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PNNL-33542

Microfluidic Uranium Microspheres Production for TRISO and Advanced Fuel Concepts

September 2022

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U.S. DEPARTMENT OF ENERGY

Prepared for the U.S. Department of Energy
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Abstract

The purpose of this project was to expand existing internal gelation sol-gel capabilities at PNNL to explore producing uranium dioxide spheres for potential use as fuel kernels in next generation Tri-isotropic (TRISO) particle fuel. This project expands on previous sol-gel efforts at PNNL by (1) increasing the size regime of sphere production from the micro-fluidic range to the milli-fluidic range, and (2) producing uranium spheres. The approach involved first scaling up the channel size of the fluidic system to the millimeter range, with radiation safety considerations in mind; testing and demonstration on non-radioactive surrogate material, cerium oxide; then transitioning to uranium production and finally optimizing system parameters. Commercially available fluidic chips in the desired size range were could not be found, therefore the project designed and fabricated a T-junction with 1mm channels for droplet production. Because the production process is temperature sensitive, prior efforts have involved performing droplet production in a lab freezer. To reduce radiological waste and footprint, two alternative chilling methods were explored using aluminum thermal beads as a chill bath and a custom aluminum block fit to reagent reservoir sizes. Both were successful in the cerium tests, however the aluminum block design outperformed the thermal bead bath and was further adapted for the radiological test and production run in the Radiochemical Processing Laboratory (RPL). Gelation trials were performed to determine an acceptable range of feed solution parameters for the uranium dioxide gels, characterized by R-values, which is determined by the ratio of uranium nitrate to Hexamethylenetetramine (HMTA)/urea in the feed solution. R-values ranging from 1.6-2 were examined in the gelation trials, with only the 1.8 condition being tested in production. The project was successful in demonstrating a proof of concept design for producing uranium dioxide spheres, however further optimization is needed to dial in production parameters and improve sphere quality and homogeneity.

Summary

Currently, sol-gel microspheres are produced using vibratory nozzles that dispense droplets into heated columns of oil or 2-ethylhexanol to gel uranium hydroxide microspheres. These traditional systems occupy a large footprint in radiological spaces, use large volumes of hot, flammable fluid, and nozzles can be prone to clogging. To increase throughput without reducing yields of particles within an acceptable size tolerance, whole additional units or increasingly larger columns are required. Oak Ridge National Laboratory (ORNL) maintains such R&D sol-gel equipment and companies including BWXT and X-Energy are standing up TRISO production lines that include sol-gel microsphere production. The use of microfluidic devices to produce sol-gel microspheres is emerging as an attractive scale-up alternative. Microfluidic devices have been applied to other materials and smaller microspheres than typical TRISO fuel kernels but has not yet been demonstrated to meet the unique demands for advanced uranium fuel production.

The objectives of this work were (1) learn more about producing U to better position us for TRISO work since the team has only worked in other material systems with sol-gel and (2) test a microfluidic approach (with scalability) as an alternative to the typical vibratory microsphere production approach. This was accomplished by determining the best chemical formulation to synthesize uranium. Also, we identified a venue to scale-up in diameter to the milli range using a T-junction customized and manufactured by PNNL and reduce the radiological footprint by using a custom-made aluminum block on a chill plate instead of a big freezer.

Acknowledgments

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Contents

Figures

Tables

Acronyms

ADUN	Acid Deficient Uranyl Nitrate
HMTA	Hexamethylenetetramine
ID	Inside Diameter
KEMA	Keuring van Elektrotechnische Materialen te Arnhem
ORNL	Oak Ridge National Laboratory
PNNL	Pacific Northwest National Laboratory
RPL	Radiochemical Processing Laboratory
R&D	Research and Development
Sol-gel	Solution-gelation
TCE	Trichloroethylene
TRISO	Tri-structural isotropic
UO_2	Uranium dioxide

Introduction

The internal gelation sol-gel method was first developed in the late 1960s at KEMA laboratory in the Netherlands as a technique to produce uranium dioxide microspheres for nuclear fuel applications using a feed solution of U(VI) nitrate. The advantages of the internal gelation process for nuclear fuel kernels of uranium include the following: (1) control of gelation time and microsphere size, (2) reproducible preparations, (3) control of uranium crystal morphology in the gel spheres, (4) homogeneous incorporation of fine particles of other materials into the microspheres, and (5) a highly developed large-scale engineering process. (Kanij et al. 1967; Kanij, Noothout, and Votocek 1974; van der Brugghen et al. 1970).

