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# *Demonstration of microfluidics for synthesis of sol-gel feedstocks*

## Nuclear Technology Research and Development

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***AL McAlister,***
***JW McMurray,***
***KM Cooley,***
***RD Hunt***
***Oak Ridge National Laboratory***

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# SUMMARY

This report details the design and processing conditions for producing hydrous cerium oxide surrogate microspheres using a microfluidics-based approach. Variables such as microfluidic chip design, exit tubing diameter, temperature, and flow rate continue to be investigated. A washing and drying procedure to remove gelation media, unreacted starting material, and unwanted reaction byproducts is under development. Samples are imaged for analysis of size and geometry.

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# ACRONYMS

| Acronym | Description |
|---|---|
| ATF | Accident tolerant fuel |
| HMTA | Hexamethylenetetramine |
| ID | Inside Diameter |
| LWR | Light Water Reactor |
| OD | Outside Diameter |
| ORNL | Oak Ridge National Laboratory |
| PDMS | Polydimethylsiloxane |
| R&D | Research & Development |
| TCE | Trichloroethylene |
| ADUN | Acid Deficient Ammonium Nitrate |

# DEMONSTRATION OF MICROFLUIDICS FOR SYNTHESIS OF SOL-GEL FEEDSTOCKS

## 1. INTRODUCTION

Sol-gel chemistry and microfluidic techniques are being combined to introduce a new method of microspherical feedstock production to support Research and Development (R&D) of Accident Tolerant Fuels (ATF). Presented in Figure 1 is ORNL first-generation microfluidics-based sol-gel system used to produce surrogate material consisting of hydrous cerium oxide microspheres via internal gelation as a proof-of-principle. The objective of this work is an investigation of whether microspheres can be made with (1) tighter tolerances, (2) a wider range in diameters, and (3) higher throughput for smaller sizes compared to conventional sol-gel techniques. This is accomplished by utilizing microfluidics hardware with either traditional broth or in-line mixing for a continuous process. While some aspects such as chip design, exit tubing size/length, and inlet tubing connections continue to be modified, the overall process flow and components remain the same as that in Figure 1.

