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THORIA-BASED CERMET NUCLEAR FUEL: SINTERED MICROSPHERE FABRICATION BY SPRAY DRYING

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ABSTRACT

Cermet nuclear fuels have been demonstrated to have significant potential to enhance fuel performance because of low internal fuel temperatures and low stored energy. The combination of these benefits with the inherent proliferation resistance, high burnup capability, and favorable neutronic properties of the thorium fuel cycle produces intriguing options for advanced nuclear fuel cycles. This paper describes aspects of a Nuclear Energy Research Initiative (NERI) project with two primary goals: (1) Evaluate the feasibility of implementing the thorium fuel cycle in existing or advanced reactors using a zirconium-matrix cermet fuel, and (2) Develop enabling technologies required for the economic application of this new fuel form.

Spray drying is a physical process of *granulating* fine powders that is used widely in the chemical, pharmaceutical, ceramic, and food industries. It is generally used to produce flowable fine powders. Occasionally it is used to fabricate sintered bodies like cemented carbides, but it has not, heretofore, been used to produce sintered microspheres. As a physical process, it can be adapted to many powder types and mixtures and thus, has appeal for nuclear fuels and waste forms of various compositions. It also permits easy recycling of process "wastes" and minimal chemical waste streams that can arise in chemical sol/gel processing. On the other hand, for radioactive powders, it presents safety challenges for processing these materials in powder form and in achieving microspheres of high density and perfection.

INTRODUCTION

This paper is one of three in this proceedings describing a 1999 NERI project designed to develop the potential and demonstrate the feasibility of a $(Th,U)O_2$ cermet fuel [1,2]. The fundamental nuclear and thermal modeling is described here and the basic fuel concept and experimental cermet fabrication method[1] and the developmental fuel microsphere fabrication method[2] will be described in the other papers.

The principal goal of this project is to demonstrate the feasibility of a metal-matrix dispersion, or cermet, fuel comprising $(Th,U)O_2$ microspheres in a zirconium matrix that can achieve high burnup and subsequently be directly disposed as nuclear waste. The potential benefits that may be gained with this fuel include high actinide burnup, inherent proliferation resistance, improved irradiation stability due to low internal fuel temperatures, low fuel failure rate, and minimal waste treatment. The cermet fuel concept is shown schematically in Fig. 1. The fuel "meat" is a fine dispersion of $(Th,U)O_2$ microspheres that have a theoretical density between 70 and 99% and a uranium enrichment below 20% U-235. Nominal values for the microsphere diameter, ThO_2-to-UO_2 ratio, fuel-to-matrix ratio, and U-235 enrichment were selected as ~50 µm, 50:50, 50:50, and ~19.5%, respectively, to provide guidance for

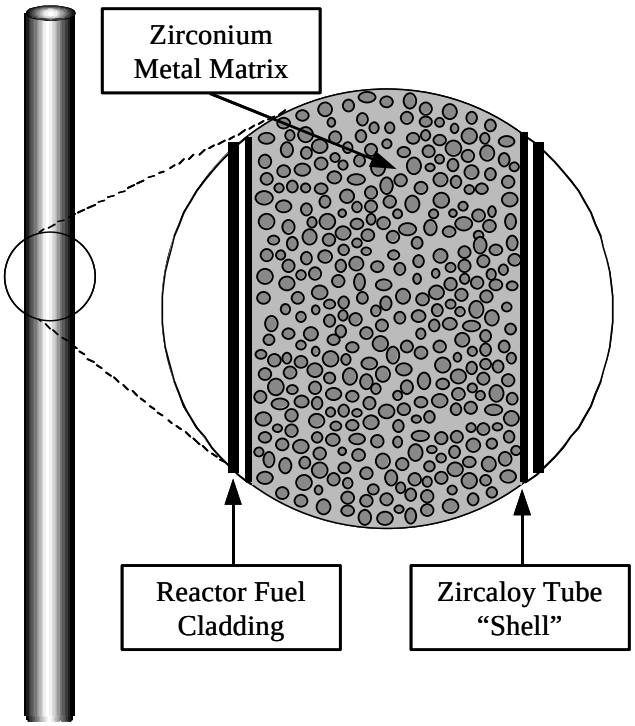

Figure 1. Concept Sketch for (Th,U)O_2 Dispersion Fuel Pin.

the calculational and experimental activities carried out within the project [3].

