Production of 75–150 μm and <75 μm of cerium dioxide microspheres in high yield and throughput using the internal gelation process¹

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Abstract

Hundreds of grams of calcined cerium dioxide (CeO_2) microspheres were produced using the internal gelation process with a focus on 75–150 μm and <75 μm diameter sizes. To achieve these small sizes, a modified internal gelation system was employed, which utilized a two-fluid nozzle, two static mixers for turbulent flow, and 2-ethyl-1-hexanol as the medium for gel formation at 333–338 K. This effort generated over 400 g of 75–150 μm and 300 g of <75 μm CeO_2 microspheres. The typical product yields for the 75–150 μm and <75 μm microspheres that were collected and processed were 72 and 99 %, respectively, with a typical throughput of 66–73 g of CeO_2 microspheres per test, which could generate a maximum of 78.6 g of CeO_2 . The higher yield of very small cerium spheres led to challenges and modifications, which are discussed in detail. As expected, when the <75 μm microspheres were targeted, losses to the system increased significantly.

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1. Introduction

Research at Oak Ridge National Laboratory (ORNL) continues to expand the utility of the internal gelation process to make a wide variety of metal oxide microspheres. This work relates specifically to the production of large quantities of very small microspheres with a narrow size distribution, which historically has been challenging. An ORNL study [1] evaluated the performance of a pneumatic drop-on-demand system for iron hydroxide and yttrium-stabilized zirconia microspheres. That technique could achieve very uniform gel diameters of 40 μm or less. However, the production rate of that technique was too low, and larger diameters were not obtainable. A more recent effort on microfluidic sol-gel process [2] demonstrated that cerium dioxide (CeO_2) microspheres could be produced over a much wider size range. However, no information on the production rate was provided. Another ORNL effort [3] produced uranium microspheres with a modified internal gelation system which utilized a two-fluid nozzle, two static mixers for turbulent flow, and 2-ethyl-1-hexanol (2EH) as the medium for gel formation at 328–333 K. The two static mixers were connected to a stainless tube union tee, and the needle was inserted into the tee and in between the static mixers. As the warm 2EH passed over the nozzle, the uranium solution broke into very small droplets which began to gel almost immediately. While the production rate from this process was more than acceptable, the size distribution was relatively wide as expected from a two-fluid nozzle system. The average diameter of the air-dried uranium microspheres was between 150 and 250 μm , and the sintered uranium dioxide (UO_2) kernels ranged from 75 to 125 μm . The flow rates of uranium feed and 2EH through the static mixers significantly impacted the average particle size.

For decades, the internal gelation process has been used in the production of UO_2 kernels with a diameter of 100 μm . The original method demonstrated by KEMA used a vibrated spray nozzle [4]. The droplets from the nozzle were collected in horizontally flowing streams of mixed hydrocarbons at 353–372 K. To make UO_2 kernels with a diameter of 10 μm , KEMA utilized an emulsion technique [4, 5]. The uranium solution was dispersed in cold Freon 113 using an ultrasonic vibrator. When the Freon was warmed to 313 K, the droplets gelled. Process controls over the size distribution were limited. More recently, the internal gelation process and the jet entrainment technique have been used to make small, dense UO_2 particles with diameters of $100 \pm 20 \mu\text{m}$ [6]. With this technique, one can control throughput and size, but the ability to produce even smaller particles is limited.

Ongoing work at ORNL required CeO_2 microspheres and uranium oxide microspheres with diameters of 150 μm and preferably much smaller; it was decided to use the internal gelation technique to attempt to make the needed microspheres. Researchers at ORNL used the internal gelation process to make CeO_2 microspheres, which were used as simulants for plutonium dioxide microspheres [7, 8]. Later, a Texas A&M University effort examined the effects of process variables such as reactant concentrations, gelation temperature, aging time, and wash conditions on the hydrous cerium oxide gel spheres [9]. These efforts [7–9] produced CeO_2 microspheres with low porosity, and the microspheres were prone to crack using the standard washing, drying and calcining procedures. The cracking problem with CeO_2 microspheres was solved recently [10] using a system, which generated up to 10 g of CeO_2 a day. For this study, the two-fluid nozzle, two static mixers, and 2EH were used. It was expected that the CeO_2 diameters would be smaller than the UO_2 microspheres produced in a previous study [3]. The maximum shrink factor of 3.74 for the Ce microspheres in this study is higher

than the maximum shrink factor of 3.14 for the uranium microspheres [3]. However, the Ce microspheres were only heated to 773 K, so they were not fully dense like the UO_2 microspheres [3]. The porosity of the CeO_2 microspheres after they are heated to 773 K was slightly more than 40 %, which reduces the estimated shrink factor down to 3.6. The results of this effort to produce CeO_2 microspheres with diameters of less than 150 μm and the needed process modifications are presented below.