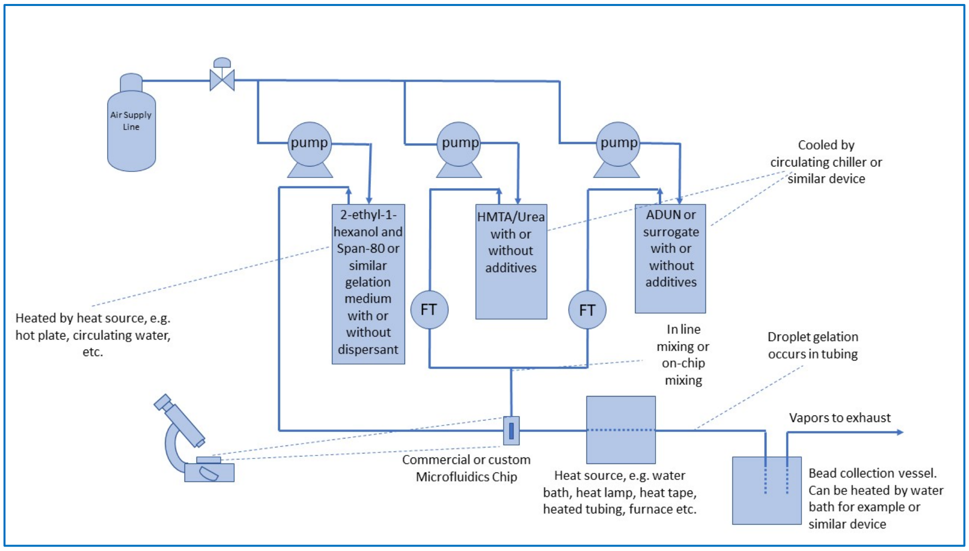

**Figure 1. Flow sheet for general microfluidics-based sol-gel system design.**

# 2. EXPERIMENTAL

## 2.1 Background

Microfluidics traces its origins to biotechnologies R&D in the early 1990's. It uses forced flow of fluids through a network of channels on the order of tens to hundreds of µm's to produce a desired outcome [1]. For the purposes of this work, that is droplets of sol-gel precursors in a flowing stream of an immiscible gelation medium, in this case 2-ethylhexanol (2EH). Silicon oil can also be used but subsequent washing in trichloroethylene (TCE) is required. TCE is toxic, therefore silicon oil was avoided; all experiments were performed with 2EH. The channels can be etched into a substrate typically in the design of a chip (Figure 2). The chips used in this work were glass with a channel diameter of 190 µm available off-the-shelf from Dolomite Microfluidics, or custom produced from polydimethylsiloxane (PDMS) by Phenomyx with a droplet channel diameter of 400 µm. Various trials to produce gel spheres ranging from 50 to 400 µm in diameter were performed using microfluidic hardware from Fluigent, and a high-speed microscope from Dolomite Microfluidics that allowed for real time adjustment of parameters (Figure 3).