We have developed a laboratory-scale facility for producing spray-dried microspheres of urania/thoria for dispersion fuel fabrication. Atomization is achieved using a two-fluid nozzle spray head; the droplets so formed are dried by heated counterflow air currents in a spray drying chamber. The microspheres that are produced are collected in a cyclone separator. The fines are first gravity-trapped, then passed through a prefilter before being removed in HEPA filter arrays. The major challenge in this process for microsphere production is to densify the drying droplets to high green density without forming hollow or broken spheres. This requires high slurry solids loading and high viscosity during droplet formation, but particle/particle re-arrangements and densification occur during drying. Thus, particle characteristics, surface chemistry, and charge state are very important. We measured the powder size distributions before and after ball-milling, and we made viscosity measurements of U,ThO_2 slurries as a function of solids loading, pH, and organic additives.

Our initial results show powder agglomeration even after wet ball-milling. The viscosity exhibits strong shear-thinning behavior, followed by Newtonian behavior at high shear rates. At present, only alumina simulant powders have been successfully spray dried using an alternate rotary atomizer to produce the droplets. These spheres were then successfully sintered and remained isolated. However, the small size of the sintered microspheres led us to develop the two-fluid nozzle approach.

MATERIALS AND CHARACTERIZATION

Detailed formal procedures and methods for characterizing and processing UO_2/ThO_2 mixtures have been established and approved by the Purdue Radiological Control Committee for (1) ball-milling, (2) viscosity and rheology measurements on slurries, (3) sintering, (4) co-precipitation, (5) particle size analysis using laser scattering, (6) surface area analysis using the BET technique, (7) X-ray diffraction, (8) stoichiometry measurement, and (9) ceramographic preparation. The spray drying procedures represented a particular challenge since they deal with the handling of loose powders. The starting UO_2 and ThO_2 powders were analyzed to determine their chemical purity with respect to "nuclear grade" purity requirements. Particle size distributions were measured for various source powders and indicated that this powder might be satisfactory.

VISCOSITY / RHEOLOGY MEASUREMENTS

For spray drying, it is important to be able to spray the maximum powder "loading" or volume fraction of solids to achieve a maximum density. However, the loading is limited by the maximum sprayable viscosity, which is typically ~1000 to 2000 centipoise (cP). To minimize the viscosity, the surface charge on the particles at the slipping plane, or the Zeta Potential (ZP), may be increased by appropriate pH adjustment. Usually, the minimum viscosity occurs near the maximum ZP. This behavior is seen in pure UO_2 at a pH of 3 and in ThO_2 at a pH of 4[4]. In a mixed powder system of UO_2 and ThO_2, we have selected the maximum ZP for the majority powder in the mix.

A second method of inhibiting particle/particle bonding and agglomeration is to use organic polymers that attach to the particle surfaces and provide stearic constraints to local bonding[5]. Thus, slurries for spray drying often contain several organics to serve as deflocculants, lubricants, dispersing agents and binders.

We have measured the viscosity of various slurries using a Haake RS-1 Rheometer/Viscometer. This instrument allows the examination of very low strain rate behavior (rheology) for a slurry that is involved in the densification of the particles in a droplet as water is removed. It also allows for cooling the slurry so as to minimize evaporation during measurement which can be a serious problem for dense slurries.

The pH for some of the slurries during initial tests described below was adjusted to 8.0 using NH_4OH addition to highly purified water following Dusek and White[6]. The slurries were sonicated for 30 min using an ultrasonic bath. However, it was evident that the thoria and especially urania dispersions were not stable, even for short periods, and in some cases caused the shear stresses to become too large for the RS-1 to operate at the higher particle loadings. All measurements were made using the 35mm/5° cone/plate sensors with increasing applied shear rates. These initial measurements were made without ball milling. (Ultimately, scanning electron microscopy and particle size measurements indicated that ball milling was necessary to break up agglomerates.)

