A Status Update on the Production of Cerium Oxide Microspheres for Space Nuclear Power Applications

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Introduction: Internal gelation sol-gel methods have been modified for processing cerium dioxide and are being analyzed at the University of Michigan for their usefulness in producing space nuclear power fuels. As a surrogate for plutonium-238 dioxide ($^{238}PuO_2$) used in radioisotope thermoelectric generators (RTGs), cerium-bearing feed solutions were used to fabricate monodisperse microspheres of cerium dioxide (CeO_2). While previous work focused on identifying ideal feed and gelation parameters to ensure gelation in the forming column and minimize cracking, a significant effort was made to increase throughput to approximately 10g of sintered cerium oxide microspheres per run for studies on scale-up. Spheres produced during this phase were encapsulated in a tungsten matrix via spark plasma sintering (SPS) in collaboration with the Center for Space Nuclear Research. Larger batches of cerium oxide were also produced for determination of density and refining washing methods. Increased throughput also enabled more recent work on the determination of trace element and carbon impurity levels in sintered spheres as well as the production of monodisperse spheres in the 50-200μm diameter range.

Background: RTGs produced in the United States for the past few decades have all used pure plutonium-238 oxide (PPO) pellets made by a process which requires the ball milling of precipitated $^{238}PuO_2$ powders to a mass-median diameter less than a micron. The ball-milling step is required due to the undesirable morphologies of the plutonium precipitates which generally form rosette and lathe shapes and are unsuitable for directly pressing into pellets [1]. Fine, ball-milled powders can be cold pressed, granulated, thermally seasoned, blended, and pressed into pellets for sintering. However, $^{238}PuO_2$ fines have proven to be an extremely hazardous material prone to contaminating equipment and facilities. The high alpha activity of $^{238}PuO_2$ accelerates corrosion, causes radiolytic degradation, and helps mobilize small fragments. [2, 3]. These distributed fines, sometimes called fleas, are also propelled by energetic alpha decay and can migrate through gloves, seals, and HEPA filters [2, 3].

While optimizing the precipitation process to generate particles that can be used directly for pellet pressing would be advantageous, previous attempts have had limited success. Trials to vary the conditions of oxalate precipitation to control the precipitate morphology in 1982 at Savannah River attempting to "grow" larger rosettes as agglomerates of 2-4μm crystals proved to be sensitive to processing conditions and yielded a high-surface-area product with varying sizes [4]. A 2008 report from the Idaho National Laboratory suggested sol-gel methods may be an attractive method for producing plutonium oxide pellets without the need for powder processing, but indicated that further development would be needed to assess its applicability [1]. Sol-gel methods are attractive because they would keep the radioisotope dissolved in solution and can yield symmetric microspheres suitable for encapsulating into an inert matrix or for directly pressing into pellets. Sol-gel feed spheres are large enough that they do not pose an inhalation hazard and gelation parameters can be tuned to produce spheres with desirable sizes and densities for pressing into pellets.

Methodology: Internal gelation sol-gel methods yield soft, gelled microspheres made from chilled solutions of cerium nitrate, hexamine (HMTA), and urea. Gelled spheres are opaque, contain water and excess reactants, and are coated with oil from the forming column, where they are gelled in hot silicone oil. After gelling, spheres are collected, aged in hot silicone oil, and then washed to remove the oil and excess reactants. Trichloroethylene, isopropyl alcohol, and ammonium hydroxide are used to wash the spheres of oil and most of the excess HMTA, urea, and reaction products. After washing, spheres are loaded into a vessel and undergo a pressurized water treatment to remove additional organic impurities.

Once impurities have been washed from the spheres, they are dried and sintered. Microspheres are typically air dried for several days at ambient temperature to accommodate approximately 200% reduction in diameter as water slowly evolves. An additional drying step to remove any remaining water is performed prior to sintering.

In the gelation column, spheres are formed at the tip of a small-gauge needle and their diameter is controlled using various needle sizes or by changing feed flow rates. A two-fluid nozzle and conditioners to remove bubbles formed in the silicone oil were employed to achieve excellent monodispersity.

Results: Scale-up efforts have resulted in approximately ten-fold increase in system throughput, allowing the production of approximately 10g of 100μm

cerium dioxide microspheres for a 4-5 hour run. The capability to produce larger batch sizes has allowed for improved analysis of spheres and testing the effectiveness of various washing techniques using a common batch of gelled spheres. This eliminated any concerns regarding batch-to-batch variations on further testing of washing methods. Similarly, densities were measured on the same batch of spheres and compared as a function of heat treatments.

Nearly 40 grams of sintered cerium dioxide microspheres were produced for SPS sintering studies and used to produce two inert matrix pellets with tungsten metal. These spheres had diameters near 100µm and were very similar to those shown in Figure 1. Pellets were sintered, sectioned, and polished for observation with scanning electron microscopy.

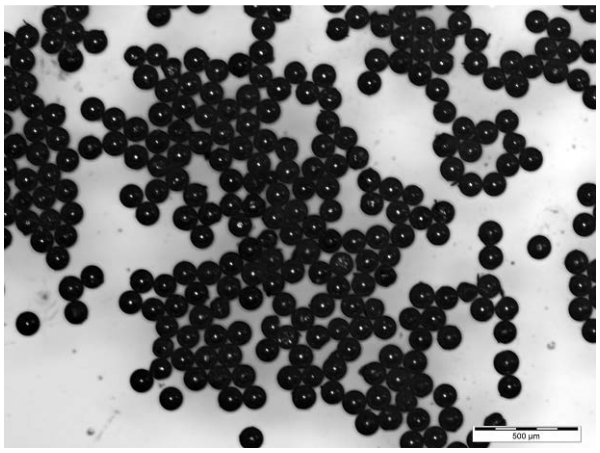

Figure 1: An optical image of un-sieved cerium dioxide microspheres produced with diameters near 100µm.

A high purity cerium feed solution was used to make a large batch of spheres for comparative impurity studies. A variety of wash treatments were assessed based on their effectiveness at removing carbon, nitrogen, and hydrogen. Additionally, spheres washed by the preferred method were subjected to glow discharge mass spectroscopy for analysis of trace impurities. The results of these wash studies and resulting impurity levels will be the subject of an upcoming publication.

An optical microscope and sizing software is currently being utilized to determine the monodispersity of several batches of microspheres prepared using different needles and flow rates. These results will be the subject of an upcoming publication as they will provide a better understanding of what sphere sizes are possible and their corresponding degree of monodispersity. To achieve this, spheres are mounted to a glass slide with a low packing density so their diameter and sphericity can be recorded using a contrast-based post-processing method. A two-dimensional scanning feature on the microscope allows for large areas containing spheres to be imaged and hundreds of spheres to be analyzed at a time.

Conclusions: Scale-up of cerium oxide sol-gel equipment has enabled several avenues of research to help determine the applicability of internal gelation methods for producing plutonium pellets without the generation of hazardous fines. Larger batches have enabled the pressing of inert matrix pellets, comparisons of density vs. heat treatment, improvement of washing methods, and analysis of sphere sizing capability.

References:

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