2. Experimental

2.1 *Preparation of stock solutions and the feed solution*

A stock solution was prepared at room temperature where the concentrations of hexamethylenetetramine (Fisher Scientific) and urea (Fisher Scientific) were both 3.2 M , and the density was 1141 kg/m^3 . The urea-hexamethylenetetramine (HMTA) solution was kept in a sealed container.

The preparation of the stock solution with ammonium cerium nitrate (Acros Organics) was slightly more involved. First, the exact concentration of ammonium hydroxide (EMD) in a new bottle was determined to be 12.7 M using a standard titration technique. Next, the ammonium cerium nitrate $((\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6)$ was dissolved in distilled water. The volume, concentration, and density of this $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ solution were determined. Then, the needed amount of the chilled ammonium hydroxide (NH_4OH) was added to the chilled $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ solution so the final molar ratio of hydroxide to cerium was 0.5. The solution of Ce and NH_4OH was heated to about 343 K to concentrate the solution. The resulting solution had a $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ concentration of 1.86 M and a density of 1600 kg/m^3 . The solution was close to

its saturation point, which minimized the water addition of the internal gelation system. In addition, the use of the prehydrolyzed Ce solution reduced the amount of HMTA/urea that was needed, and it further reduced the amount of water that was added to the system.

Prior to the start of each internal gelation experiment, three 127.5 g samples of the HMTA/urea stock solution and three 131.0 g samples of the $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ solution were chilled at 273 K for 0.5 h. Then, a chilled HMTA/urea sample was added to the $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ solution and shaken by hand. This combined solution was then transferred to the internal gelation system, and the internal gelation experiment was initiated. The molar ratio of HMTA/urea to cerium in the combined solutions was 2.35. Each combined solution took approximately 18 min to pass through the internal gelation system. After approximately 90 % of the broth empty was empty, the second set of HMTA/urea and Ce solutions was combined, mixed, and added to the broth pot. The same steps were applied to the third set solutions when sufficient space in the broth pot became available. These three combined solutions should generate up to 78.6 g of CeO_2 microspheres.

2.2 *Experimental apparatus and conditions*

A detailed description of our internal gelation system, which utilizes the two-fluid nozzle technique, is provided elsewhere [11]. However, due to the small droplet size required in this effort, changes to the internal gelation apparatus were needed. The key modification involved the use of two Stratos Tube Mixers (Koflo). The static mixers were connected to opposite ends of the stainless steel Swagelok® tee. A 17-gage blunt-end hypodermic needle (Cadence) was positioned in the side connection of the tee using a small section of Tygon R-3603 tubing, which was replaced frequently due to its tendency to shrink and alter the position of the needle tip. The

tip of the needle was positioned in the center of the channel in the tee. A sleeve was placed on the needle to ensure that the placement of the needle tip in the channel was reproducible as shown in Fig. 1. A calibrated gear pump (Micropump) was used to transfer the feed solution from the broth vessel to the hypodermic needle. Another calibrated gear pump was used to circulate 2EH (Sigma-Aldrich) and Span™ 80 (Sigma-Aldrich), which was added when the gel spheres would agglomerate in the transfer line. The flow rates from these gear pumps determine the size distribution of the particles. The 2EH in the system was maintained at 333–338 K.

Fig. 1. Needle inserted in the horizontal portion of the T fitting above the top of gelation column and the static mixers above and below the needle tip.