Figure 2 shows the results of the ofshear stress and viscosity for UO_2 at a 15 vol % loading and a pH of 8. It is seen that there is marked "shear-thinning" behavior over this range of shear rates, indicating strongly non-Newtonian behavior, especially at low shear rates, which is probably related to flocculation in the slurry. The very high shear stresses at low shear rates can also lead to problems of occlusion of the peristaltic pump feed system during spray drying. Figure 2 also shows that if the same slurry is measured a second time, the viscosities are considerably lower. Figure 3 shows another sample of UO_2, at the same solids loading, with even stronger shear thinning behavior than seen in Fig. 2.

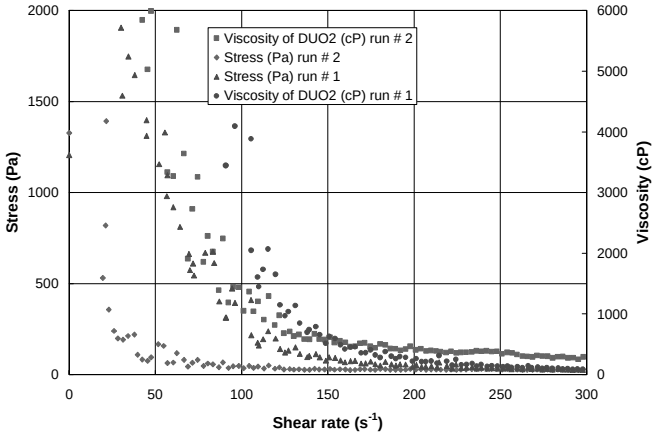

Figure 2. Shear Stress and Viscosity in Urania (UO_2) Slurries at 15 Vol % Loading and pH 8 for Successive Trials.

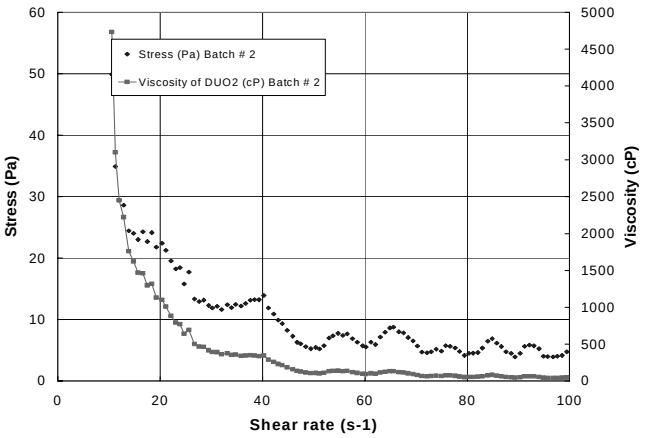

Figure 3. Shear Stress and Viscosity in Urania (UO_2) Slurries at 15 Vol % Loading and pH 8 for an Independent Batch.

Summarizing the data for UO_2 at 12, 15 and 17.5% vol % loadings for the conditions investigated, the viscosity at a shear rate of 200 s^{-1} was 3, 60 and 300 cP, respectively. The latter viscosity approaches what might be spray dried, but we feel that we should attempt to increase the powder loading in order to obtain high green and sinter densities.

Thoria dispersions were somewhat better behaved, as shown in Fig. 4. Above a shear rate of ~60 s^{-1}, the slurry approaches Newtonian behavior. We therefore focused on the maximum solids loading that can be achieved with commercial thoria and urania powders, their mixtures, and powders of our coprecipitated 70 wt % thoria, 30 wt % urania. In order to study the variation of viscosity of the slurry with pH, slurries of pure ThO_2 and UO_2 and coprecipitated powders were prepared by mixing the powders with aqueous hydrochloric acid solutions of pHs from 1 to 5 and sonicating with an ultrasonic bath for 30 min.

