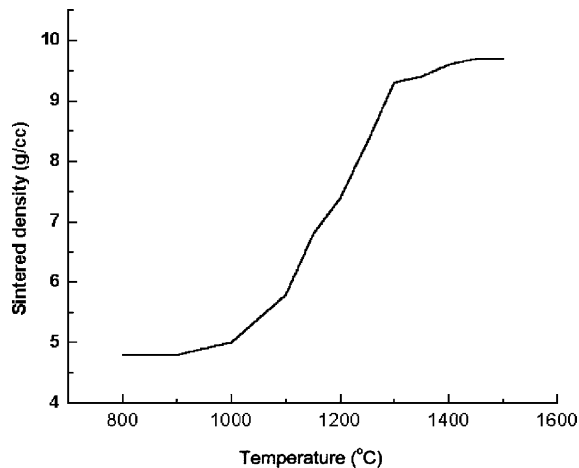


Fig. 3. Variation of sintered density of $(\text{Th,U})\text{O}_2$ pellet in air atmosphere with temperature.

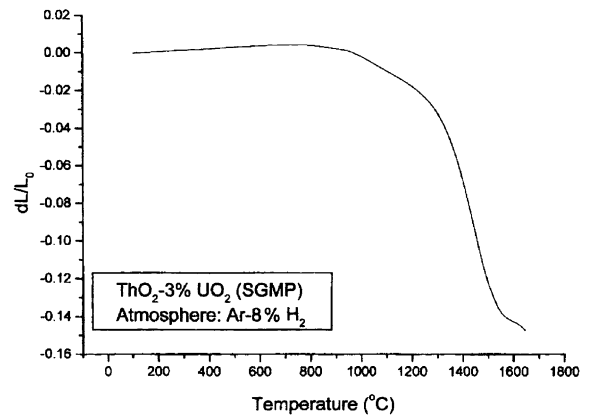


Fig. 4. Shrinkage behaviour of $(\text{Th,U})\text{O}_2$ pellet with temperature in $\text{Ar} + 8\% \text{H}_2$ atmosphere.

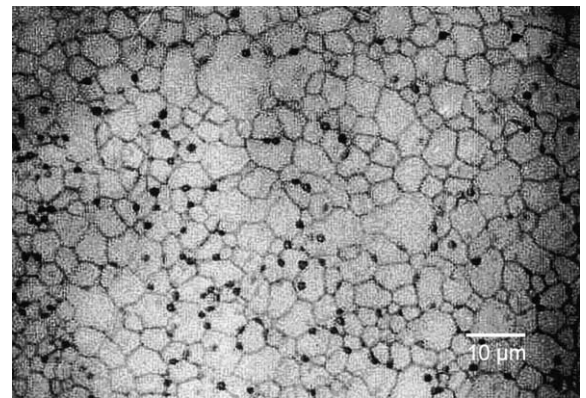


Fig. 5. Micrograph of $(\text{Th,U})\text{O}_2$ pellet polished and etched in vacuum at $1350 \text{ }^\circ\text{C}$ for 5 h.

by heating the pellets in air at $1350 \text{ }^\circ\text{C}$ for 4 h. The optical microscopic examination of the polished surfaces of sintered pellets showed defect free surface without any berries. Figs. 5 and 6 show the typical microstructures of the pellet obtained using an optical microscope and SEM, respectively. The grain size in these pellets varied from 3 to $5 \text{ }\mu\text{m}$. Uniform pores of size $< 1 \text{ }\mu\text{m}$, homogeneously distributed across the pellet cross-section, could be seen in the microstructures.