After the small spheres were formed, they were transported through a vertical glass column and then through flexible tubing into a collection system as shown in Fig. 2. The system was composed of two glass vessels and a stainless steel mesh basket. Each glass vessel had an overflow tube, which was 3 cm below the top of the vessel. The heights of the glass vessels were 29 and 25 cm. The overflow tube directed the 2EH flow from one chamber to the next. Each glass vessel had a removable glass plate that extended to the center of the vessel and partitioned the vessel vertically. Therefore, nearly all of the 2EH and gel spheres were directed toward the bottom of the glass vessel before the 2EH was allowed to exit through the overflow tube near the top of the vessel. The gel spheres were collected at the bottom of the collection vessels via gravity settling. As expected, the effectiveness of the gravity settling was a function of the diameter of the gel spheres. When the target for the calcined CeO_2 microspheres was 75–150 μm in diameter, 90–95% of the gel microspheres were collected at the bottom of the first glass vessel. Most of the remaining gel spheres were collected in the bottom of the second glass vessel, and a small amount of gel spheres was collected from the mesh basket. When the CeO_2 microspheres in the <75 μm diameter range after calcination were sought, 60–70% of the microspheres was collected in the first vessel. 25–35 % of the collected gel spheres were in the second vessel, and <5% of the microspheres were collected from the basket. During the experiments for the smallest microspheres, the mesh basket became plugged to the point that the 2EH would flow out of the top of the basket.

For both size distributions, the experiments resulted in many of the extremely small microspheres, which remained suspended in the 2EH for many hours. For the experiments with the slightly larger microspheres, the 2EH would clear enough overnight so the 2EH could be reused several times. In the tests with the smaller gel spheres, most of the suspended particles

Fig. 2. Collection system for the very small gel spheres

took more than a day to settle out. Whenever the gelation system was not to be used for a few days, the 2EH was transferred out the system into holding vessels. The last two liters of the 2EH, which had the highest concentration of the suspended particles, were transferred to a glass graduated cylinder. Even after a week of settling in the graduated cylinder, the 2EH still appeared to contain suspended particles. Due to concerns that the suspended particles would become powders as they were continually passed through the pumps, the 2EH with the higher percentages of suspended particles was frequently replaced. However, the images from Motic digital microscope indicated that nearly all of the collected microspheres remained spherical.

The presence of the very small microspheres led to more frequent cleaning of the gelation system. Fortunately, a large fraction of the suspended particles were eventually trapped near the bottom of the gelation column where the 2EH was pumped up between the walls of the gelation column. The static mixers were routinely cleaned with dilute nitric acid and then distilled water since they played one of the most critical roles in the size distribution of the microspheres.

2.3 Aging, washing, and subsequent heat treatment

At the end of each test, the chambers remained in the warm 2EH reservoir at 333–338 K for 15 min. Unlike our previous 2EH experiments with uranium microspheres [3], the Ce gel spheres were aged in a static solution of 2EH. This change was designed to keep water from the aging microspheres in the Pyrex chambers and to assist in the removal of water from the 2EH. After the bulk of the 2EH and water was removed from the Pyrex chambers, the wet gel spheres were transferred to a series of plastic beakers. The gel spheres were washed several times with 200 mL of 2-propanol (BDH). In our previous study with uranium microspheres [3], they could be transferred to the Pyrex column, which had a coarse frit near the bottom and stopcock below the frit, for the subsequent wash steps. When the Ce gel spheres were transferred to the column, the flow through the column was extremely slow even if air pressure was applied to the top of the column. Therefore, the gel spheres were kept in the beakers and then gently swirled by hand. Most of the remaining of 2EH and water was removed through decantation. Next, the spheres were washed several times with an equal-volume mixture of 2-propanol and 0.5 M NH_4OH . Again, the gel spheres were washed using gentle swirling. Then, the wash step was repeated using 0.5 M NH_4OH . The washed gel spheres were then transferred into the Pyrex column. Then, 0.5 M NH_4OH was sent down the column to remove reaction impurities such as HMTA, urea, and ammonium nitrate. The effectiveness of this wash step was monitored by measuring the electrical conductivity of the spent NH_4OH solution with a YSI model 3100 conductivity instrument.

The next series of treatments performed was based on a procedure for amorphous yttrium stabilized zirconium microspheres [12] and for Ce microspheres with air-dried diameters of 300 μm and greater [10]. The microspheres were washed with distilled water until the electrical

conductivity of the spent water was below 0.4 mΩ. Then, the washed microspheres were placed in the Teflon container with thick walls and covered with distilled water. After the Teflon container was sealed, it was placed in an oven (Barnstead-Thermolyne) and heated at 473 K for 3 h. The microspheres were then returned to a Pyrex column using distilled water. Then, the microspheres were treated with Dowanol PM (Aldrich Chemical Company). Next, the microspheres were washed with distilled water until the electrical conductivity of the spent water was below 0.1 mΩ. Finally, the microspheres were spread out within a stainless steel pan, and they were dried using a heat lamp for 15 h.

