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Pneumatic drop-on-demand generation for production of metal oxide microspheres by internal gelation

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ABSTRACT

Drop-on-demand generation is an alternative approach to the traditional vibrating nozzle used for the production of nuclear fuel microspheres via the internal gelation method. We integrated a low-cost pneumatic setup and demonstrated that the drop-on-demand approach has some advantages, such as low inventory of feed solution (attractive for laboratory-scale research), improved drop diameter control, reproducibility, scale-up to desired throughput by simple multiplication of the number of dispensing units, and simple remote operation. However, limitations on reproducibility and drop diameter control still exist due to the intrinsic variation of physical properties, viscosity, and dispensing-tip wettability during the internal gelation process. These adverse effects can be mitigated, to a certain extent, by carefully controlling the temperature of the feed as uniformly as possible. We validated the drop-on-demand generation method by producing solid kernels of yttrium-stabilized zirconia and soft gel microspheres of iron hydroxide. In addition, we have measured the diameter change at each principal process stage. Based on the observed gas entrainment/absorption in the gel spheres, we conjectured that aging and washing are likely the critical stages determining the final precision to which microspheres can be made. Finally, we comment on potential improvements that add robustness to the method for handling other metal precursors in aqueous solutions.

1. Introduction

The US Department of Energy (DOE) is exploring various process options for the transuranics (TRUs) in spent fuel elements from light-water reactors. One option is to make TRU fuel kernels, which will contain 90% plutonium and 10% minor TRUs, via the internal gelation process. The TRU kernels would then be coated with carbon and silicon/zirconium carbide and converted into tri-structural-isotropic (TRISO) coated fuel particles, which could be used in high-temperature gas-cooled reactors as part of the Deep-Burn project [1].

Past work on the internal gelation process created kilogram quantities of uranium fuel kernels with diameters of 350 μm and 500 μm [2], which were made into TRISO coated fuel particles. However, the use of the internal gelation process with TRUs presents several challenges. At the first stage of the process, plutonium dioxide (PuO_2) is amorphous, and amorphous microspheres from the internal gelation process tend to crack during subsequent heat treatment. In a previous attempt, essentially all of the PuO_2 microspheres from the internal gelation process failed due to cracking during subsequent heating. The cracking was probably caused by insufficient removal of residual organics and ammonium nitrate from the gel spheres. Recently, a new wash procedure [3] was developed to eliminate the cracking problem of amorphous microspheres from the internal gelation process. In addition to standard washes with trichloroethylene and ammonium hydroxide, this process employed water washes, pressurized water at 200 °C, and Dowanol PM rinses.

Another challenge for the internal gelation process involves small kernel size. The target size for the TRU kernels is from 150 to 300 μm in diameter. The primary reasons for the small size are to reduce self-shielding in the transuranic Pu–Np fuel kernels and to increase reactivity [4]. With a vibrating tube or nozzle system, the standard methods to reduce the final kernel size are to increase the frequency of the vibrator, reduce the diameter of the nozzle, decrease flow rate to the nozzle, and reduce the metal concentration (increase shrinkage factor) of the gel spheres. Using our vibrating tube system, yttrium-stabilized zirconia kernels with a diameter size range of 288(22) μm were obtained [3] by employing the aforementioned first three methods. However there exist practical limitation problems. For instance, at the laboratory scale, Pu/Np production runs use less amount of feed material for a constant amount of unused material at the startup and end of the process. Therefore, the product yield is expected to drop probably by 20%

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in shorter runs. Recently, uranium kernels in the size range of 100(20) μm were produced by reducing the metal concentration in the feed [5]. However, it is not known if a similar feed adjustment with plutonium would produce quality Pu/Np fuel kernels, because of the lack of existing data.

As a result of these potential challenges with the vibrating nozzle system and Pu/Np, alternative production equipment was considered. The primary requirements for the alternatives were the production of monodispersed Pu/Np kernels in the size range of 150 to 300 μm in diameter, suitable for short production runs with TRUs, and a small range of particle size, which is very desirable for subsequent coatings for the TRISO coated fuel particles. A leading candidate identified by this evaluation was the drop-on-demand (DOD) method [6], which typically uses direct electric pulses via piezoelectrics, acoustic beams, or electrohydrodynamics. Here we experimented with a pneumatically actuated microvalve of common use in the fluid dispensing industry but not intended for DOD generation. The availability of robust, low-cost, off-the-shelf pneumatic components is attractive for assembling a method for the production of microspheres for nuclear applications. The combination of pneumatic DOD and the internal gelation process was tested using yttrium-stabilized zirconia as a typical Pu surrogate. The experimental results of this evaluation are presented below.