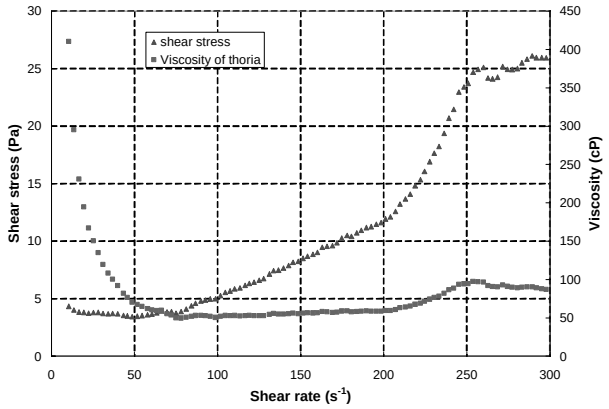

Figure 4. Viscosity of Thoria (ThO_2) Slurries at 15 Volume Percent Loading as a Function of Shear Rate.

In order to measure the viscosity, the slurry must be "flowable" to spread it evenly over the specimen plate of our viscometer. No flowable slurries of pure urania without additives could be prepared above a maximum solids loading of 17.5 vol %. However, flowable slurries of pure thoria and of the coprecipitated $(U,Th)O_2$ powders contained as much as 20 and 23 vol % solids loading, respectively. The pH did not appear to affect the flowability to any noticeable extent. This again indicates that UO_2 tends to agglomerate.

Figure 5 shows the results for pure UO_2 slurries as a function of shear rate at three values of pH. The shear rate was ramped up at a constant rate from ~$10s^{-1}$ to $300s^{-1}$, held for 30s, and ramped down. At pH = 3 the solids loading was 16.5 vol % as compared with the loading of 14.6 and 15.3 at pHs of 1 and 5, respectively. The measured viscosities appear to be dominated by solids, loading since we would expect the viscosity to be a minimum at pH = 3 at the maximum ZP. All slurries showed strong initial shear thinning for all values of pH. This indicates strongly non-Newtonian behavior at low shear rates, which is probably related to flocculation in the slurry. At higher shear rates the behavior became Newtonian with viscosities approaching that for water. It should be noted that the initial data is at a very low but finite value of shear rate. For non-flowable slurries, the initial torque values sometimes exceeded the torque limitations of the viscometer.

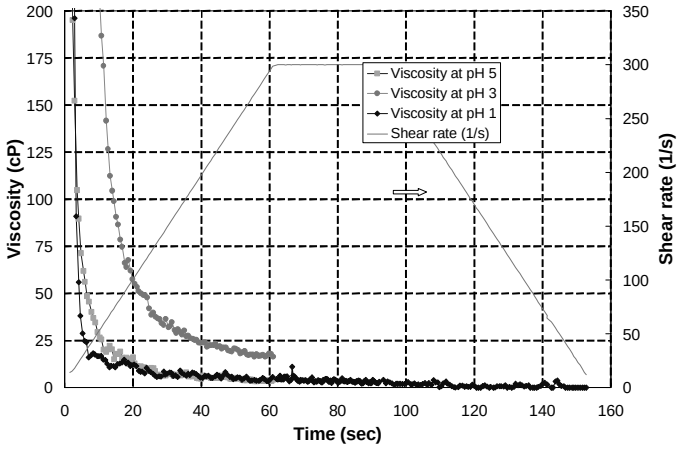

Figure 5. Viscosity of Urania (UO_2) as a Function of pH and Imposed Shear Rate.

An important feature shown in Fig. 5 is that the flow behavior of UO_2 appears to be non-reversible. As the shear rate decreased back to zero, the viscosity did not increase, but remained at the low Newtonian value. This might indicate that once agglomerates had been broken up, they did not reform readily. However, the slurry was always being sheared, even at the lowest shear rates shown.

Figure 6 shows similar shear-rate-cycling experiments for pure thoria at 20 vol % solids loading and a wider pH range. In this case, the shear rate was cycled beyond one cycle to examine the question of reversibility in more detail. Similar initial shear thinning behavior was observed, but in this case the shear-thinning behavior appeared to be reversible. This behavior is in contrast with our observation that subsequent ramps with the same powder often resulted in lower viscosities on subsequent runs. In view of the scatter in the data, there was no obvious change of viscosity with pH, but at the minimum viscosity, the pH 3 slurry appeared to have the highest viscosity of 3 cP for a very high solids loading of 21.2 vol %.

