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

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ABSTRACT

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 for mechanized processing. Occasionally it is used to fabricate sintered bodies like cemented carbides, and has been used to produce sintered fuel and actinide microspheres [1]. As a physical process, it can be adapted to many powder types and mixtures and thus, has appeal for dispersion nuclear fuels, and waste forms of various compositions. It also permits easy recycling of unused powders, and generates minimal chemical waste streams that can arise in chemical sol/gel processing. On the other hand, the containment of the radioactive powders, present safety challenges that need to be addressed [2]. Detailed formal procedures and methods for characterizing and processing UO₂/ThO₂ 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, (9) zeta potential measurements and (10) ceramographic preparation. The spray drying procedures represented a particular challenge since they deal with the handling of loose powders.

Studies were carried out to formulate suitable stable, dense and homogeneous aqueous slurries of urania and thoria powders for the production of urania-thoria microspheres by the spray drying method. The studies included (a) particle size distribution after ball-milling, (b) viscosity, (c) zeta potential, (d) slurry flowability, stability and cleanability, (e) microsphere green strength, and f) effects of organic dispersants on the above properties. After formulating the slurry, U,ThO₂ microspheres were produced using a commercial, laboratory-scale spray dryer modified for handling these radioactive materials. The microspheres thus obtained were dried at 473 K for 4 hours, presintered at 1173 K for 2 hours and sintered at 1923 K for 10 hours.

INTRODUCTION

Cermet nuclear fuels 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 using thoria based cermet nuclear fuel in 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. This paper is one of three in these proceedings describing a 1999 NERI project designed to develop the potential and demonstrate the feasibility of a (Th,U)O₂ cermet fuel [3,4]. The fuel microsphere fabrication method will be described here.

The cermet fuel concept is shown schematically in Fig. 1. The target fuel design is a fine dispersion of (Th,U)O₂ microspheres that have a theoretical density between 70 and 95%, and a uranium enrichment below 20% U-235. Nominal values for the microsphere diameter (~50 to 100µm), ThO₂-to-UO₂ ratio of 50:50, fuel-to-matrix ratio of 50:50, and U-235 enrichment of ~19.5%, were selected to provide guidance for the calculational and experimental activities carried out within the project [3].

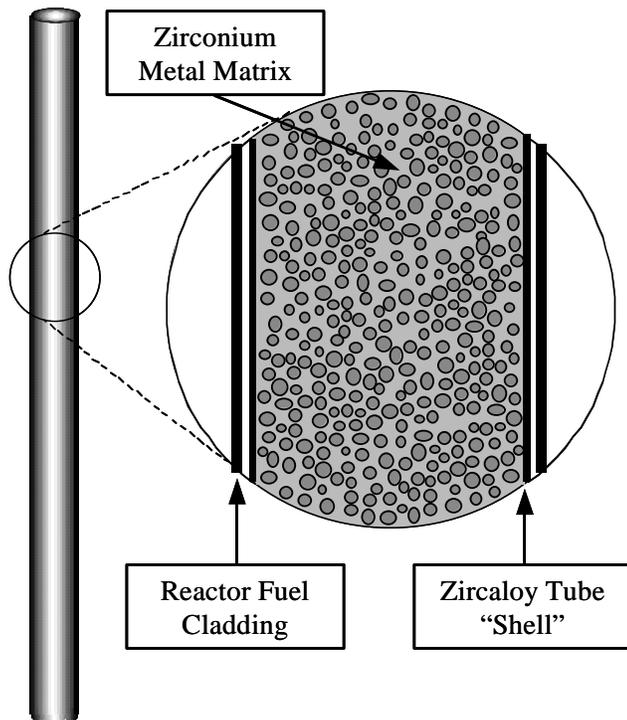


Figure 1. Concept Sketch for (Th,U)O₂ Dispersion Fuel Pin.

We have developed a laboratory-scale facility described more fully below for producing spray-dried microspheres of urania/thoria for dispersion fuel fabrication. 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 that occur

during drying require appropriate rheological characteristics of the powder. Thus, particle size distribution, surface chemistry (organic additives), and charge state (zeta potential) are very important for these properties. We measured the powder size distributions before and after ball milling, and we made viscosity measurements of urania-thoria slurries as a function of solids loading, pH, and organic additives.

MATERIALS AND CHARACTERIZATION

The starting UO₂ and ThO₂ powders were analyzed to determine their chemical purity with respect to “nuclear grade” purity requirements. As-received Particle size distributions were measured for various source powders and indicated that this powder might be satisfactory but required ball milling.