2. Experimental procedure

The pneumatic DOD system consisted of the following six main components (Fig. 1): (1) pneumatic microvalve and dispenser tip (741 MD-SS; PTFE-lined crimped tip or PTFE-coated tip, EFD East Providence, RI, USA); (2) solenoid valve (8202 kit, EFD); (3) solenoid valve controller (ValveMate 8000 Controller, EFD); (4) waveform generator (Model 3390 Arbitrary Waveform Generator, Keithley, Cleveland, OH, USA); (5) cooling unit (ProcessMate 6500 Temperature Control System, EFD); and (6) 100-psi air supply, filters and pressure regulators.

A 10 cm^3 syringe barrel was directly connected to the pneumatic microvalve and used for holding the feed solution under pressure (typically held at the starting pressure of 55 psi). The syringe and feed solution were jacketed and chilled by a one-pass-through cool airflow from the cooling unit at 5 °C; no attempt was made to cool the stainless steel body of the valve. It was sufficient to cool only the feed solution as long as the light shed against the camera lens was cool (Fig. 1). Heat emitted from lighting disrupted the generation of drops even with simple fluids such as glycerin probably because of the change in physical and transport properties, such as density and viscosity. The pneumatic valve was actuated by pressure from the solenoid valve at 75 psi. The solenoid valve controller was set to keep the valve open for 10 ms each time it received a 5-V signal from the waveform generator, which was used to set the desired period for the drop generation.

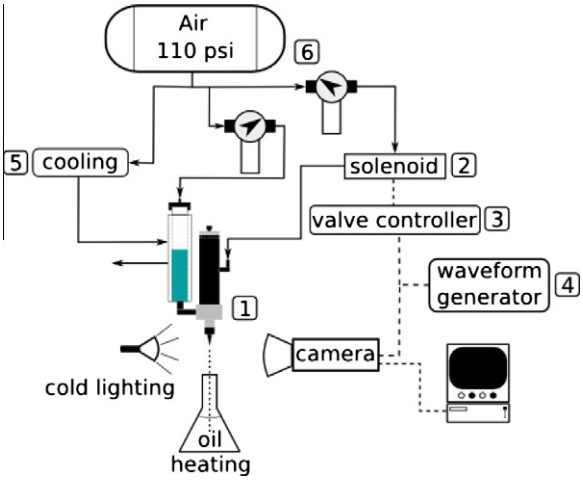

Fig. 1. Main components of drop-on-demand pneumatic setup. A high-speed video camera, lens, lighting, and a computer/monitor were used as auxiliary components. Drops were allowed to fall into a heated silicone oil tank.

Two types of dispenser tips were used. A Teflon-lined, crimped needle with an internal diameter of 150 μm and external diameter of 690 μm was the best off-the-shelf tip available for the zirconium nitrate solution. A stainless steel, Teflon-coated blunt tip with internal diameter of 330 μm and external diameter of 692 μm was used for the ferric nitrate solution. Other types of tips were tested, namely chamfered and general-purpose blunt shape. However, they were problematic since fluid from the ejecting orifice spread and climbed the outside surface of the tip; this flow configuration did not allow for a stable generation of monodispersed drops.

The tips had a lip with length equal to the wall thickness, which is typically (but not always) fully wetted by the feed solution. Therefore, the outside tip diameter (not the inside diameter) was one of the principal quantities determining the final size of the generated drop (Fig. 2).

A 5-V rise pulse function with a period ranging from 100 to 500 ms was programmed into the waveform generator, and the stroke control knob of the pneumatic valve was set to fully closed. The pulse generation was started with the desired period, and the stroke of the valve was slowly increased until fluid was ejected from the dispensing tip. The successful ejection of a single drop at each pulse depended on the simultaneous adjustment of the pressure on the syringe barrel and the stroke of the valve. This adjustment was made possible with the assistance of a high-speed video camera synchronized with the waveform generator and connected to a computer and monitor. Each pulse sent to the solenoid controller was also sent to the camera which was set in burst mode. The arriving signal triggered the camera to record a burst of fixed number of frames and subsequently to return to standby mode to wait for the next voltage rise. The images sent to the computer monitor were refreshed sufficiently fast to allow visualization on screen of the effect of changing the stroke of the valve and the pressure in the fluid feed.