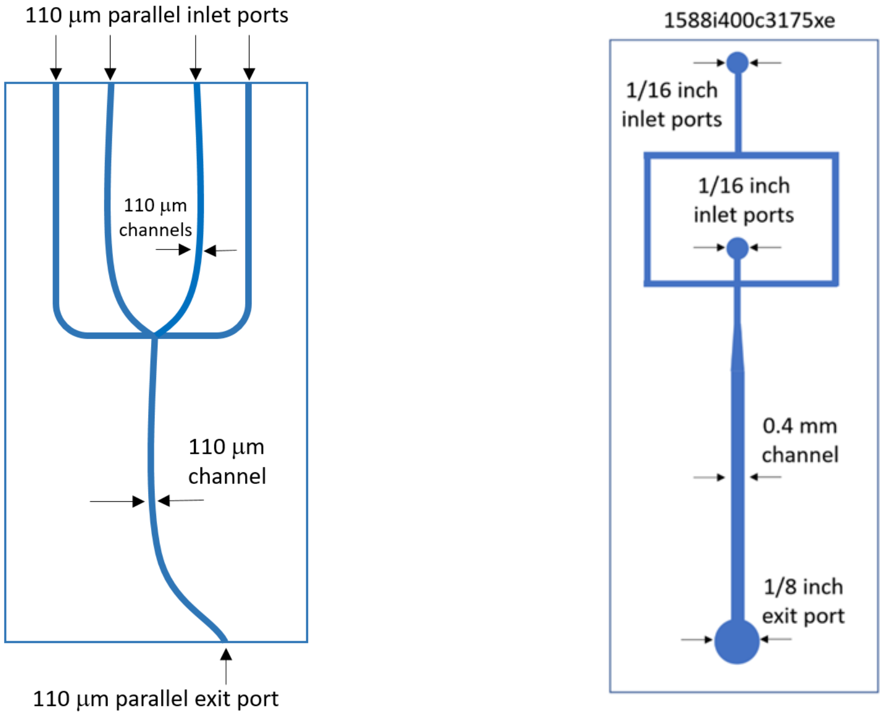

**Figure 2. Glass mixing chip (left) and PDMS x-junction (right) designs.**

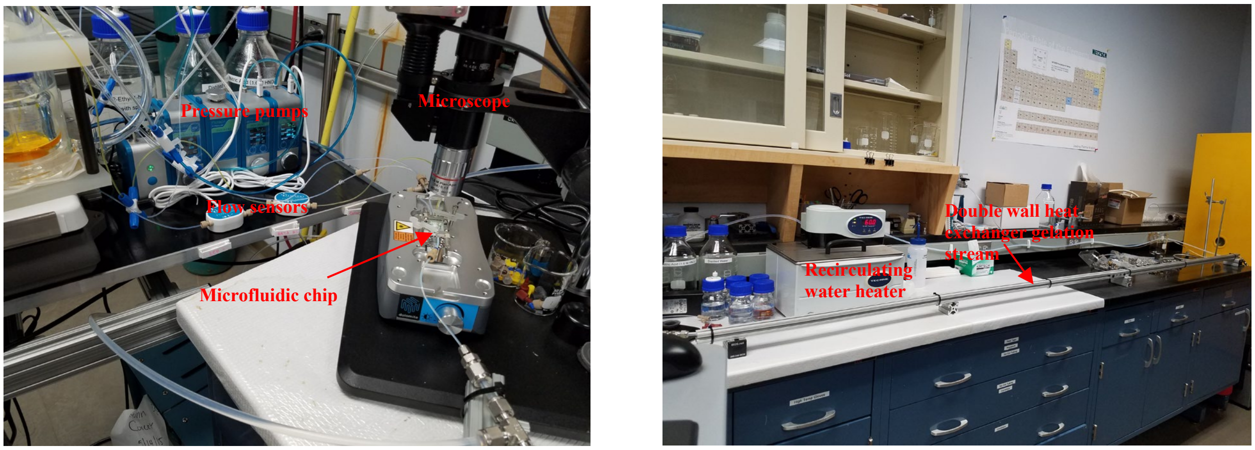

**Figure 3. Lab setup for the microfluidics-based sol-gel system.**

## 2.2 Procedure

A solution of a metal nitrate, hexamethylenetetramine (HMTA), and urea is either mixed *a priori* in a broth pot or in-line on the chip where it flows into a junction, is pinched into a droplet as shown in Figure 4, and then carried downstream where it is heated to initiate the gelation reaction. A double wall heat exchanger was designed using a circulating hot water jacket along the entire length of the exit stream, shown in Figure 5, in order to improve gelation of the microspheres. For this work, the gelation temperature was maintained at 60ºC since 2EH vapor pressure precluded going any higher. The process is similar to the sol-gel system and process at ORNL described in detail in [2-6] and used extensively to produce $UO_2$, UN, UC, $UO_2$-UC, and $UO_2$-$UC_2$ for advanced nuclear fuel concepts [7-20]. The major differences are the use of microfluidics hardware as well as the size and orientation of the gelation stream, in this case a double wall heat exchanger with a circulated water jacket (60 °C) shown in Figure 5 was added to the entire length of the exit stream. With this design, at higher flow rates the spheres will be exposed to enough heat to gel before reaching the collection vessel.