4. Discussion

4.1. Variation of gel characteristics with feed composition

The characteristics of gel microspheres largely change with the feed composition as depicted in Table 1. For a given metal ion concentration, the formed gel changed from soft opaque to hard transparent appearance with the increase in molar ratio R . Similar results were re-

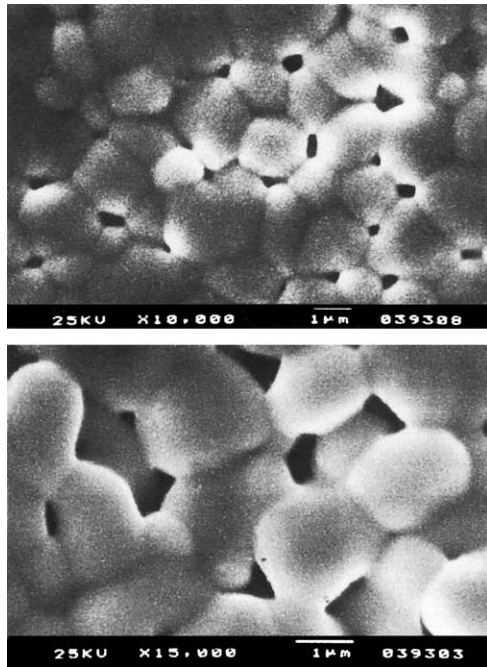


Fig. 6. Scanning electron micrograph of (Th,U)O₂ pellet with different magnifications.

ported by several workers for urania [9–12] and by Kumar et al. [6] for ThO₂ microspheres preparation by internal gelation process. Lloyd et al. [13] studied these aspects for urania and attributed this effect to crystal habit and crystallization behaviour of urania. Based on their electron microscopic studies on urania gel microspheres, they reported that with the increase in R for a given $[U]$, the microspheres progressively became smaller, less opaque and darker in colour suggesting that the crystallite size of the precipitated urania decreases as R increases. A probable explanation for similar behaviour in the case of thoria–urania system has been given in the present investigation on the basis of kinetics of the hydrolysis reaction. The rate of reaction for a given concentration of metal ion, increases with the increase in concentration of gelation agent i.e.; HMTA+urea. This rate of reaction governs the size of crystallites formed in the gel. The high reaction rate caused by high R restricts the extent of growth of crystallites yielding hard translucent gel microspheres. On the other hand, the low reaction rate from low R yields soft opaque gel particles. This effect is also reflected in the ammonia washing characteristics of the gel microspheres. Table 1 shows the time required to leach NO₃⁻ from gel microspheres for different fuel compositions. The rate of the NO₃⁻ removal is much slower for A category gel compared to B and C category gel suggesting the presence of a large number of small pores in the A type gel matrix formed due to small crystallites. The physical characteristics of

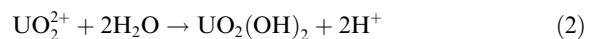
the dried microspheres listed in Table 2 also indicate formation of small crystallites for higher values of R . It can be seen that for $[M]=1.25$ and higher values of R , the microspheres had higher values of specific surface area, tap density and crush strength. All these properties point towards the formation of small crystallites. Among the different values of R used, the most suitable value for SGMP is one for which the gel microspheres did not leach any metal ion during ammonia washing and yielded defect free calcined gel microspheres having minimum crush strength and reasonable specific surface area and tap density values. For each metal ion concentrations from 1.15 to 1.3 M, at least one such value of R could be obtained and the characteristics of the gel microspheres for SGMP were improved with increase in metal ion concentration as shown in Table 2.

Another important observation from Table 2 is that the optimum R value decreased with increase in metal ion concentration for obtaining gel microspheres suitable for SGMP. This observation is in contradiction to general stoichiometric equivalence, which suggests that for the hydrolysis of higher concentration of metal ion higher values of R should be required. A detailed investigation was carried out by Collins et al. [14] on urania system to understand the basic chemistry involved in this reaction. They reported that four principal reactions are involved in hydrolysis and precipitation of uranyl nitrate solution. The four reactions are

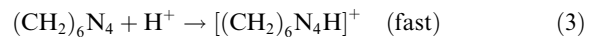
Decomplexation:



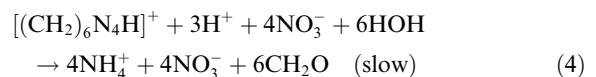
Hydrolysis:



HMTA protonation:



HMTA decomposition:



The hydrolytic acid formed in reaction (2) is neutralized by reactions (3) and (4) resulting in precipitation of metal ion. Similar reactions are supposed to take place during hydrolysis of thorium nitrate solution. The R values used in the present study is much higher than the amount stoichiometrically required as per the above reactions. According to reaction (4), 0.25 mol of HMTA can neutralize 1 mol of nitrate. However, the minimum amount of HMTA required per mole of nitrate in the present study was 0.38 mol. The requirement of such high values of R must be dictated by the need of gel

formation. The various steps involved in the formation of gel are

- (a) Nucleation of crystallites with a certain minimum threshold density.
- (b) Growth of the nuclei.
- (c) Formation of a stable gel network.