Figure 7 shows the behavior of the coprecipitated powder during shear-rate-cycling similar to that done on pure thoria. Again the shear-thinning behavior seems reversible, but in this case the pH 1 slurry had the highest viscosity of 3 cP.

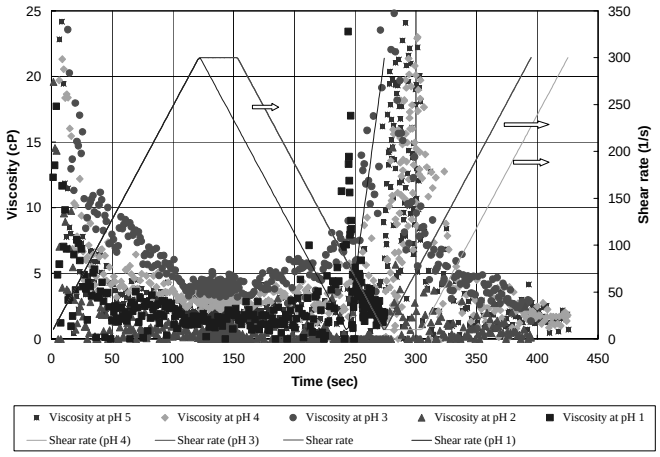

Figure 6. Viscosity of Thoria (ThO_2) as a Function of pH and Imposed Shear Rate.

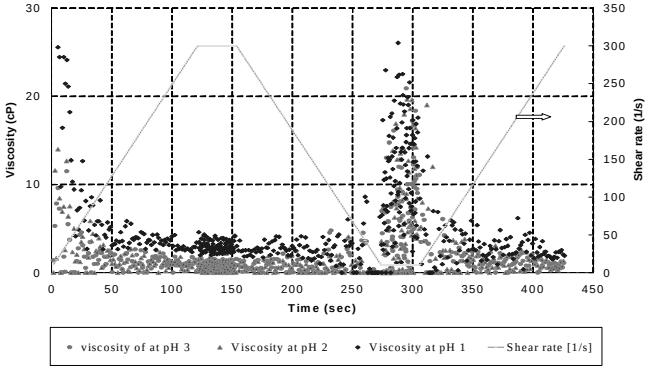

Figure 7. Viscosity of Coprecipitated $(U_{0.3},Th_{0.7})O_2$ as a Function of pH and Imposed Shear Rate.

One question needs to be raised about the viscosity measurements, however, that became more evident in the slurry flow tests that we have conducted: are the slurries stable? We have already mentioned the problem of water evaporation, which we attempt to control by lowering the plate temperature to 15°C using a Peltier plate and surrounding the cone and plate with a cup to prevent evaporation and the spread of contamination. A second problem concerns settling of the powders. Although the liquid meniscus that is measured is quite thin, there still may be settling of the larger agglomerates. The low viscosities that were measured might indicate that some settling is occurring. On the other hand, the reversibility of the viscosity during strain rate cycling suggests that it may not be important. One final note of clarification is that all of the viscosity curves shown here were obtained without calibration of the viscometer against known standards. All measurements discussed here should be considered qualitative only, but calibration efforts are underway to enable quantitative measurements that will assist in sorting out the unusual behavior at low shear rates.

We have also conducted semi-quantitive flow tests of $(Th,U)O_2$ slurries using our peristaltic pump that is intended for spray drying and simulating the restriction of the two-fluid nozzle with a hypodermic syringe needle. We initially combined the coprecipitated powders of solids loading from 10 to 20 vol % with aqueous solutions of hydrochloric acid of pH=3 and mixed in an ultrasonic bath for five minutes, as was done for the viscosity measurements. We then attempted to pump from the transfer jar with the peristaltic pump while the jar was immersed in the ultrasonic bath. However, in larger quantities of slurries used for this test, the slurries were clearly not stable against settling. A 70/30 mix of commercial powders was then ball-milled for 24 h with 1 vol % polyethylene glycol; it was sufficiently stable, at least for the period of time it takes to make a spray drying run.