The following four reactions are the essence of the internal gelation process. A clear broth is formed when a chilled solution of concentrated hexamethylenetetramine (HMTA) and urea is mixed with a chilled concentrated solution of acid-deficient uranyl nitrate (ADUN). The gelation process is driven by temperature and pH. Urea acts as a complexing agent in reaction (1) and prevents precipitation from occurring while lower temperatures are maintained. When the droplets of stock solution are introduced into a heated stream of immiscible organic [trichloroethylene (TCE)] medium, heating leads to decomplexation [reverse of reaction (1)] and drives the hydrolysis [reaction (2)]. The HMTA, a weak base, acts as the consumer of protons generated by reaction (2). The HMTA protonates by reaction (3) and decomposes by reaction (4), resulting in the precipitation and gelation of the uranium. Also, the urea acts as a catalyst by causing the decomposition of protonated HMTA molecules, which helps to accelerate reaction (4) .

Complexation/Decomplexation:

$$2CO(NH_2)_2 + UO_2^{2+} \leftrightarrow UO_2[CO(NH_2)_2]_2^{2+}$$

Hydrolysis:

$$UO_2^{2+} + xH_2O \leftrightarrow UO_2(OH)_2\cdot(x-2)H_2O + 2H^+$$

HMTA Protonation:

$$(CH_2)_6N_4 + H^+ \leftrightarrow (CH_2)_6N_4\cdot H^+$$

Protonated HMTA Decomposition:

$$(CH_2)_6N_4\cdot H^+ + 3H^+ + 6H_2O \leftrightarrow 4NH_4^+ + 6CH_2O$$

PNNL has produced large diameter spheres using cerium as a uranium surrogate and an in-house, custom-made T-junction and aluminum block. Also, we determined an acceptable range in the formulation (R-value) for the uranyl nitrate stock solution.

Production of uranium-based microspheres for TRISO fuel involves both internal gelation sol-gel chemistry as well as specialized equipment for microsphere production and processing. Traditional approaches to making uranium microspheres for TRISO used vibratory nozzles for regular breakup of droplets, which fall into a column of heated, immiscible fluid. This approach poses challenges for scale up beyond the pilot scale since many nozzles are required and past efforts to manifold feed solutions across multiple nozzles significantly degraded the product microsphere size uniformity. As fuel fabricators consider moving beyond the pilot scale used for DOE AGR tests and aim to produce ton-quantities for new nuclear reactors, additional approaches for microsphere production with better scaling potential are desirable. For this reason, we proposed to examine a T-junction microfluidic droplet production approach. Microfluidic, or in this case millifluidic, droplet generation systems have been the topic of considerable research over the past decade, with a variety of approaches and devices for producing uniform droplets demonstrated. While these microspheres are typically much smaller than those needed for TRISO fuel, this project aimed to test similar principles using a single T-junction with the understanding that a successful outcome would have potential for scaling into parallelized T-junctions to increase droplet production rates. Our hypothesis is that hydrodynamic forces in small channels can provide more uniform droplet sizes in a manifolded system than vibratory assisted droplet production across manifolded needles.

Experimental Data

Equipment description

To test the applicability of a scalable, millifluidic approach to making kernels for TRISO fuel, a new millifluidic sol-gel apparatus was developed as a modification to a microfluidic version currently used at PNNL. The microfluidic sol-gel apparatus, shown in Figure 1, uses a miniature freezer to chill feed solutions, transfer lines, and the sphere forming device. A microscope is also located inside the freezer to visualize microsphere production on a microfluidic chip. It also uses a pressure controller for precise flow control and a hot plate for microsphere collection and gelling.