The density of the crystallite nucleation must be controlling the characteristics of the gel. Below a certain threshold density, the gel network formation is not possible. Beyond the threshold value, stable gel network formation is facilitated. However, very high density nucleation will finally result in small crystallites in the gel because the crystal growth will be limited with the given concentration of metal ion.

The nucleation step has to be controlled by adjusting the feed composition to obtain suitable characteristics in the gel. Since the overall kinetics of the hydrolysis reaction is governed by the product of the concentration of metal ion and HMTA, the increase in metal ion concentration leads to decrease in the requirement of HMTA to maintain optimum rate of nucleation as shown in Table 2. However, this effect is not very prominent in the case of $[M]$ of 1.15 and 1.2, because of decrease in pH associated with increase in metal nitrate concentration.

The improvement of the gel characteristics with increase in metal ion concentration may be due to the fact that in case of higher metal ion concentration where requirement of R is reduced, smaller fraction of hydrolysis occurs through reaction (3). Since reaction (3) is very fast, reduction of its contribution to hydrolysis must have brought down the overall rate of the reaction resulting in formation of the gel spheres with larger crystallite size. Similar results have been reported by Suryanarayana et al. [5] for the preparation of urania pellets via the SGMP route. However, the feed composition range for SGMP in the case of urania is much higher than that in the case of thoria. This is mainly due to large difference in their gelation temperature. The gelation temperature for obtaining hard and opaque gel, in the case of thoria is 60–70 °C [6] compared to 25–50 °C for urania [12]. This can be explained on the basis of the following major differences in these two systems. A high nitrate to metal ratio of 3.0 is used in case of thoria as compared with 1.5–1.6 for urania. Also crystallites are rod type for thoria [15] as compared to platelet type crystallites for urania [13].

The higher nitrate to metal ratio results in low pH of the broth, requiring higher gelation temperature for optimum hydrolysis for gel formation. The rod type crystallites of thoria may be less amenable for the formation of a rigid gel network than platelets type crystallites of urania, which necessitates higher density of crystallites for thoria for desired gel formation. This

requirement further hints the need of higher gelation temperature. Since gelation is occurring at higher temperature, where the rate of hydrolysis is quite high, the control of nucleation and growth of crystallites becomes difficult bringing down the suitable range of feed composition.

4.2. Heat treatment of microspheres

The main purpose of calcination is to obtain the required tap density without losing the softness of the microspheres significantly. The decrease in the specific surface area of the 300 °C dried gel microspheres with increase in $[M]$, as shown in Table 2 could be explained on the basis of increase in crystallite size of the gel. As the crystallite size increases, the pore size increases and the number of pores decreases causing a decrease in specific surface area. This decrease is larger for higher temperature of heat treatment but is related also with the hardness of the gel microspheres. Since the decrease in surface area is due to collapse/merging of pores, this process proceeds faster at higher temperatures but lower for hard microspheres. For the gel microspheres obtained from different compositions heated up to 600 °C, the specific surface area decreased to different extent. For the variation of feed composition from Serial no. 2 to 4 of Table 3 the decrease in percentage of the observed specific surface area for 600 °C from that for 300 °C was around 48%, 75% and 82%, respectively, indicating that the hardness of the microspheres decreased with change in composition of feed broth from Serial no. 2 to 4. This observation is in agreement with the measured hardness of the microspheres listed in last column of Table 3.

