Production of depleted UO_2 fuel kernels for the NASA NCPS Program Cermet Fuels Development using an Ammonium Alginate process

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Introduction: Initial work performed at the Center for Space Nuclear Research (CSNR) in 2011 – 2012 examined the production of small (10-20 g) batches of microspheres composed of surrogates for uranium compounds using a sodium alginate drip casting process. This work adapted techniques that are similar to those used in pharmateuticals production. Specifically, CeO_2 and HfO microspheres were produced in batches with the final size ranges from 200 μm – 600 μm ± 50 μm-100 μm respectively. The drip-casting process is performed by the discharging of an water-alginate based slurry of the desired compound (e.g. depleted uranium dioxide) through an appropriately sized resonating nozzle. The resonance of the nozzle produces harmonic instabilities within the discharged slurry stream and results in the formation of discrete droplets. High droplet sphericity is achieved in free fall over a space of approximately 6 inches. The droplets, once spheroidized are allowed to submerge into a CaCl hardening solution where Calcium ions are rapidly exchanged from the hardening solution to cross link an alginate polymer chain. Dripcasting is performed within a purpose built HEPA filtered enclosure. The initial results achieved at the CSNR indicated that the drip casting process offered a potential for a significantly higher mass throughput rate over traditional sol-gel and internal gelation processes while maintaining low eccentricity and high overall sphericity. The small batch results also indicated potential throughput rates ranging between 100g/hr to ~450 g/hr (product diameter dependant) using a single drip casting nozzle.

For the scale up of the process to batch sizes of up to 500 grams, several challenges were initially anticipated and engineering approaches in addition to work control protocols were developed under contract to NASA Marshall Space Flight Center in support of the Nuclear Cryogenic Propulsion Stage (NCPS) program [1]. A selection of the technical challenges and their solutions are discussed.

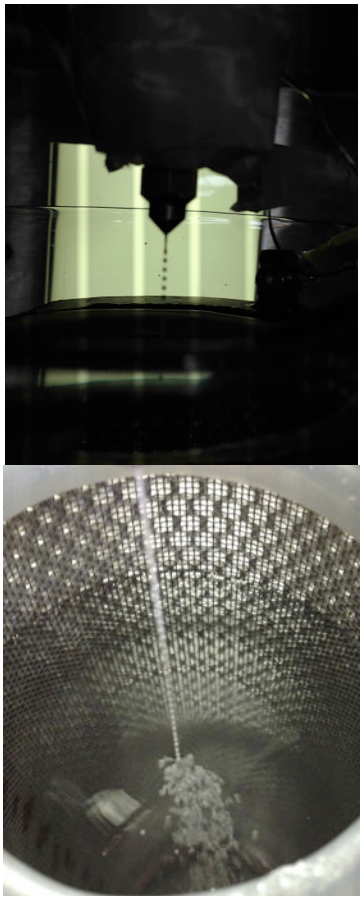

Figure 1: (Top) Dispensing and harmonic droplet formation of microspheres from a dripcasting nozzle. (Bottom) Submersion of

Conversion from a sodium alginate to an ammonium alginate based drip-casting process: While initial research at the CSNR was performed using food grade sodium alginate, it was understood that sodium contamination of the product microspheres would be undesirable for NTR fuel research applications due to sodium activation. Therefore, by changing the alginate scaffold used to support the structure of the microspheres in their "green" state to an ammonium alginate, Na contamination can be eliminated. The conversion to ammonium alginate was not anticipated to be significantly challenging, however when coupled to the pH change attributed to the uranium oxide slurry chemistry, significant experimental effort for stable slurry recipe development was required. Specifically

several small batches and several larger (100 g dUO_2) batches of depleted uranium oxide suspension slurries had to be produced prior to successful use of ammonium alginate and refinement of the final recipe that has been adopted. Segregation of ammonium alginate powder components occurred during transit from the vendor to the CSNR which led to inconsistent results initially, thus consistent results were obtained after re-mixing the alginate powders prior to use.