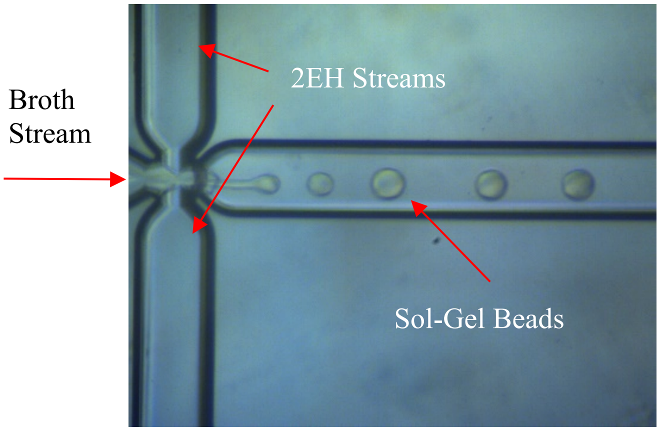

**Figure 4. In-line mixing chip produced smaller microspheres (~ 80 µm).**

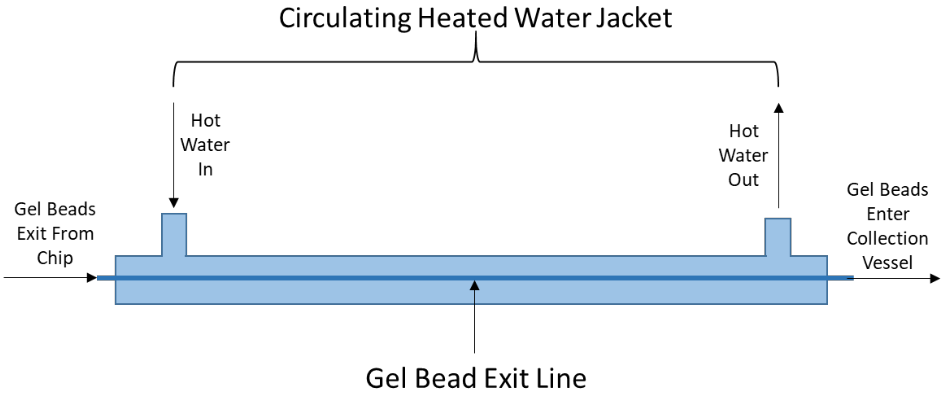

**Figure 5. Double wall heat exchanger with circulating water along entire gelation exit stream.**

Ceric ammonium nitrate, chemical formula $(NH_4)_2Ce(NO_3)_6$,was used as a surrogate for Acid Deficient Uranyl Nitrate (ADUN). Both chemicals can be mixed in appropriate ratios with a HMTA/urea solution to form a broth mixture which can be chilled to delay gelation. The process to produce hydrated Ce-bearing oxide gel spheres is described in detail in [21-23]. The feedstock for this work uses standard solution concentrations for HMTA (Fisher Scientific) and urea (Fisher Scientific) at 3.2 *M* each. Once prepared and filtered, the density was measured to be 1,141 $kg/m^3$ and the pH ranged from 9 to 10. The ceric ammonium nitrate solutions had a density of 1,594 $kg/m^3$ with a pH of 0.5-0.3 and a Ce concentration of ~1.85-1.86 *M.* Ammonium hydroxide is added to the cerium nitrate solution and the ratio of hydroxide to cerium can affect how quickly the spheres can gel. A lower $OH^{1-}/Ce$ ratio improves broth stability and requires longer gelation times.

Droplet size is principally dependent upon channel size; however, flow rates can be manipulated to produce smaller diameters within the limits of the chip design. For this study, two channel sizes were investigated. Pressure[1] values of the streams were investigated. A washing and drying procedure continues to be developed to yield hydrated cerium oxide beads that can be subsequently converted to $CeO_{2-x}$ microspheres without breaking apart.

## 2.3 Parameter adjustment and results

To delay gelation while flowing through the chip, the broth was chilled to ~5 °C. As pointed out above, to further prevent premature gelation, an OH ratio of 0.6 was used. Span 80 was added to the 2EH to prevent agglomeration of the smaller microspheres as has been observed previously [24].

Initial trials were done using flow controllers to read and manipulate flow rates (via the pressure pumps) for both the 2EH and broth streams. Fluctuating or unstable flow rate readings were observed while using direct flow control, but were resolved when manipulating pressure values only. This could be due to insufficient flow resistance. Flow controller stability is currently being explored through means of software settings and increasing resistance by decreasing outlet tube diameter as well as other system modifications.