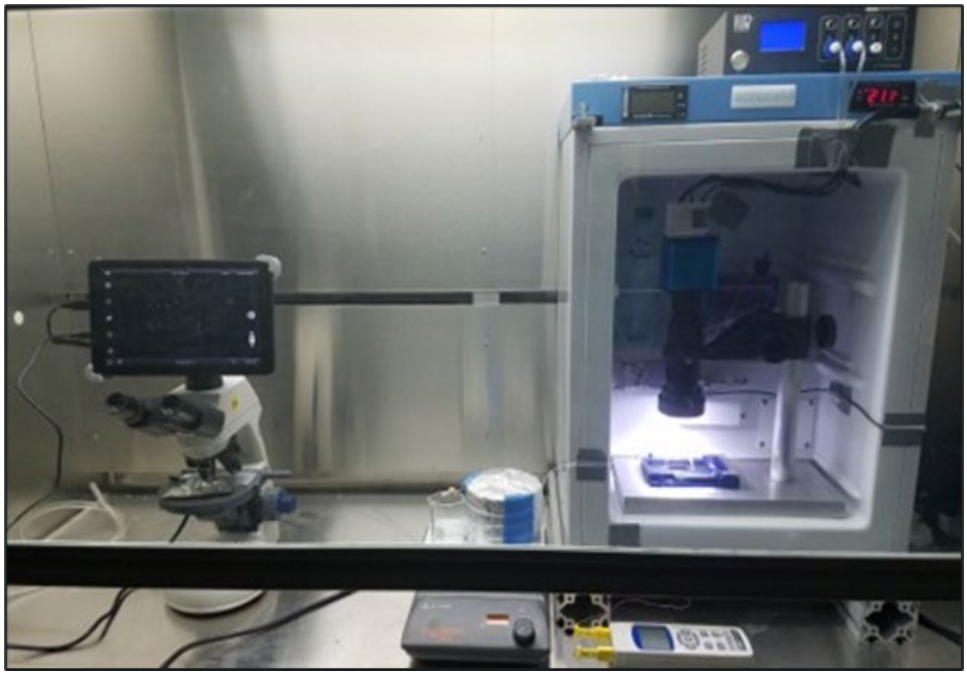

Figure 1: The microfluidic sol-gel apparatus, which is used for other applications at PNNL, provided the basis for a revised, more compact version for this project.

The new hardware similarly used a pressure controller and hot plate but did not require a microscope and replaced the cumbersome freezer with a smaller Peltier chill plate and aluminum block. The aluminum block, illustrated in Figure 2, interfaced with the chill plate, and contained holes for feed solutions as well as a mounting point for the T-junction.

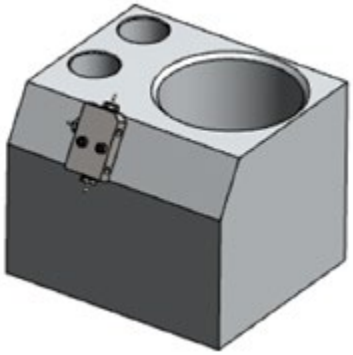

Figure 2: A SolidWorks model of the aluminum chill block with the T-junction attached to the front of it.

A stainless-steel T-junction was designed and fabricated for this effort to produce large droplets consistent with the size needed for TRISO fuel kernels. This revised sol-gel apparatus was more compact than previous equipment and was used for both the non-radiological cerium oxide and subsequently the radiological uranium dioxide microsphere production testing. Theoretically, the T-junction device could be designed to include a manifold with many sphere forming junctions and a larger outlet line to increase the production throughput while maintaining a small equipment footprint.

Synthesis of cerium dioxide spheres in a non-rad, scalable device

The sol-gel team decreased the footprint of the current set up from the big freezer to first, a tray full of aluminum thermal pellets and then, with a custom aluminum block that holds all the stock solutions on a chill plate. In April 2022, the team tested the first setup in a non-radiological laboratory fume hood using cerium ammonium nitrate as a surrogate. This set up used the thermal bead bath (Figure 3) atop two chill plates to cool the solutions, and used the custom fabricated stainless steel T-junction.