Particle size analysis

The size distributions of the oxide particles in the slurries were measured by dispersing the powder in distilled water and using the Small Volume Module of the Beckman/Coulter LS230 Particle Size Analyzer. The results of the measurements are shown in Figs. 2-5. Figs. 2 and 3 show the particle size distribution on a number basis at different slurry pump speeds with or without concurrent “sonication” (using a low energy ultrasonic horn). The data are for a 30/70 mol% UO₂/ThO₂ slurry with and without Polyethylene Glycol, PEG. It appears that the slurries are monodispersed and have a mean size of about 1µm. However, from Figs. 4 and 5, which show the size distribution on a volume basis, it is seen that the mean of the particles is about 2µm, even though a very small fraction of agglomerates appear at about 50µm during higher values of pump speed or sonication. In general, the slurries are monodispersed and have a mean particle size of less than about 2µm. This indicates that wet milling produces a superior milling compared to our previous dry milling experience. Fig. 6 and 7 show the size distribution for 50 mol.% urania-thoria slurries (with 0.5 vol.% triethanolamine, TEA, as a dispersant) as a function of milling time. Increase in milling time does not appreciably alter the size distribution of the oxide particles. Hence 24 hours milling time appears to be an adequate milling time.

Slurry Preparation and Characterization

One of the most important steps in the production of (U,Th)O₂ microspheres by the spray drying method is the preparation of stable, homogeneous aqueous slurries of urania and thoria powders with maximum solids loading for maximum microsphere size, and also possessing suitable viscosity and rheological properties to form high green density spheres. In order to increase the flowability, slurry stability, green strength and final sintered density of the microspheres, numerous binders, lubricants, surfactants and dispersants are typically

added to the feed slurry. The final mixtures are usually only arrived at after extensive experimentation, and often become closely guarded proprietary formulations. The particle surface charge or zeta potential is also controlled to prevent flocculation or coagulation of the powders.

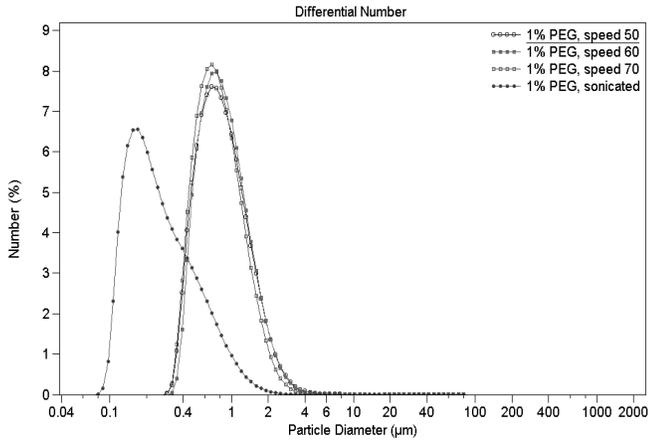


Fig.2. Particle number distribution of 30/70 mol% Urania/Thoria slurry with 1% PEG, pH=3

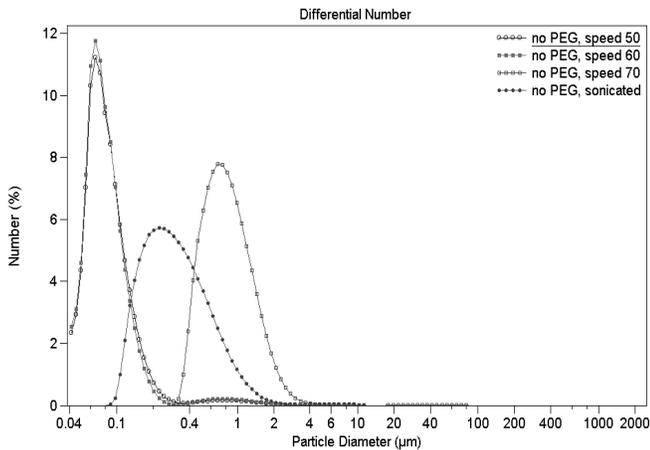


Fig.3. Particle number distribution of a 30/70 mol% Urania/Thoria slurry without PEG at pH=3

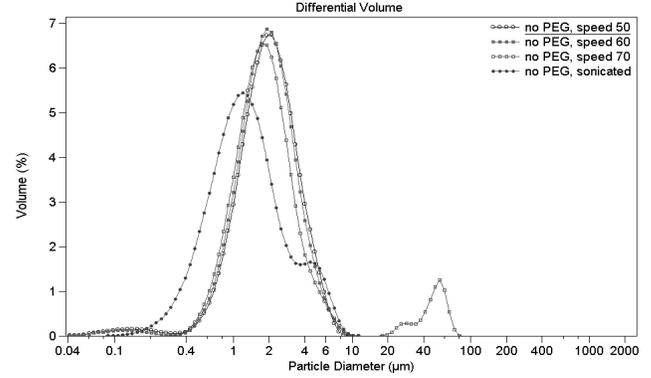


Fig.4. Particle volume distribution of 30/70 mol% Urania/Thoria slurry with 1% PEG at pH=3