Once the stroke knob was sufficiently open, a cylindrical jet of fluid emerged from the tip. Next, the feed pressure was adjusted to reduce the length of the jet until it broke up into a segment that evolved into a single drop. The portion of the jet that remained connected to the tip retracted into an oscillating pendent drop attached to the lip of the dispensing tip (Fig. 3). This pendent drop, with diameter spanning the outside diameter of the tip, was the precursor of the next ejected drop. Therefore, the final diameter

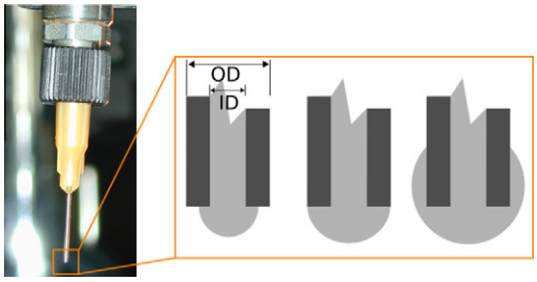

Fig. 2. Wetting of the dispenser tip by the feed solution. Left: Partially wettting; acceptable but unstable. Center: Fully wetting where contact line is pinned at the outside diameter rim; ideal case. Right: Overwetting with climbing film; undesirable.

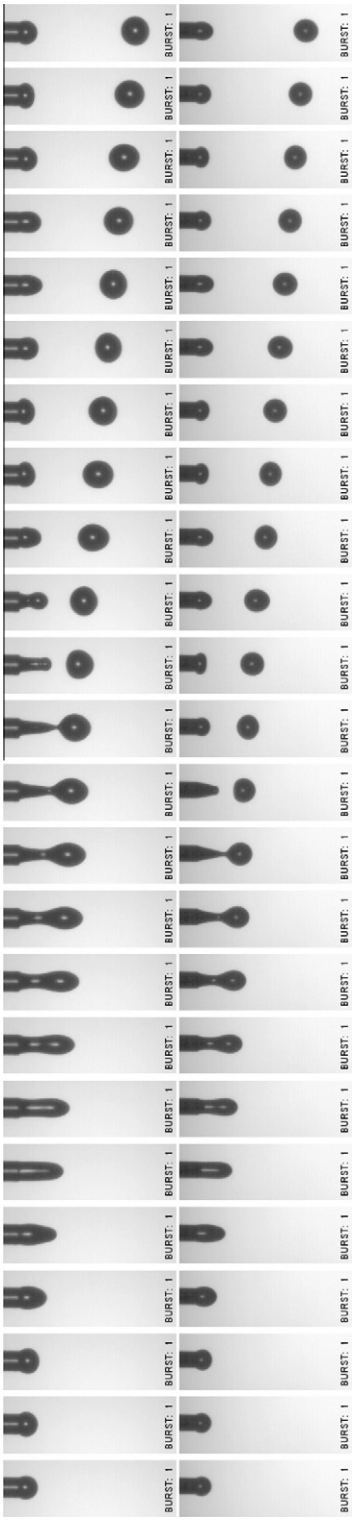

Fig. 3. Single period of drop-on-demand generation at 0min of a production run. Top row: Aqueous feed solution: hexamethylenetetramine (HMTA) 0.96 M, urea 0.96 M, nitric acid 0.52 M, yttrium nitrate 0.066 M, and zirconium nitrate 0.74 M [3]. Period of generation: 200 ms. Feed pressure: 55 psi. Interval between frames: 625 μs. Jet length without constriction: 1725(35) μm (seventh frame from the left). Drop diameter: 1000(35) μm; speed: 0.38 ms^{-1}. Bottom row: Aqueous feed solution: HMTA 1.72 M, urea 1.72 M, and ferric nitrate 1.15 M [7]. Period of generation: 500 ms. Feed pressure: 60 psi. Interval between frames: 625 μs. Jet length without constriction: 1301(41) μm (sixth frame from the left). Drop diameter: 977(41) μm; speed: 0.46 ms^{-1}.

Fig. 4. Drop free fall into oil Drop free fall and bubbly oil. Left and center: Drop of zirconium solution falling into heated bath of silicone oil; bubbles were formed as the drops sank to the bottom. Right: Drops of ferric solution falling into heated silicone oil; fewer bubbles are generated.

of the generated drop, was largely determined by the volume of the existing pendent drop and the outside diameter of the tip.