In the next year, the important role of organic and inorganic additives will be examined to determine their impact on the viscosity/shear rate behavior, settling behavior, and binding behavior in our next set of experiments. Some typical organics used in spray drying have been selected for trial, as well as some more advanced compounds.

SPRAY DRYING SYSTEM

The spray drying system, shown schematically in Fig. 8, is a commercial, laboratory-scale spray dryer made by Niro Inc. It

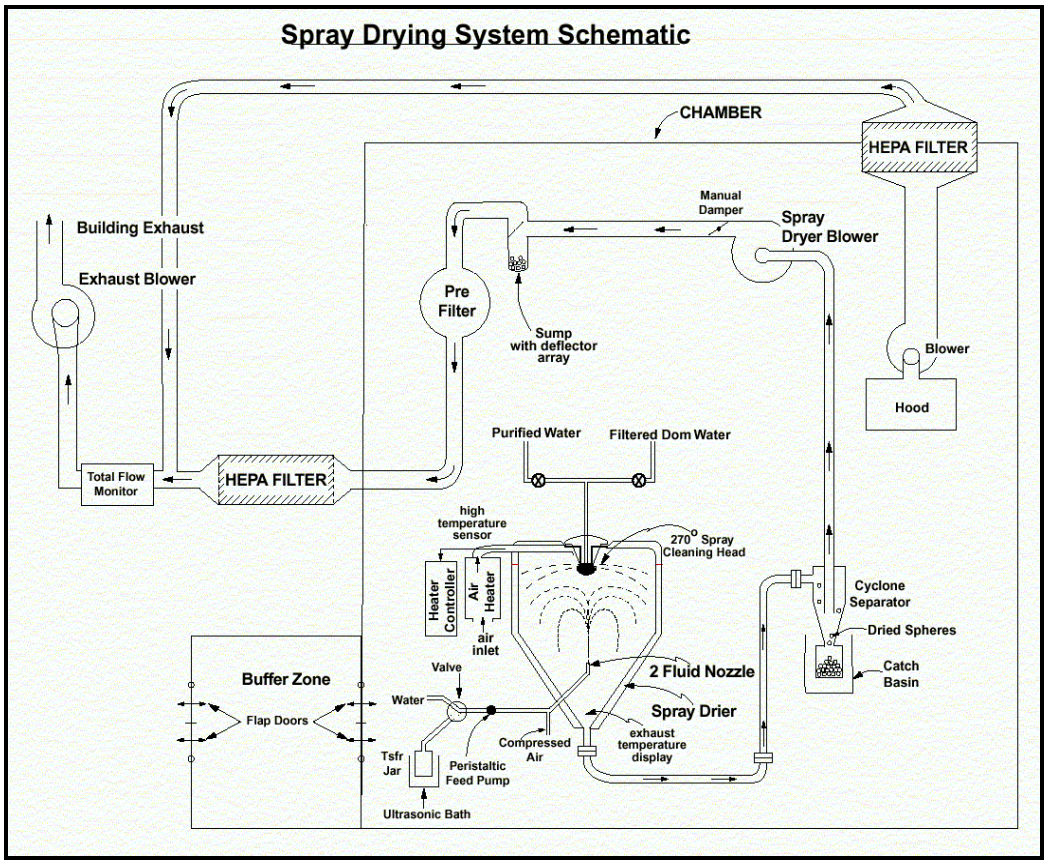

Figure 8. Schematic Diagram of the $(Th,U)O_2$ Microsphere Spray Drying System.

consists of a funnel-shaped chamber approximately 1 m in diameter with an insulated stainless steel double wall. To increase particle sizes, we added a vessel extension at the top, also fabricated by Niro and shown more clearly in the photograph of our facility, Fig. 9. The extension has viewing windows, which aid considerably in the operation of the system. The system also has the important safety feature for handling radioactive powders: it operates at negative pressures because of the location of the spray dryer blower at the exit. The exit is fed to a collection sump with a deflector array that is intended to trap the larger particles, through a high-temperature polyester Consler Prefilter with 98% efficiency down to 1 micron, and finally through typical HEPA filters with 99.97 % efficiency for 0.3-micron particles. As an additional safety precaution, the pressure in the exhaust line of the spray dryer (after the manual damper) is sensed by a photohelic gauge which turns off the spray dryer heater and blower motor if pressures above atmospheric are detected.