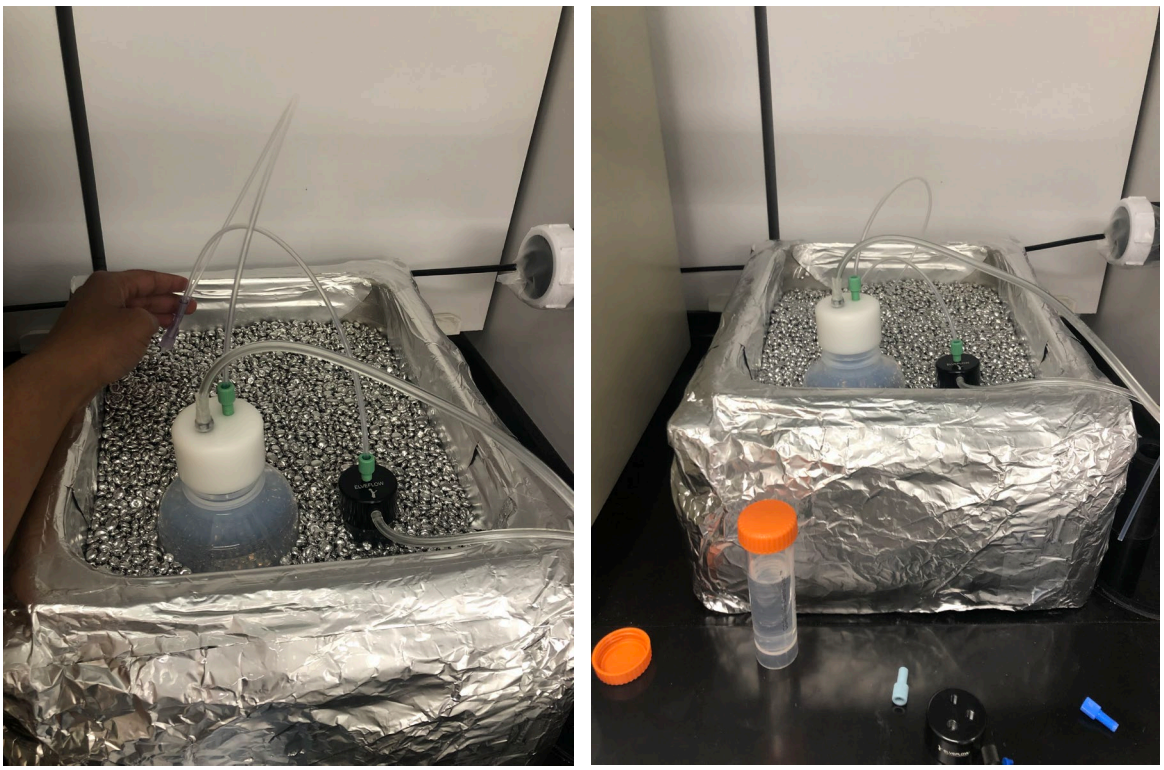

Figure 3: Aluminum thermal pellet chill bath with reagent reservoirs and fluidic system tubing connections.

Solution parameters were determined by referencing prior publications which produces cerium oxide microspheres. The test was successful in chilling the solutions, demonstrating the viability of the newly fabricated T-junction, and producing spheres in the desired size regime. Post processing included washing the spheres to remove process impurities, pressurized water treatment (PWT) and calcination. This post processing causes the spheres to shrink considerably. The resultant cerium oxide spheres were at the expected size and showed no evidence of degrading or bursting, indicating that the washing was successful, and the calcination was performed at appropriate ramp and dwell rates. The spheres, however were not as smooth as anticipated and showed some irregularities in the surface. This was not unexpected, as the formulation conditions were optimized for a different carrier solvent than was used in this test.