4.3. Pelletisation and sintering

The pellets obtained from the heat treated microspheres with average crush strength of >3.5 N/particle at 300 MPa pressure had a berry structure. The pressure was not high enough for the microspheres with this hardness to merge them into one another. Use of higher pressure resulted in lamination/end chipping of the pellets. These pellets could not be densified to $>80\%$ of TD on sintering. In such cases intra microsphere sintering prevents the closure of pore between the microspheres resulting in formation of pellets with poor sintered density. The microspheres with crush strength values ≤ 3 N/particle were soft enough to be pelletised into green pellets free from berry structure. It can be seen from Figs. 3 and 4 that the rate of densification is much faster during sintering in air atmosphere compared with Ar + 8% H₂ atmosphere. The optimum feed composition range for SGMP of thoria–3%urania is very narrow and limited to feed broth composition of $[M]=1.25$ M, R varying from 1.15 to 1.3. The pellets of (Th,U)O₂ could

be sintered to >97% of TD in air atmosphere at 1350 °C in 4 h without using any sintering aid. This sintering temperature is much lower than the temperatures required for ThO₂ in any atmospheres [8] or (Th,U)O₂ in a reducing atmosphere [3]. It is well known that the addition of aliovalent cations accelerates the sintering of thoria [16,17]. In the present case during sintering, uranium is in higher oxidation state (>4⁺) in air, which acts as a sintering aid. The presence of uranium of higher oxidation state in UO_{2+x} matrix is known to incorporate cationic vacancies in the matrix, which is responsible for the enhanced cation diffusivity [18]. From Fig. 4 it is clear that the sintering process started at 1100 °C, which is much lower than the temperatures adopted for pellets preparation by conventional powder route. The difference may be attributed to the higher surface area of the sol-gel derived microspheres and homogeneous distribution of uranium which acts as a sintering aid. Recently Ananthasivan et al. [19] systematically studied the sintering characteristics of thoria doped with group VB elements. They reported the formation of pellets with a sintered density of 97% of TD below 1300 °C from the powders synthesized through wet chemical route. They concluded that the sintered density of the final product is influenced both by the nature of the dopant and the method by which it is doped. When dopant is added through a wet chemical procedure, homogeneity in mixing is achieved down to ionic scale thus accelerating the sintering process.

5. Conclusion

The process flow sheet is given for the preparation of dense (Th,U)O₂ pellets via SGMP route through characterization of press feed (gel microspheres) prepared from various feed compositions, subjected to different heat treatment. The gel microspheres were characterized with respect to physical appearance of the gel, rate of NO₃⁻ leaching through the gel, tap density, specific surface area and crush strength of the heat treated microspheres. The following conclusions were obtained:

- (1) The nature of the gel formed depends upon the crystallite size, which in turn depends on the density of nucleation during hydrolysis reaction. Also a certain minimum density of nucleation is required for the formation of stable gel.
- (2) For a fixed set of experimental conditions and a given metal ion concentration with increasing *R* (increasing density of nucleation) the gel microspheres texture changes from soft opaque (C) to hard translucent (A) via hard opaque (B). Hard opaque gel gives the best final product for that [M].
- (3) With the increase in metal ion concentration the *R* value required for obtaining good gel microspheres decreases such that the rate of nucleation, which depends upon the product of [M] and [HMTA, Urea], is optimum.
- (4) The size of the crystallites governs the characteristics of the gel microspheres that play an important role in SGMP process.
- (5) (Th,U)O₂ microspheres containing 3 mol% uranium could be sintered at 1350 °C in air for 4 h to 97% of TD. Here uranium acts like a sintering aid.
- (6) The feed composition range that could be used for obtaining defect free high density (Th,U)O₂ pellets via SGMP route is rather smaller.

Acknowledgements

The authors are thankful to Dr V. Venugopal, Head, Fuel Chemistry Division for his keen interest in the work and Shri H.S. Kamath, Director, Nuclear Fuels Group for his constant support. The authors sincerely thank Dr K.T. Pillai, FCD, BARC for Surface area measurements and Shri K. Kutty of NMSCD, BARC for Scanning Electron Microscopy. We express our sincere thanks to Dr T.R.G. Kutty, RMD for his kind help in processing the Dilatometric data. Thanks are also due to Shri N. Kumar, FCD, BARC for valuable discussion during the course of investigation.

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