Figure 9. Photograph of the Spray Drying System Showing the Chamber and HEPA Filtration System.

Figure 10. Photograph of the Two-Fluid Nozzle Assembly.

The two fluid nozzle assembly is shown in Fig. 10. The slurry is propelled as it is being fed by the peristaltic pump by compressed air at ~40 psi. Since there was no compressed air source available, we purchased a compressor capable of operating the rotary atomizer or the two fluid nozzle.

Spray-dryed spheres are separated in the cyclone separator and collected in the sampling jar. Typically about 10% of the batch passes beyond the cyclone separator as fines. A major advantage of the spray-drying process, which is a physical granulation process, is that it does not generate waste streams that occur in chemical or sol/gel granulation methods. The material trapped in the sump and even in the prefilter can be recovered and recycled with no further treatment. For larger batch sizes, most prefilters have a reverse pressure pulse capability for cleaning the filter and recuperating the powders. As seen in Fig. 8, inlet air passes through a 6 KVA heater; the heated air enters the vessel at the top and is eventually exhausted out the bottom with the dried spheres.

There are two methods commonly used to generate droplets of slurry. Last year, we reported our preliminary results on alumina spray drying using an air turbine driven “rotary atomizer”, the first method. Slurries are gravity-fed to a 30,000 rpm wheel, which ejects streams of slurry that break up into droplets by Rayleigh instability. Our experience with this approach was mixed: with alumina, a relatively large fraction of slurry reached the wall and was difficult to remove. Nevertheless, we were successful in obtaining alumina spray dryed powders and sintering them to spheres of ~30 microns.

We subsequently chose the second approach of droplet formation which involves a so-called “two fluid nozzle”. Compressed air and slurry are simultaneously fed to a nozzle at the bottom of the vessel that ejects droplets in an upward direction, which gives the droplets greater residence time and counter-flow in part of their trajectory to effect more complete drying of the droplets and less momentum toward the wall causing them to stick. Additionally there is a larger final microsphere size with this approach.

Because of the very low DAC for thorium of 5E-13 μCi/ml, special steps were taken to limit the spread of airborne contamination. The entire system was enclosed in an isolation chamber kept at negative pressure with respect to the surrounding room by the use of a separate hood and blower system with an independent HEPA filter. The hood was fabricated to aid in cleaning operations especially for the two-fluid nozzle. The chamber also has a buffer zone with monitors and other safety equipment.

The method of cleaning the spray dryer after a run was particularly important because of the possibility of airborne powders during any manual cleaning operation. As seen in

Fig. 11, the chamber is cleaned by a special tank-cleaning spray head that is first fed ~6 gal filtered domestic water at 40 psi, then ~1gal DI or distilled rinse water using a diaphragm pump. After each wash, the water that collects at the bottom of the vessel is pumped to a carboy using a rubber hose that is fed to the bottom of the vessel exhaust line. This procedure is intended to avoid removing the top of the vessel, which is usually done for cleaning.

REFERENCES

[1] S.M.McDeavitt, T.J. Downar, S. Revankar, A.A. Solomon, M. C. Hash, and A. S. Hebden "Thoria-Based Cermet Nuclear Fuel: Cermet Fabrication and Behavior Estimates," 10th International Conference on Nuclear Engineering, Arlington, VA, April 14-18, 2002, Paper No. ICONE10-22317.

[2] T.J. Downar, S.M. McDeavitt, T.K. Kim, S. Revankar, and A.A. Solomon, "Thoria-Based Cermet Nuclear Fuel: Neutronics Fuel Design and Fuel Cycle Analysis, 10th International Conference on Nuclear Engineering, Arlington, VA, April 14-18, 2002, Paper No. ICONE10-22305.

[3] S.M. McDeavitt, T.J. Downar, M.C. Hash, S. Revankar, A.A. Solomon, Y. Xu, A.S. Hebden, W. Robey, and J. Xiu, "Development of a Mixed-Oxide Cermet Dispersion Fuel Using $(Th,U)O_2$ in a Zirconium Metal-Matrix," ANS Transactions 83 (2000) 205.