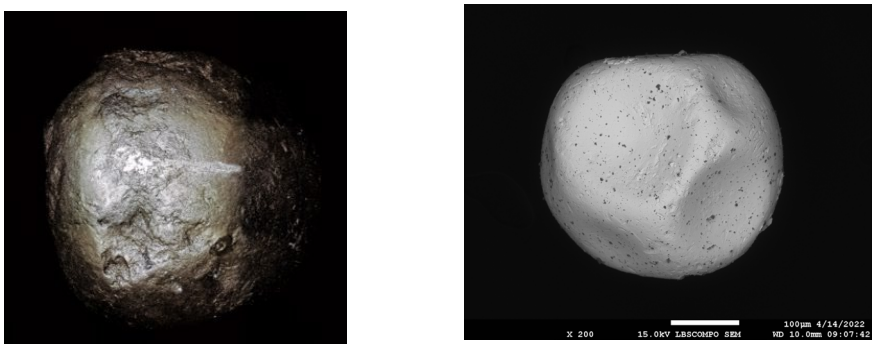

Figure 4: CLSM image of cerium oxide sphere after PWT (left) and SEM image of cerium oxide sphere after calcination.

It was suspected that these irregularities in sphere surface and lack of sphere homogeneity were due to spheres not warming sufficiently during the production process before being collected in the collection vessel. As such, the product line, or the channel downstream of the T-junction, was extended and coiled around a heated cylinder to warm the gelled spheres between the T-junction and collection vessel .

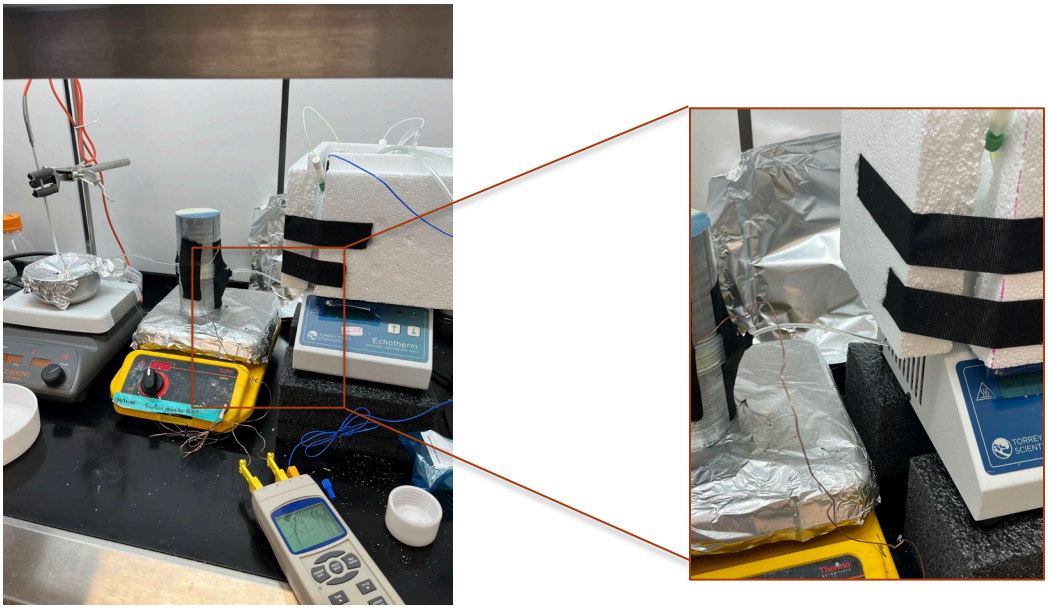

Figure 5: Non-radiological setup using aluminum block for chilling and heating the product line with an aluminum cylinder.

To verify reproducibility, the team tested the surrogate two additional times: first, using the old set up with the tray and the final time using the new aluminum block. A large batch of cerium oxide spheres were produced (Figure 6).

Figure 6: Cerium oxide spheres during non-rad surrogate testing

After the tests were successful, the capability was transferred to the Radiochemical Processing Laboratory (RPL).

Gelation studies for uranyl nitrate

Once the non-rad set-up was reproducibly tested, the capability was transferred and set up in RPL. Before transitioning from cerium feed solution to uranium feed solution, the uranium formulation had to be determined. To do so, gelation tests were performed to identify an acceptable reagent formulation and temperature for production.

Stock solution of acid deficient uranium nitrate (ADUN) was prepared by partially neutralizing uranyl nitrate with NH_4OH to give NO_3^-/U mol ratio of 1.6. The uranium concentration of the stock solution was 2.49 M. A stock solution of HMTA and urea was prepared in which each component concentration was 3.18 M.