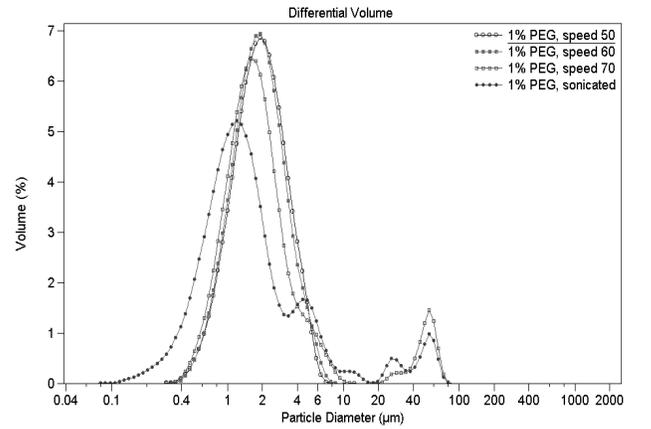


Fig.5. Volumetric Particle size distribution of 30/70 mol% Urania/Thoria slurry without PEG, pH=3

For spray drying of radioactive powders, there is the additional requirement that the chamber and Two Fluid Nozzle be easily cleanable after spray drying. Thus, in order to shorten the developmental process, the many parameters both in slurry preparation and properties and spraying parameters need to be optimized using various quantitative methods of characterizing the slurry including viscosity, rheology, and zeta potential measurements.

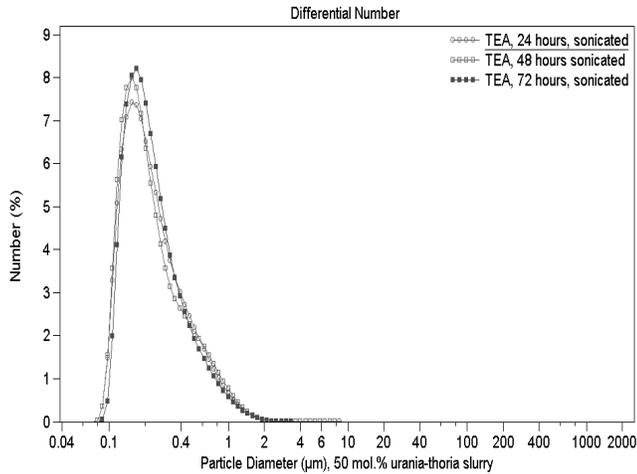


Fig.6. Particle number distribution of a 50/50 mol% Urania/Thoria with 0.5 w/o TEA, pH=6

Accordingly, slurries of various formulations and properties were prepared and their flow properties were measured with our Haake RS-1 Viscometer/rheometer. In addition, our Peristaltic Pumping System was used to examine the problem of slurry feeding. Although PEG is commonly used in dry processing, TEA is a simpler more easily cleanable binder compared to PEG. Figs. 6 and 7 shows that the TEA yields excellent monodispersed distributions on both a number density and volume distribution, which can be further improved with ball-milling.

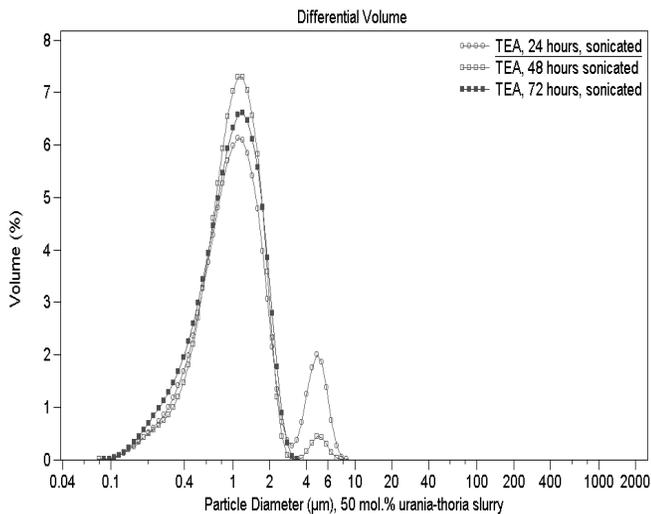


Fig.7. Particle volume distribution of a 50/50 mol% Urania/Thoria slurry with 0.5% TEA, pH=6

Slurries were prepared by mixing urania and thoria with a known amount of high purity deionized water. HCl or aqueous ammonia were used to adjust the pH of the slurry. The pH could

be measured directly in these concentrated slurries with a specific ion electrode pH meter supplied by IQ Scientific Instruments. After adding the desired binder/dispersant, the mixture was wet ball-milled for 24 hours, employing WC balls. In some cases the slurry pH changed after organic addition.