Two microfluidic channel diameters, 190 µm and 400 µm were investigated to produce small (< 150 µm) and large (300 µm < 400 µm) sol-gel spheres. Ceric ammonium nitrate, urea, and HMTA were chilled to ~ 5 °C and mixed to form a broth. This mixture was continuously stirred and maintained at ~ 5 °C in a broth pot. An exit line length of ~1 m was used with a portion immersed in a circulated water bath at 60 °C.[2] Only pressure values were manipulated due to flow controller variability. For the chip with a 190 µm diameter channel, after 30 minutes of run time, irregular and decreasing flow was observed. The pressure was increased to investigate throughput limits. The 2EH stream was increased in steps from 350 mbar to about 756 mbar, while the broth stream was increased from 310 mbar to 555 mbar. At that level, pressure limits were reached resulting in a contiguous broth stream that extended to outside the exit port. The spheres were washed with ammonium hydroxide and dried at 400 °C. The sol-gel beads were then calcined at 400°C in air to convert to Ce oxide microspheres. A small sample taken after the washing and air-drying procedure (Figure 6) had an average bead diameter of about 104 µm. After calcination, samples from the same batch measured about 74 µm.

Throughput limits from the previous experiment showed that pressure values for the 2EH and broth streams were most stable around 490 mbar and 375 mbar, respectively. Using the same parameters, the next experiment had a 5 hour run time at 105 µL/min with 40 mL of mixed and continuously stirred, chilled broth. Manipulating the pressure values showed that changes to the 2EH stream had a significant impact on all fluid flows; therefore, the broth stream was found to be more effective for fine-tuning flow rates and maintaining stability. The microspheres were washed with ammonium hydroxide and calcined at 400 °C in air. The yield was 6.2 g of calcined Ce oxide microspheres.

The chip with a 400 µm channel with a 0.7937 mm ID (1.5875 mm OD) tubing was just large enough for single file droplets. Choke points in the line, i.e. perpendicular runs or turns, caused pile up and coalescence that produced slugs shown in Figure 7. When the outlet was increased to 1.5875 mm ID (3.175 mm OD), disk-like beads were produced for all flow rates (Figure 9), likely due to the perpendicular outlet orifice. A new customized design using a horizontal exit orifice and a 4.625 mm ID (6.35 mm OD) outlet tubing is the subject of continued investigation and is shown in Figure 9

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[1] Pressure and flow rate are coupled and can therefore be used interchangeably.

[2] This was done prior to upgrading to a ~3m double walled heat exchanger shown in Figure 5.

below.

Premature gelation resulting from backflow of 2EH into the broth line was identified as a major issue to address. The problem was resolved by first priming the broth lines with distilled water. As the broth is an aqueous solution, $H_2O$ can be used to equilibrate flows and establish good droplet formation. It was observed that these flows are consistent with the required flows for broth droplet formation.

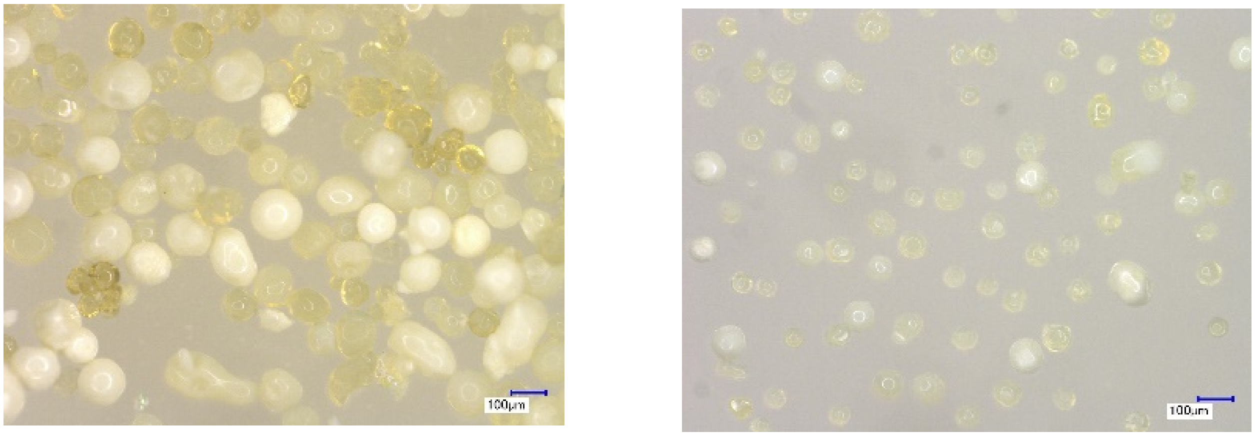


**Figure 6. Microspheres after ammonium hydroxide wash and air drying at room temperature (left), and washed spheres sintered at 400 °C (right).**