Mixing of large batch feed solutions: Consistent small batches were initially obtained via a combination of heating and magnetic stirring of the water-ammonium alginate prior to the heated magnetic stirring of uranium oxide powders into the solution. It was found that as batches were enlarged into greater than 100 g dUO_2, traditional magnetic stir equipment was incapable of adequately agitating and maintaining a stable suspension of the dense dUO_2 powder granules within the ammonium alginate solution. In order to rectify these challenges, three engineering solutions were developed. Firstly, a rare earth magnetic stirrer / hot plate was acquired and rare earth stir bars were purchased to ensure sufficient strength was available to counter act the initial resistance experienced when transitioning to the mixing of dUO_2 powder. Secondly, small additions of an ammonium polyacrylate dispersant was added to the recipe incrementally in experimental batches until a more stable and uniformly mixed solution was achieved. The addition of ammonium polyacrylate presents a negligible impact upon the overall purity of the product microspheres since this is broken down into ammonia, CO and CO_2, and are out gassed during calcining and final sintering. Finally, a large volume hermetically sealed feed vessel with self-sealing high-pressure connections was designed and constructed. This feed vessel is capable of handling up to 6 liters of feed solution for batches up to 500 g. This feed vessel is loaded with dry powder in an inert atmosphere glovebox and is transferred to a radiological fume hood for filling with the ammonium alginate solution.

Drying of microspheres: In their drip cast "green" state, microspheres are composed of approximately 96 % water and alginate scaffold by volume. The water content is removed to harden the product by drying within an inert atmosphere glovebox. Once dried, the microspheres are approximately 25 % of their "green" state volume. While small batches of microspheres were successfully dried within aluminum foil weighing dishes, drying larger batches in this same manner proved unsuccessful. Specifically, the dUO_2 microspheres formed rigid agglomerates that were unable to be broken up without damaging the morphology of the individual microspheres. Therefore, an experimental design and construction of a cylindrical rotary drier was undertaken at the CSNR. This design allowed free flowing of the wet/"green" microspheres between agitating paddles while drying. Thus, reducing the opportunity for agglomerate formation during the drying process. The main cylindrical body of the drier was designed to serve as both a basket for the collection of the drip cast microspheres and as a vented tumbler. The cylindrical basket was manufactured using a 316 stainless steel frame surrounded by multiple layers of stainless steel mesh with a minimum pore size of 75 μm. The internal agitation paddles were manufactured within an internal removable frame using PLA plastic. These PLA components in addition to a chassis and end cap for the drier were manufactured using a 3D printing technique. A low voltage high-torque motor was installed into the drier chassis and linked to a drive & support axel via a double U-joint. A second, non-driven axel is used to support the opposite underside of the rotary drier basket. The assembled rotary drier is operated within a lined spill tray as a precautionary engineering control to mitigate contamination of the fume hood.

Calcining and sintering of microspheres: Following drying, the microspheres are transferred to a box furnace housed within an inert atmosphere glovebox. The microspheres are calcined at 600 °C and sintered to final diameter under a flow of argon at 1550 °C. While surrogate work was initially performed inside a small tube furnace, the work with large batches of dUO_2 microspheres is only accommodated within a box furnace. A multi-layered Zirconia crucible was designed by the CSNR and manufactured by Astromet Inc. to sinter each batch of microspheres.

Summary: By undertaking experimental development, the CSNR has been able to refine the process of ammonium alginate drip casting of depleted uranium oxide microspheres to allow for large batch production. With the process refined, the CSNR is now in production of batches of material that will fulfill the contracted order of dUO_2 microspheres for the NCPS program.

References:

[1] Houts M. G., Borowski S. K., George J. A., et al, "NUCLEAR CRYOGENIC PROPULSION STAGE" *Nuclear and Emerging Technologies for Space conference* (2012), Abstract #3093.