It was often possible to obtain two drops for each pulse by breaking up a longer jet into two segments. The leading segment evolved into the main drop while the second segment generated a smaller satellite drop. This regime could be used to generate a bimodal distribution of drops; this innovation was not systematically explored but it could be useful for SPHEREPAC fuel applications. In addition, it was easy to create larger drops once a single drop regime was obtained. It was just a matter of reducing the fluid pressure such that a drop was ejected every other pulse cycle. This would effectively double the size of the pendent drop in order to generate a final ejected drop of about twice the original diameter. This is an attractive way to create larger drops without increasing the diameter of the tip.

The system was fully troubleshot at room temperature with a mixture of glycerin and water (65 wt%; viscosity of 15 cp) which simulated the dynamic viscosity of the chilled feed solution for internal gelation.

The drops were created in ambient air and were allowed to fall (by gravity) into a wire basket inside a beaker (10-cm diameter; 18-cm tall) filled with silicone oil at 92 °C (80 °C for the ferric solution) (Fig. 4). The oil was kept at uniform temperature by a temperature-controlled heating tape tightly wrapped outside the beaker wall; a thermocouple was inserted in the oil and connected to the heating tape controller. The reservoir was cylindrical and long enough (11.5-cm diameter and 20.0-cm height) to allow gelation to occur (zirconium solution only); therefore, the drops acquired sufficient rigidity to avoid coalescence (for the most part) when touching other drops at the bottom of the reservoir.

Finally, the microspheres were removed from the beaker by removing the wire basket and further processed [3] to produce solid oxide microspheres.

3. Results and discussion

It is sufficient to present and discuss results for the zirconium solution (0.74 M Zr, 0.066 M Y, 0.96 M HMTA, 0.96 M urea, and 0.52 M H^+). Production runs were made by setting up the system as described in the previous section and letting it run while the drops were visualized through the high-speed video camera and the feed pressure was adjusted to keep a single drop produced at each valve aperture cycle.

A typical run used about 8 ml of feed solution and took about 45 min. During this time, the changes in physical properties of the solution were insufficient to require major changes in the

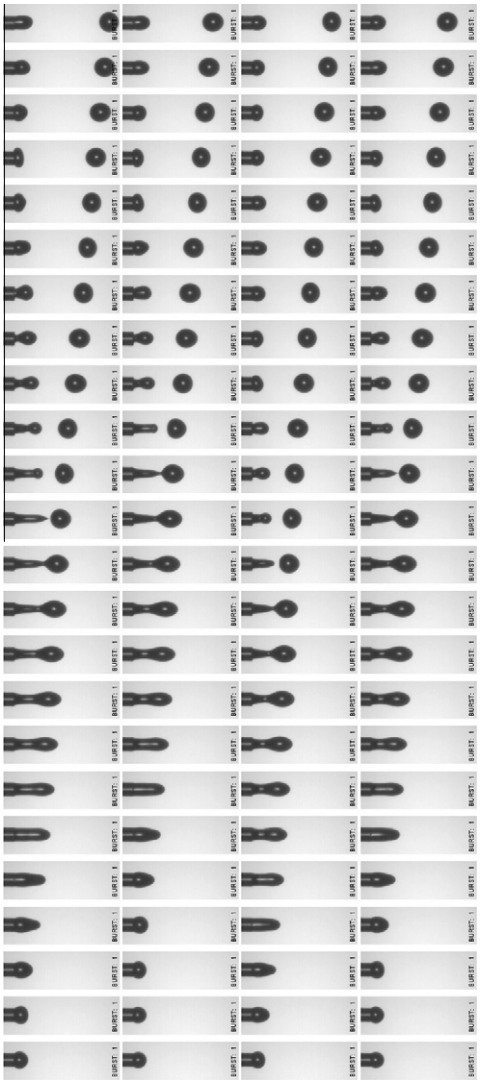

Fig. 5. Single period of drop-on-demand generation at 10, 20, 30, and 40 min of production (top to bottom rows, respectively). Corresponding feed pressures: 45, 41, 35, and 32 psi. Other parameters are the same as those listed for the top row of Fig. 3.

original system parameters used at the onset of the production. As the level of the feed solution in the syringe barrel lowered, the feed pressure had to be reduced to compensate for the reduced total pressure head and reduced resistance to flow. Fig. 5 presents a comparison of the ejection of one drop at four different times during production with respective adjusted feed pressure values.