The set-up consisted of a chill plate, hot/stir plate, and Al blocks test tube holders (Figure 7). During each experiment the temperature of the hot plate was controlled to 65°C.

Figure 7: Gelation Trials set up

The broth was prepared by mixing 5 mL of uranyl nitrate with 0.3279 g of 13.80 M of NH_4OH. Then, 992 μL aliquot of the ADUN solution was added to each pre-labeled test

tubes: R=1.6, 1.7, 1.8 and 2.0. To each test tube and aliquot (1.164-1.454) mL of the HMTA/urea stock solution in a chilled test tube. After allowing time for temperature equilibrium, each test tube was transferred to the stir/hot plate and a video was recorded to determine the gelation time. See Table 1.

Table 1. Uranium gelation trials with volumes, R-values, and gelation times

Trail no	Volume of HMTA/urea (µL)	R-Value	Gelation time (minutes)
1	582 (2 times)	1.6	1: 16
2	618 (2 times)	1.7	0:47
3	654 (2 times)	1.8	0:40
4	727 (2 times)	2.0	0:40

The gels were evaluated for hardness and inverted to see if any liquid was observed. All of them were considered good gels but R-values 1.8 and 2.0 were more homogenous in color and in hardness.

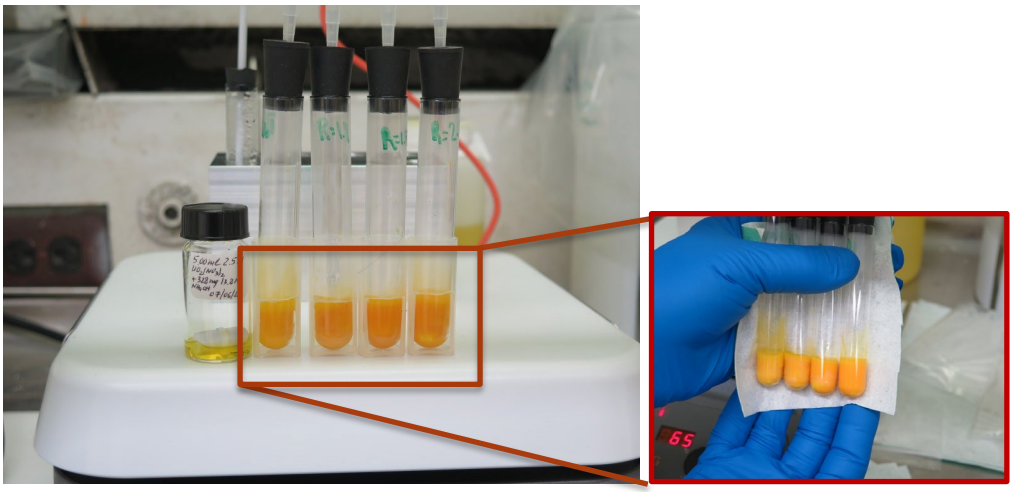

Figure 8: From left to right: ADUN solution, test tubes with R-values 1.6, 1.7, 1.8 and 2.0.

The selected formulation was R-value 1.8. A stability test was performed, and the broth solution was stable for more than 3 hours.