The microspheres were then sieved using 300, 212, 150 and 75 μm sieves. For the microspheres larger than 75 μm, a pan with a slit cut out at one edge was used to segregate the nonspherical microspheres. The spherical microspheres were rolled down the length of the pan and out of the pan through the slit into another pan. The nonspherical microspheres that remained in the pan were then removed. Typically, the rejects were 2 wt % or less of the total sample. The weight of each sieve fraction was then measured. For the largest fraction, approximately 9.5 mL of the microspheres were slowly transferred to a previously weighed graduated cylinder. The weight and volume of the microspheres were determined, and the slow pour density of the sample was estimated. For these tests, the slow pour densities ranged from 1700 to 1900 kg/m³. The sieved fractions were combined into alumina crucibles and placed into a furnace (Barnstead-Thermolyne). The microspheres were heated at a rate of 100 K/h until the microspheres reached 773 K. As soon as a temperature of 773 K was reached, the power to the furnace was shut off. The microspheres were cooled in the furnace in air, and then they were sieved again. The slow pour density of the largest fraction was determined again, and the densities increased only to 2200 to 2600 kg/m³.

3. Results and discussion

3.1 Flow rates vs particle size distribution

While many factors can affect the size distribution of spheres from a two-fluid nozzle system, only two main variables were evaluated in a quantitative manner for this study: (1) the flow rates of the 2EH and (2) feed solution into the static mixers. The results of the size distribution of calcined CeO_2 microspheres with a target diameter of 75–150 μm are presented in Table 1. If all of the microspheres were collected and converted to CeO_2 , the total mass would be 78.6. The maximum yield in the target diameter of 75–150 μm was 73.5 % when the microspheres that were lost to the system were not included. It would be expected that an increase in the 2EH flow rate, which should increase the turbulence at the point of gelation, should lead to smaller gel spheres. The reasons for the decrease in size distribution with the increase in the feed flow rate are not currently well understood. However, the gear pump may produce smaller variations in the feed rate, which should decrease the size distribution. The size distribution for each sequential experiment in Table 1 became smaller, which may suggest the presence of another variable such as the 2EH age or the amount of suspended solids in the 2EH. For experiments with a targeted size of the calcined CeO_2 microspheres <75 μm , the feed flow rate was apparently the most important variable as shown in Table 2. When the feed flow rate was 7.2 mL/min or less, the product yield of <75 μm calcined CeO_2 microspheres was 99% when the microspheres that were lost to the system were not included. It is likely that essentially all of the lost microspheres would have produced <75 μm CeO_2 microspheres. Even before the calcination step, the yield of the air-dried hydrous cerium microspheres was >96%, so nearly all of the CeO_2 microspheres would have diameters <35 μm if they were fully sintered.

Table 1. Size distribution of calcined CeO₂ microspheres with a primary target diameter of 75–150 µm as a function of feed and 2EH flow rates

Feed flow rate (mL/min)	2EH flow rate (mL/min)	<75 µm Wt % (total Ce) Wt % (recovered Ce)	75–150 µm Wt % (total Ce) Wt % (recovered Ce)	150–212 µm Wt % (total Ce) Wt % (recovered Ce)
8.9	169	14.9	66.0	8.8
		16.6	73.5	9.8
9.7	169	18.7	63.5	8.8
		20.5	69.6	9.6
10.4	169	25.6	65.4	0.0
		28.1	71.9	0.0
9.9	183	38.3	52.4	0.8
		41.9	57.3	0.8
9.0	195	36.6	50.8	0.8
		41.6	57.6	0.8

Table 2. Size distribution of calcined CeO₂ microspheres with a primary target diameter of <75 µm as a function of feed and 2EH flow rates

Feed flow rate (mL/min)	2EH flow rate (mL/min)	<75 µm Wt % (total Ce) Wt % (recovered Ce)	75–150 µm Wt % (total Ce) Wt % (recovered Ce)
8.0	195	64.6	28.2
		69.6	30.4
5.5	183	82.7	1.0
		98.8	1.2
7.2	183	82.7	1.1
		98.6	1.4

The production of the very small Ce microspheres also led to a 16 wt % loss of gel spheres to the 2EH and the internal gelation system. Most of these gel spheres could have been recovered if the 2EH and suspended solids were transferred to another vessel and permitted to settle for several days. Alternatively, a centrifuge could have potentially been used to separate the solids from the 2EH. However, this technique could negatively impact the sphericity of the gel spheres. Unlike the uranium microspheres [3], the Ce gel spheres that were lost to the gelation system would form a film in the reservoir, which would be difficult to remove, when the gelation system was not used for a week or more.