If the fluid pressure was not reduced within intervals of 10 min, smaller satellite drops started to form since the effective feed pressure was higher and longer jet lengths were formed. However, the corresponding effect of pressure adjustment on the final drop diameter was insignificant within the accuracy (35 μm) of the camera lens (Fig. 6). The only noticeable effect was on the length and time of jet pinch-off as indicated in Fig. 5 by which compares the detailed ejection phenomenon at different times during production. The need to change the feed pressure during production adds complexity to any attempt at automation of the process. However, we believe that this difficulty can be minimized or eliminated if the feed solution is made to flow nearly at a constant flow rate, as opposed to constant pressure.

The soft gel microspheres were allowed to cool to room temperature overnight in silicone oil and removed from the beaker to show a bimodal size distribution, indicating that some level of

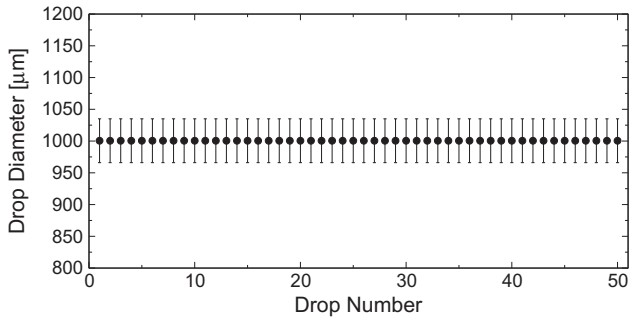

Fig. 6. Drop diameter of a sample of ten consecutive drops ejected at 0, 10, 20, 30, and 40 min of production. Measurements were made at a distance of 15 drop diameters downstream of the dispenser tip at a resolution of 35 μm.

coalescence occurred as the drops traveled inside the silicone oil bath. This could have been caused by the rising bubbles (Fig. 4 center), which may have decelerated some of the falling drops, providing an opportunity for drop collisions within the oil. Alternatively, there may have been coalescence of gel spheres at the bottom of the beaker as they piled on top of one another.

The average diameter of the dominant population of smaller spheres was 709(34) μm (95% confidence level) and the diameter of the larger spheres, 33% greater (943 μm). Therefore, there exists approximately a 300-μm reduction in diameter of the liquid drops when they undergo gelation and aging in the oil bath.

The ideal diameter of the larger spheres, resulting from the coalescence of two smaller spheres of the same diameter, would be 26% greater than the diameter of the precursor spheres. However, in view of the substantial size reduction of drops immersed in silicone oil, it is not realistic to expect the ideal value be to obtained. In fact, a closer look at the gel microspheres (Fig. 7) after they are washed and air-dried reveals small entrained bubbles. These bubbles suggest either that air entrainment during the mixing of the HMTA-urea and the zirconium–yttrium nitrate solutions persisted in the feed stream or that the absorption of gases by the feed solution in the pressurized syringe barrel was sufficient to lead to bubble nucleation when the drops were exposed to a hot environment. There is also a possibility of mechanical bubble injection inside the pneumatic microvalve. However, this scenario cannot be investigated at present because of lack of information on the internals of the valve.

Entrained bubbles in the gel spheres may cause rupture problems during the subsequent processes of washing and heat treatment and therefore should be removed (to the extent possible) from the feed. In this work the feed solution was simply allowed sit in a vial for 15 min before loading into the syringe barrel, in an attempt to allow for disengagement of the air bubbles. No effort was made (if at all possible) to circumvent the problem of gas

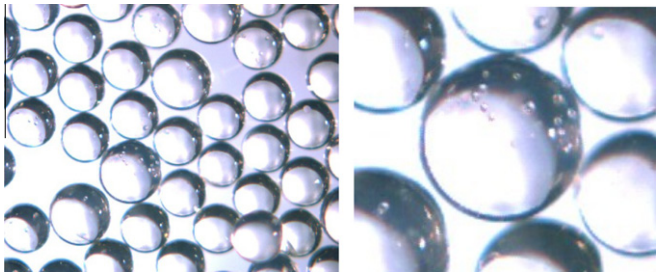

Fig. 7. Gel microspheres after washing and air-drying. The bimodal distribution is probably the result of coalescence in the oil bath container. Left: smaller size diameter, average 503(30) μm (95% confidence level). Right: Close-up of bubbles entrained in the gel microspheres.