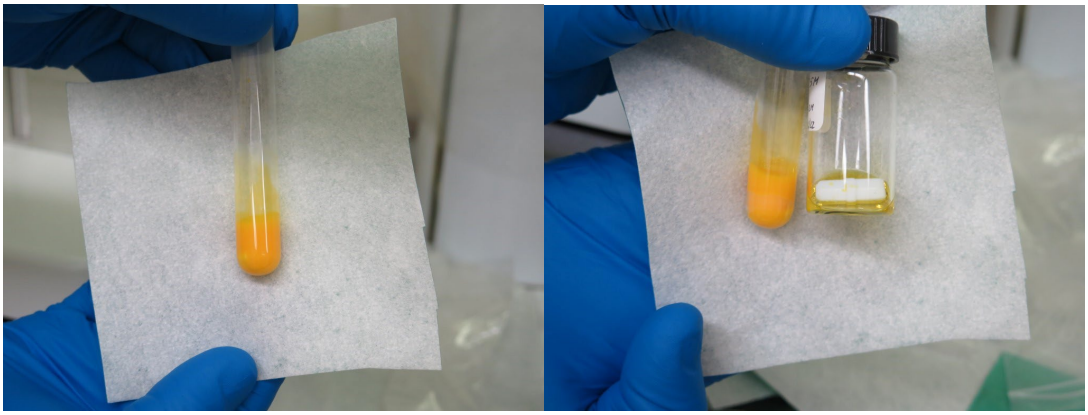

Figure 9: Uranium gelation trial showing R-value of 1.8, which was chosen for production test.

Once chosen, this feed formulation with R-value of 1.8 was used in two uranium sphere production runs in RPL.

Uranium Synthesis

After successful non-rad testing, and gelation trials were used to choose a uranium formulation, the sol-gel production rig was set up in RPL and two production runs were performed. The first run was a partial success. The set up was successful in keeping the solutions chilled, passing material through the T-junction, and finding operable pressures and unit configuration. However, the material produced was not spherical in the collection vial. The uranium droplets at the outlet seemed to distort as they traversed the product tubing and appeared to have frayed into irregular flattened shapes. Many factors were suspected to have contributed to this behavior, including the length and orientation of the outlet tubing, the flow parameters, and the chemical behavior of the feed solution itself.

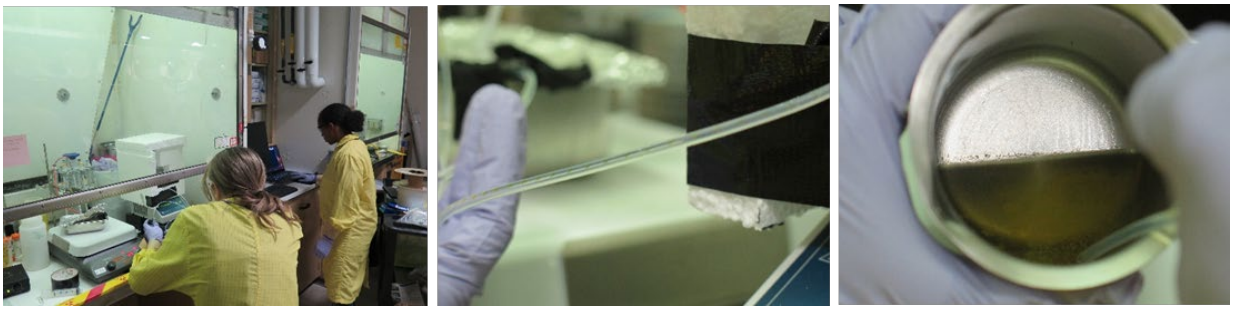

Figure 10: Testing the system with ADUN/HMTA/urea solution in TCE/Span 80.

The second test attempted to address a few of these suspicions by reducing the length of the outlet tubing, reducing the diameter of the tubing between the source reservoirs and the T-junction to better control the pressure, and more strictly monitor the

temperature in the collection vessel. Material flow in this new configuration was improved. Spheres were observed in the collection vessel alongside irregular shaped product. Further development is needed to optimize this system for producing millimeter diameter uranium spheres (uranium milli-spheres) to prepare precursor material for uranium fuel kernels for use in TRISO fuel.

Discussion

The undesirable behavior of the uranium feed solution after droplet formation was unexpected and additional investigation is necessary to confirm why the equipment did not perform as well for uranium as for cerium. Based on observations that the microspheres were spherical at the T-junction outlet but increasingly distorted as they proceeded through the outlet tubing, we presume that the challenge is related to differences between the flow conditions experienced by cerium and uranium feed solution microspheres. Potential sources of discrepancy in the behavior of the solutions include 1) different solution density, 2) different solution viscosity, 3) different interfacial tension between the feed solution and the forming fluid, and 4) different gelation speed, based on the feed solution parameters. Additionally, there may have been differences in the size of the microspheres produced during the cerium and uranium sphere-forming runs due to different flow settings needed to generate stable droplet production. Differences in wet droplet size in the outlet tubing could have resulted in different shear forces on the wet droplets due to friction forces near the tubing inner surfaces and the resulting impact on the radial velocity profile of the liquid inside the tubing.