Slurry flow measurements

We have measured the flow rate of 30 mol.% urania-thoria slurries at various pumping speed of our peristaltic pump. We wanted to insure that the slurries were flowable through our system using 1/8" I.D. tubing and two parallel pumping heads on our Peristaltic Pump. The two heads permit out-of-phase pumping which smoothes out the pulsations considerably. Pumping was done with a capillary tube at the end to simulate the restriction of the Two Fluid Nozzle. The results of the semi-quantitative flow tests are given in Fig.8. We first discovered that sufficiently stable slurries could not be obtained without the addition of binder/dispersant. Hence, the flowability of these slurries could not be reliably measured. In the case of slurries with binder/dispersant, increase in solids loading decreased the flowability of the slurry, as expected. However, ball-milling considerably enhanced the flowability of the slurry. Even though a stable slurry with good flow properties was obtained at pH=10 or at pH=1, a slurry at pH=3 was thought to be preferred

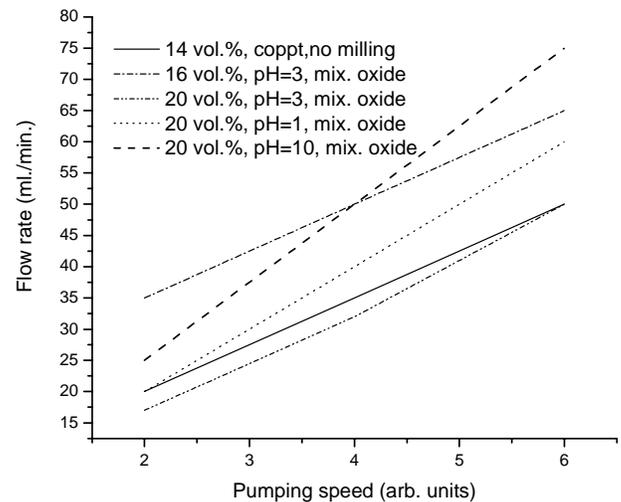


Fig.8 The results of the flow tests

for the spray drying because the maximum zeta potential is reported to occur at pH=3 for pure dilute urania slurries, and at pH=4 for pure dilute thoria slurries [6]. However, the zeta potential is a function of the concentration of solids and additives. We therefore measured the zeta potential using the Zeta Probe which is based on an electroacoustic method that permits concentrated dispersions to be measured as discussed in the following section.

Zeta Potential (ZP) of Concentrated Slurries.

Using the acoustophoretic technique employed in the ZetaProbe, the zeta potential can be measured at the high slurry concentrations used in spray drying. An example of a titration using HCl or KOH to adjust pH in a 10 v/o solids loading of pure urania, thoria and a 50/50 mol% urania-thoria mixture 15 v/o solids loading, is shown in Fig. 9. It is seen that the Isoelectric Points, IEP, where the effective charge on the particles goes to zero, are at pH=6 and 9.6 for UO_2 and ThO_2 respectively. (The IEP is generally the point at which the suspension becomes unstable and flocculation occurs.) For the 50/50 mixture the IEP occurs at pH=6.5. The IEP's are similar for the pure urania and the 50/50 mixture so that the large differences in IEP between thoria and urania does not appear to adversely affect the mixture which could lead to serious problems of coagulation of oppositely-charged particles. Also, the ZP rises to quite acceptable values at both low and high pH values.

A second example involves titration of TEA. Organics can serve to stabilize powder slurries by both electrostatic repulsions and by steric constraint when organic molecules attach to particle surfaces and prevent strong VanderWaals bonding. The results of such a titration is shown in Fig.10. It is seen that the zeta potentials of a 50 mol.% urania-thoria slurry (15 vol.% solids loading) decrease with increasing TEA concentration. However, the decrease in the zeta potentials with addition of TEA is not very significant. For example, the change in zeta potential is only about 8 mV when the concentration of the TEA is changed from 0.1 vol.% to 1.0 vol.%. A reasonable quantity of TEA is required in the slurry (and hence in the green microsphere) for further processing.