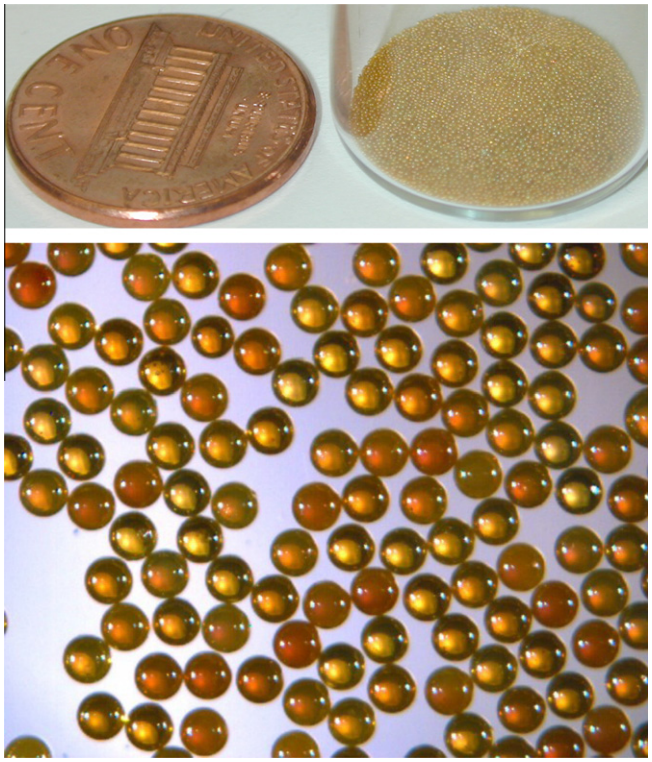

Fig. 8. Yttrium-stabilized zirconia microspheres after heat treatment at 1165 °C. Average diameter: 257(14) μm. Total shrinkage factor: 3.9 (from flying drop to partially sintered kernel).

absorption in the syringe barrel. It appears that the bulk of the absorbed gas escaped the forming gel spheres in the form of bubbles during the immersion in hot oil (Fig. 4, center).

After fully washing the gel spheres, applying an appropriate heat treatment [3] (which resulted in an average sphere density of 5.4 g mL^{-1}; Quantachrome pycnometer 1000), and mechanically separating nonspherical beads (approximately 5%), random samples from the nonsieved total production were measured (Fig. 8). The average diameter value was 257(14) μm (95% confidence level). The shrinkage factor obtained from the wet gel sphere stage, after removal from the silicone oil and prior to any treatment, to the heated (but nonsintered) solid oxide was 2.7. The shrinkage factor from the drop diameter to the final kernel diameter was 3.9. Past work [3] using a vibrating nozzle system with the same feed solution resulted in an average diameter of 288(22) μm for the sieved population of spheres and a shrinkage factor of 4.

In view of the accuracy (35 μm) of the measurements of the drop diameter, we were not able to clearly identify the critical step in the production process that controls the diameter variation of the final oxide microspheres. However, our observations demonstrate that gas absorption and/or gas entrainment play a role in determining the precision to which microspheres can be produced. This adverse effect seems to be mitigated by the gas released in the hot oil bath which led to the encouraging results obtained without sieving the test production.

4. Conclusions

The oxide microsphere production by internal gelation explored in this study had four stages that defined the final kernel diameter: namely, the drop generation (1000(35) μm), the gelation/aging in the hot oil bath (709(34) μm), the washing of residues (503(30) μm), and the final nonsintering thermal treatment (257(14) μm). There exists significant change in diameter from one stage to the next. However in view of the implications of gas entrainment/absorption in the sol/gel stage, it is likely that the aging in hot oil and the washing procedures dictate the final precision to which the process can produce monodispersed microspheres. The thermal treatment applied to the microspheres resulted in a density near to the theoretical limit (5.55–5.82 g mL^{-1} depending on the concentration of ZrO_2) therefore further sintering may not be sufficient to improve the precision to an acceptable limit.