[4] P.J. Anderson and P. Murray, Zeta Potentials in relation to Rheological Properties of Oxide Slips, J. Am. Ceram. Soc. 42 (2) (1959) 70.

[5] F. Lange, "Colloidal Processing of Powder for Reliable Ceramics," Curr. Opin. Solid State Mater. Sci (UK) 3(5) (1998) 496-500.

[6] J. T. Dusek and G. D. White, "Fabrication of Uranium Dioxide Helices for Irradiation Creep Measurements", Bull. Amer Ceram Soc. 51(2) (1972) 149.

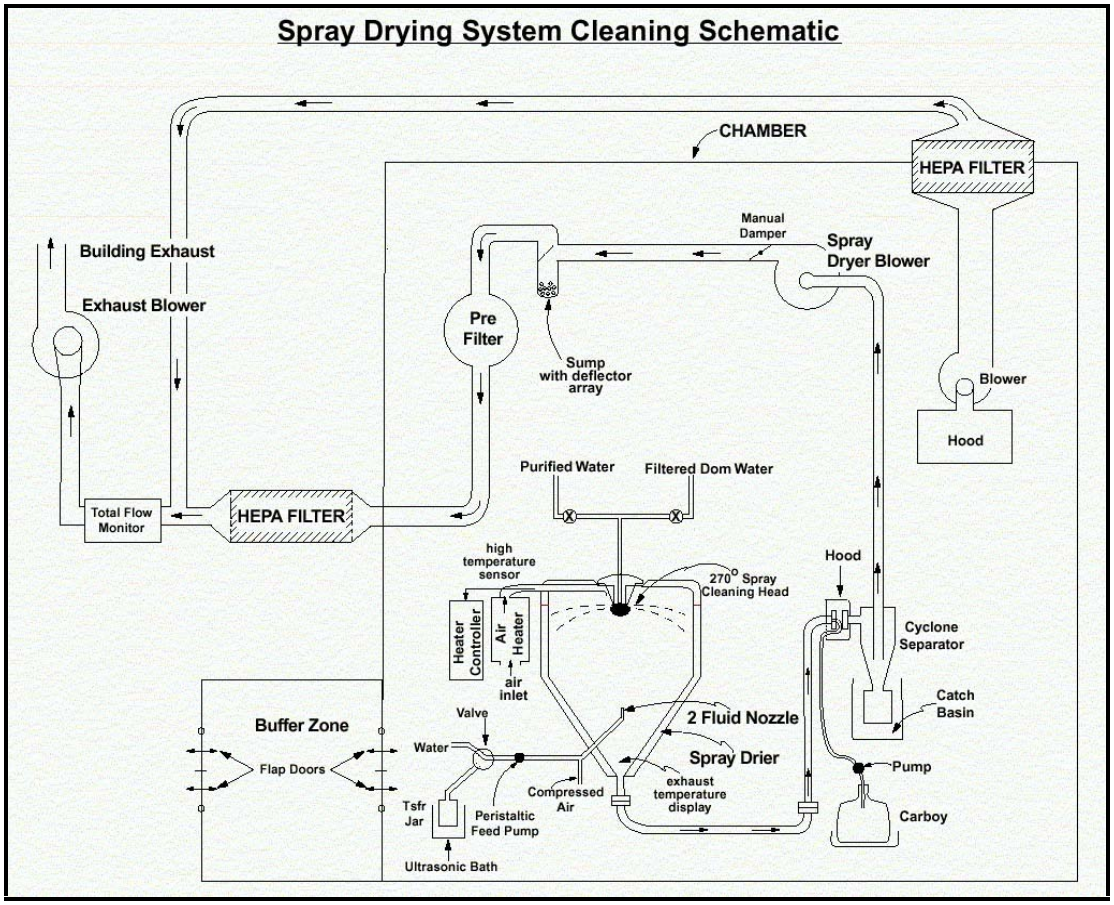

Figure 11. Schematic Diagram Showing the Method for Cleaning the Spray Drying System.