Based on observations of how quickly the uranium droplets in the outlet line distorted, it's unlikely that a faster gelation time would entirely resolve the problem. Although uranium feed parameters are meant to result in a slower gelation time than the cerium feed parameters, neither gelation is rapid, particularly for larger sphere sizes.

Minor modifications to the equipment, particularly the outlet line, have potential to resolve the issues observed with uranium microsphere production. Changes to the feed solution parameters or choice of forming fluid may also influence the result. However, it's also possible that our observations reflect a tendency for flow-related forces to have a more substantial impact on spheres at the millifluidic scale than at the microfluidic scale.

Summary and Future Work

This project represented a first attempt to expand existing internal gelation using the sol-gel method capabilities at PNNL to produce uranium oxide TRISO fuel kernel material. The approach to this method first involved increasing the diameter of the sol-gel droplet producing chip from the microfluidic range to the millifluidic range. With radiation safety and space considerations in mind, this project also used this opportunity to develop a system in which to perform droplet production under a decreased footprint by replacing the freezer apparatus with a chill bath or chilled block design. Non-radiological surrogate testing was performed to ensure the system worked properly prior to engaging in radiological work using uranium nitrate in the feed material. Milestones achieved over the course of this project are summarized in the bulleted list below:

- Developed millifluidic droplet formation T-junction
- Reduced footprint for sphere production apparatus
- Demonstrated ability to produce mm diameter spheres with non-rad surrogate material in both thermal bead bath and chill block design
- Tested ability to produce uranium dioxide spheres with novel sphere production apparatus

Further optimization is needed to enhance this capability to reproducibly produce uniform, millimeter diameter uranium oxide spheres comparable to those produced using the cerium surrogate material.

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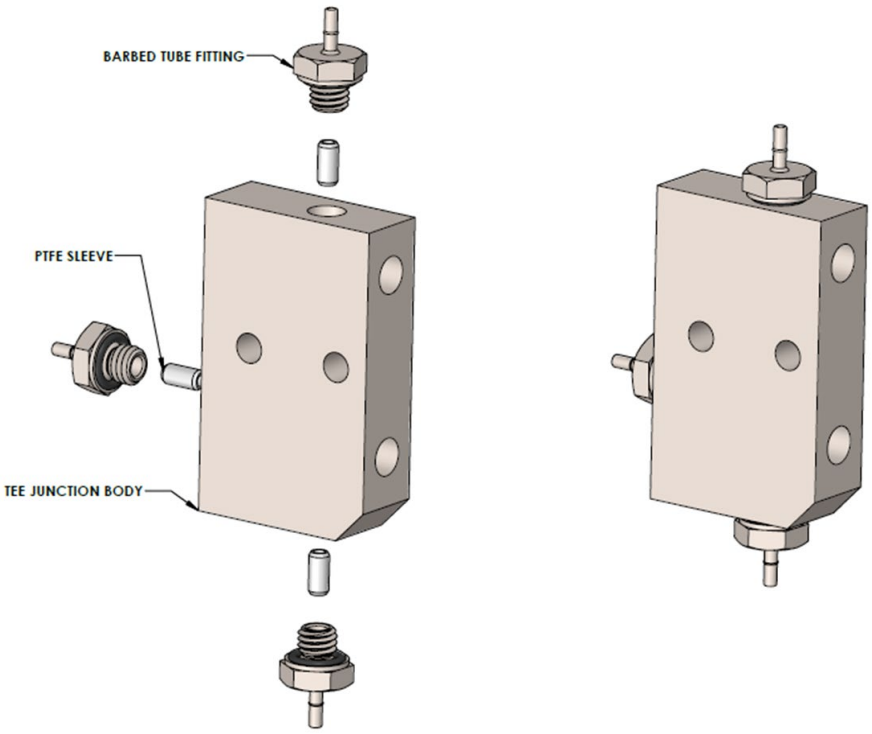
Appendix



Tee junction diagram

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