The components of the pneumatic setup are items readily available in today's fluid dispensing technology. However we integrated these components for DOD generation, which is not the original intended application of the equipment. Therefore we demonstrated the usefulness of the components for production of oxide microspheres and identified significant improvements to further optimize the system. First, the dispenser tips used were off-the-shelf items that can be greatly improved in material and shape. Better design of the tip can help improve control of drop diameter and reproducibility. Second, smaller drop sizes can be achieved by reducing the stroke and valve aperture time with increased operating pressure levels. These custom modifications could be made by the manufacturer of the components upon specific requirements from the end user. Finally, uniform cooling of the feed solution during its entire travel path until the drop formation will help reduce the adverse effect of viscosity and mass density changes during gelation.

At this time there exists a number of tip shapes commercially available for the most promising types used in this work, namely, Teflon-lined or Teflon-coated. We have used those with the smallest external diameters, that is, 690 μm (EFD PTFE-lined 5125TLCS-B) and 692 μm (5123PC-B), respectively. If tips with smaller diameters are custom made, the system developed here should be able to produce smaller microspheres, possibly by a factor of two. However, the solenoid valve aperture time has to be reduced correspondingly. In our case the ValveMate 8000 Controller could not be set to a smaller aperture than 9 ms. Larger microdrop diameters can be easily created with either larger tips or by other means discussed in the Section 2. We expect that with these adjustments the range of final microdrop diameters delivered by such a system to be approximately 128–514 μm.

The proposed system is easily scalable, remotely operable, and simple to shield against radiation; only the pneumatic valve and feed need to be confined. The solenoid valve and valve controller we used can operate four pneumatic valves simultaneously; therefore, a fourfold increase in drop generation frequency can be obtained on our system by adding three pneumatic valves. Our typical drop generation frequency was 5 Hz for one valve. Hence, it is conceivable to set up a system with a 500 Hz total frequency by simply adding extra valves and controllers. An additional bonus is the economy of scale obtained by building identical pneumatic valve units, wherein the cost of the equipment scales sublinearly with increased throughput.

We used high-speed video monitoring synchronized with the drop generation process. Typically a total of 40 frames at 1600 frames per second is sufficient to record the generation of a single drop. We have used 8-bit, gray, 256×96 pixel resolution per frame, with storage of 27 kilobytes. Thus, 1 terabyte of storage could record the detailed ejection of 1 million drops. Considering the low cost of today's digital disk storage, accurate information regarding the generation of all drops in a typical run could be obtained via image processing of the acquired images. In fact, the drop size distribution could be obtained in real time by segmenting the images and determining the diameter of the drops "on the fly." In addition, the sphericity of the drops could be determined, and the real-time information could also be used as feed-back control

signal. Last but not least, the image data obtained could be used to keep a tight inventory of the material used for nuclear applications.

Acknowledgements

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References

[1] R.M. Versluis, F. Venneri, D. Petti, L. Snead, D.W. McEachern, Project deep-burn: development of transuranic fuel for high-temperature Helium-cooled reactors, in: ASME (Ed.), Proceedings of the Fourth International Topical Meeting on High Temperature Reactor Technology, vol. 1, American Society of Mechanical Engineers, Three Park Avenue, New York, NY 10016-5990, USA, 2009, pp. 167–170.
[2] R.D. Hunt, J.L. Collins, Uranium kernel formation via internal gelation, Radiochim. Acta 92 (2004) 909–915.
[3] R.D. Hunt, F.C. Montgomery, J.L. Collins, Treatment techniques to prevent cracking of amorphous microspheres made by the internal gelation process, Radiochim. Acta, submitted for publication.
[4] Oak Ridge National Laboratory TM-2002-135, Deep-Burn Modular Helium Reactor Fuel Development Plan, Oak Ridge, TN 37831, USA, Co-authored with General Atomics GA-224-0-TRT-000167, 2002.
[5] V.R. Ganatra, N. Kumar, S. Suryanarayana, Y.R. Bamankar, N. Reghu, V.N. Vaidya, S.K. Mukerjee, Process and equipment development for the preparation of small size UO_2 microspheres by jet entrainment technique, J. Radioanal. Nucl. Chem. 275 (2008) 515–522.
[6] E.R. Lee, Microdrop Generation, Nano- and Microscience, Engineering, Technology, and Medicine Series, CRC Press, Boca Raton, Florida, 2003.
[7] J.L. Collins, R.J. Lauf, K.K. Anderson, Method for preparing hydrous iron oxide gels and spherules, United States type 6599493, 29 July 2003.