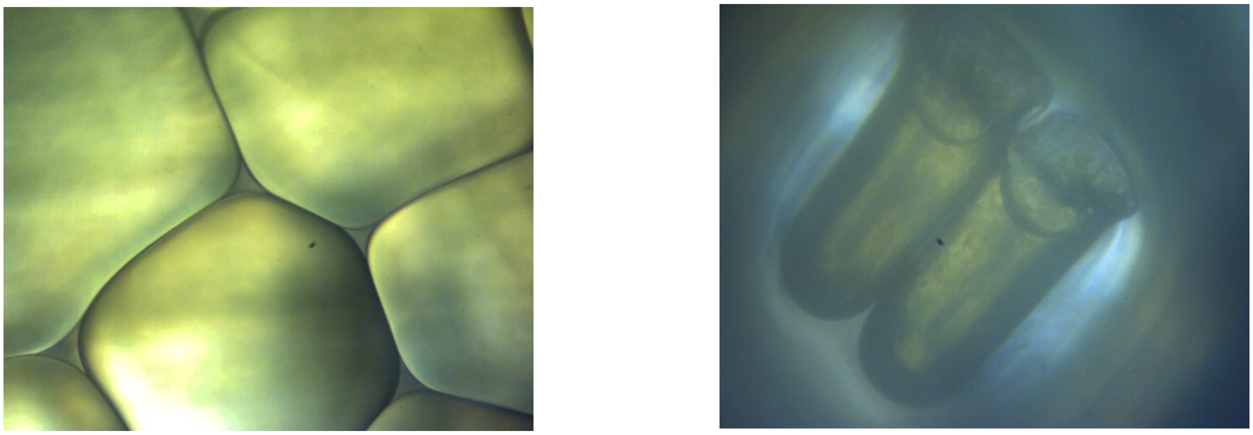
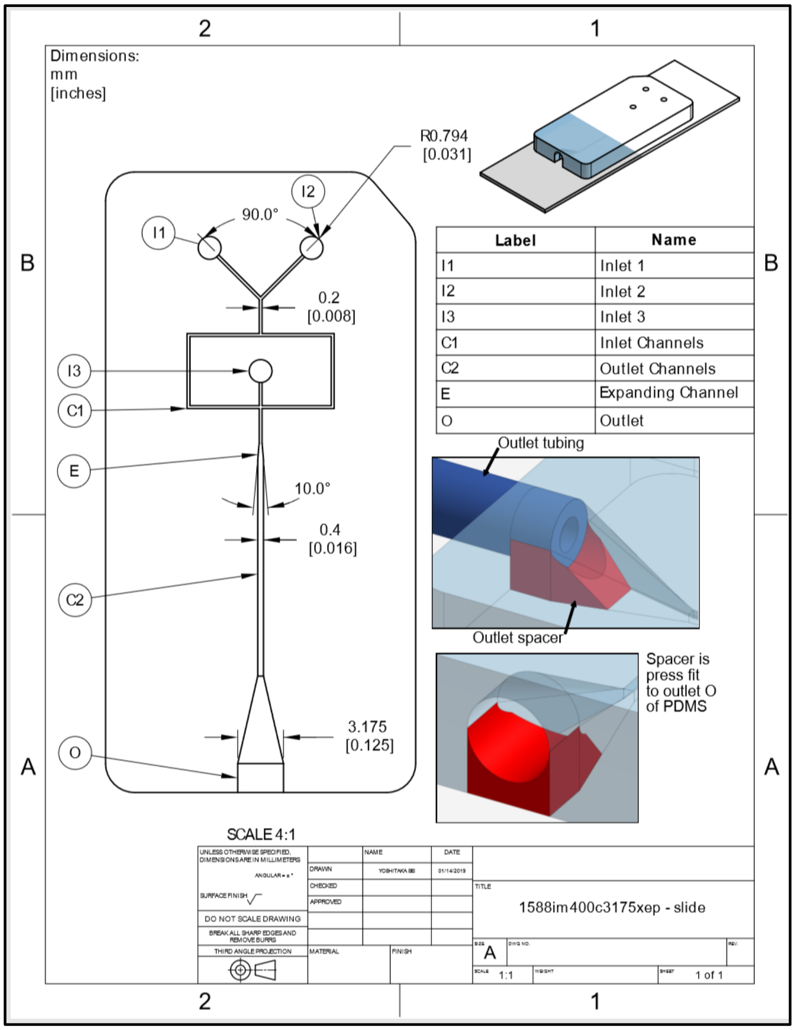