3.2 Other potential factors in the size distribution

Other potentially significant parameters that may affect the size distribution include the Ce concentration in the feed, the position of the needle tip in the channel between the static mixers, and the length and internals of the static mixers. Due to our initial success producing $<75\text{ }\mu\text{m}$ CeO_2 microspheres, a thorough evaluation of these variables was not needed. However, these initial results indicate that this technique could be used to make even smaller microspheres through the use of these process variables.

In the earlier study with uranium microspheres [3], the 2EH was replaced as it became cloudy. It was thought the presence of water with the 2EH would retard the gelation process and lead to agglomeration of the microdroplets before they could gel. Therefore, this effort tried to maximize the Ce concentration in the feed solution and thus minimize the water concentration so the presence of water from the feed with the 2EH would be less problematic. Typically, 200 mL of the 13 L of 2EH in the gelation system was replaced after each experiment. This 200 mL of 2EH, which came from the bottom of the reservoir, contained the highest percentage of the

suspended particles as expected. Since water was not a significant problem, a more dilute Ce feed could have been used. Although the size of the Ce gel spheres would not have changed significantly, their shrink factor could increase significantly since the shrink factor is inversely related to the Ce concentration in the feed solution.

In our previous study of small uranium microspheres [3], it was demonstrated that the position of the needle tip in the channel between the static mixers was a key variable. If the needle was placed close to the back wall of the channel, a smaller size distribution was observed, but this position also increased the likelihood of operational problems such as a plugged needle. The smaller size distribution may be due to increase in turbulence at the needle tip. When the needle tip was placed in the center of the channel, no operational problems related to the static mixers or the needle were observed, so the position of the needle tip was normally inserted into the middle of the channel. However, one test with Ce evaluated the effect of the needle placement with respect to the channel. The needle was placed near the back wall of the channel and in the middle of the channel during the same test with the same gelation temperature and feed solution. Noticeably larger gel spheres were produced when the needle was placed in the middle of the channel. Gel spheres from this test were examined using a Motic digital microscope, and the size difference of the microspheres from the two needle positions was slightly more than a factor of 2. In addition, it should be noted that the placement of the needle close to the back wall of the channel significantly reduced the flow rate of the feed solution even though the setting for the gear pump had not changed.

3.3 Water treatment at 473 K and the Dowanol wash to prevent cracking during calcination

For smaller microspheres, the need for crystal growth steps such as the water treatment at 473 K and additional wash steps such as the Dowanol wash to prevent cracking during calcination should be reduced because the distance for the evolved gases to escape from the microspheres had been reduced significantly. In one Ce test, these additional treatment steps were not used before the Ce microspheres were air dried and then heated to 773 K. As expected, the percentage of rejected microspheres from the tests with and without the additional treatment steps was the same if the microspheres were only air dried. If the microspheres had the additional treatment steps, essentially no additional microspheres were rejected because of the heat treatment to 773 K. However, when the water treatment at 473 K and the Dowanol wash were skipped, at least 5 wt % of the microspheres failed after the heat treatment to 773 K. Due to the time consuming nature of the water treatment at 473 K and the Dowanol wash, it may be reasonable to skip these steps if the product specifications allow a small percentage of cracked microspheres, which was not permitted in this study.

4. Conclusions

Hundreds of grams of CeO_2 microspheres with the diameters of 150 μm or less were produced using the internal gelation process. In order to achieve these small sizes, cerium microspheres were prepared using a modified internal gelation system which utilized a two-fluid nozzle, two static mixers for turbulent flow, and 2EH as the medium for gel formation at 333–338 K. The typical product yields for the two desired size distributions, 75–150 μm and <75 μm , were 72 and 99 %, respectively, for the collected and processed microspheres and with a typical mass of 66–73 g of collected and processed CeO_2 microspheres per experiment, which could produce a maximum of 78.6 g of CeO_2 . These initial results indicate that this technique

could be used to make even smaller microspheres. As the gel spheres become smaller, the need for effective ways to collect the gel spheres and to reject nonspherical particles became more apparent. Finally, as the microspheres become smaller, the need for crystal growth steps such as the water treatment at 473 K and additional wash steps such as the Dowanol wash to prevent cracking during calcination was reduced significantly.

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