**Figure 7. Insufficient gelling of microspheres can lead to deformation of spheres (left); fused spheres coalesced to form slugs in lines which disrupts flow (right).**

**Figure 8. Droplets formed flattened pucks.**



| Label | Name |
|---|---|
| I1 | Inlet 1 |
| I2 | Inlet 2 |
| I3 | Inlet 3 |
| C1 | Inlet Channels |
| C2 | Outlet Channels |
| E | Expanding Channel |
| O | Outlet |

Spacer is press fit to outlet O of PDMS

|  |  | NAME | DATE |
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Figure 9. Next generation custom large bead chip design with horizontal outlet orifice to be provided by Phenomyx, LLC.

**Figure 10. Microspheres show improper gelling (larger white spheres) and powder formation.**

Since the broth is unstable at room temperature, in-line mixing is required for a continuous process. In-line mixing involves combining the ceric ammonium nitrate and HMTA/urea solutions within the chip just before the junction whereby the 2EH pinches off a droplet of the now mixed broth. This was performed using the glass in-line mixing chip with a 190µm channel from Dolomite Microfluidics with all solutions at room temperature. The pressure values were manipulated until stable, with flow rates for the cerium nitrate and HMTA/urea streams around 15 µL/min and 10 µL/min, respectively. After about 4 hours of run time, the pressure decreased due to gelling in the lines. A sample was washed with ammonium hydroxide and dried in air before imaging. As can be seen in Figure 10 a lot of powder and agglomerations were produced. The Ce microspheres are composed of very small crystallites, which makes the removal of the HMTA, urea, and ammonium nitrate more difficult. If these chemicals are not removed before the calcination, they will generate gases, which will break apart the microspheres if they cannot escape. The small microspheres are more difficult to wash because they are transferred to a column, which can lead to channeling. Therefore, a more rigorous washing/drying procedure was attempted that included washing with $NH_4OH$, immersion in 200 °C water. These were then calcined in air at 400 °C. Two calcined samples were taken, one with and the other without the more rigorous washing procedure (Figure 12). The total yield was about 0.5 g of cerium microspheres with diameters ranging from 50-70 µm.

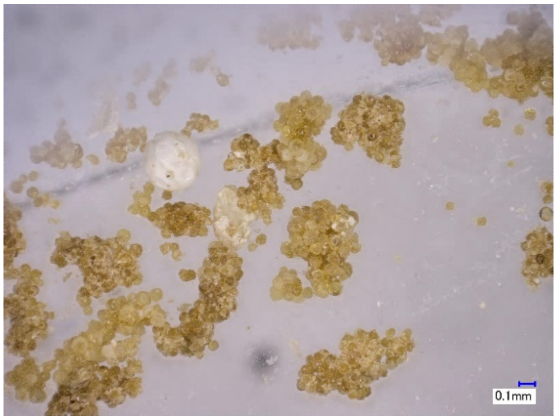

**Figure 11. Gelled cerium nitrate-based microspheres (~53-100 µm) washed in $NH_4OH$ and air dried.**

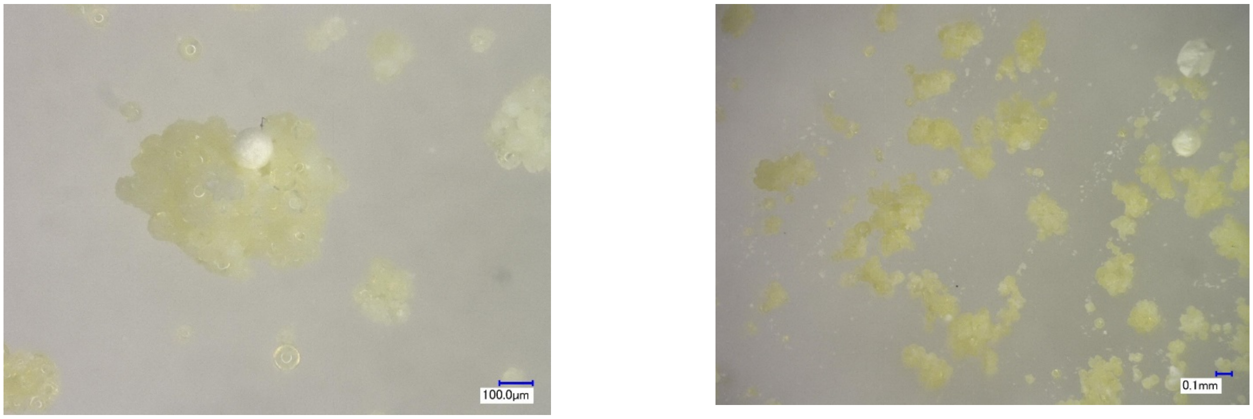

**Figure 12. Washed in $NH_4OH$ and dried at 400 °C (left); Washed in $NH_4OH$, treated with 200 °C water, and dried at 400 °C (right).**

## 3. SUMMARY AND CONCLUSIONS

The focus of this effort was a proof-of-principle processing design to produce large and small sol-gel derived beads for feedstock preparation of ATF ceramic fuel R&D. The latter was accomplished while the former is the subject of continued investigation. However, a washing and drying procedure still needs further development. Also, fine tuning processing parameters continues for improved sol gel bead geometries, e.g. avoiding the formation of dimples that can be seen in Figure 6.

Another goal was to determine throughput limits. The smaller beads (<190 µm) were produced at a rate of 13.3 ml/hr or about 1g/hr of Ce based surrogate. This would translate into 0.93 g/hr of air-dried sol-gel derived $UO_3 \cdot 2H_2O$ typically used as feedstock for ceramic fuel fabrication [7-20]. While an analysis of the size distribution of a statistically significant set of sol-gel beads and/or calcined microspheres was not performed, the Fluigent system claims a coefficient of variance of <2% is possible [1]. Therefore, the size distribution of calcined Ce oxide microspheres will be the subject of ongoing efforts.

This report summarizes the ongoing R&D for a microfluidics-based sol-gel system to produce Ce oxide microspheres of various sizes with a high throughput and tighter size distributions. System parameters are continuing to be fine-tuned in order to achieve an automated process and improved gelled bead geometries. A washing and drying procedure for the small gel beads is still being developed. Custom, experimental PDMS chips are being used for R&D. While they tend to tear from repeated use and PDMS is not chemically inert to dilute nitric acid[3], it is a quick and inexpensive way to test chip designs. Ultimately, glass chips will be used due to chemical resistivity. In addition, a new PDMS gel chip design will include in-line mixing ports, and a 4.625 mm ID horizontal exit port.

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[3] Dilute nitric acid dissolves hydrous metal oxides and is used for cleaning.

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