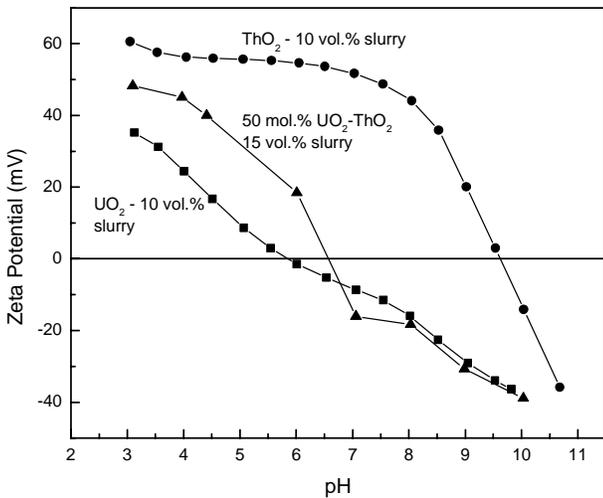


Fig.9 Zeta potentials of Urania, Thoria and Urania-Thoria slurries

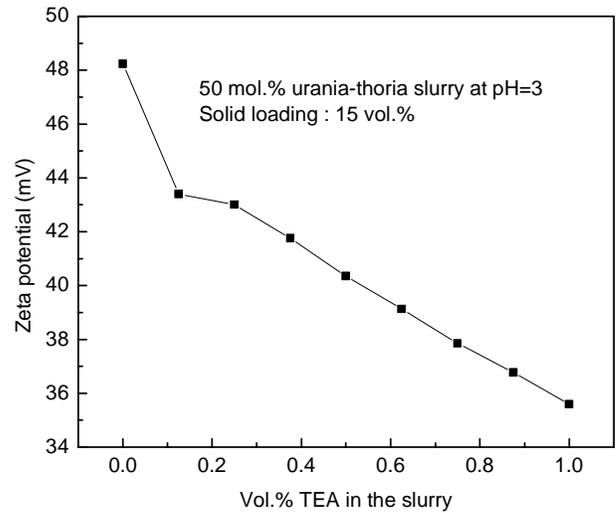


Fig.10. Zeta Potentials as a function of TEA concentration

Slurry Cleanability and Stability Tests

To verify that droplets of slurry that dried on the hot walls of the Spray Dryer could be cleaned by our tank spray cleaning system, droplets of the following samples:

- i) PEG solution,
- ii) TEA solution
- iii) Urania-thoria slurry without any binder/dispersant
- iv) Urania-thoria slurry with above binder/dispersants

were sprinkled on a stainless steel plate and heated at 473 K for about four hours. After cooling, the plates were washed with flowing water using a standard laboratory wash-bottle. After heating, it was observed that pure PEG completely charred, and the black carbonaceous residue on the stainless steel plate could not be removed even after washing and brushing. However, TEA completely evaporated at these temperatures, and no carbonaceous residue was observed on the stainless steel plate. In the cases of iii) and iv), a major portion of the dried sample could be removed by washing with flowing water. However, it appeared that repeated heating and washing steps are required in the spray drying system to completely remove urania-thoria samples that may stick to the walls of the spray dryer. Therefore, the inlet temperatures in the Spray Dryer must be kept as low as possible.

Slip Casting

An estimate of the green density of the microspheres that would be obtained through the spray drying method is an essential input in formulating suitable urania-thoria slurries for spray drying. In order to obtain this estimate, urania-thoria slurries were slip cast into cylindrical Plaster of Paris molds, by simply filling the mold, but not pressurizing the slip as we normally do. The interior of the plaster mold was coated with 0.5 wt% ammonium alginate solution which functions as a mold release agent when removing the green body. The mold was

pinned together and the slurry was poured into the mold through an injector. The specimen was removed from the mold after 24 hours and baked in air at 373 to 425 K for about 24 hours. For difficult-to-pour slurries, green specimens were also prepared by pouring the slurries into 10 mm diameter polyethylene cups and dried for 4 days. The dried specimens were again baked at 373 to 425 K for about 24 hours. It was found that large bubbles were entrapped in the slurry making geometric densities meaningless. Therefore, the slurries need to be degassed before spray drying. Also, the poor flowability of some of the slurries without pressure slip casting resulted in poor mold filling. Therefore, the geometric densities had to be obtained from the plastic cup casting which probably resulted in lower green densities. However, both PEG and TEA binder/dispersants appeared to give good green strength. When we tried to determine whether the good green strength would be retained after heating in the spray dryer, we attempted to bake in air at 200°C for 4 hrs, but the pellet fractured because of UO_2 oxidation.

Viscosity / Rheology Measurements

In order to achieve high densities through spray drying, slurries with high solids loading need to be sprayed. However, the loading possible is limited by the maximum sprayable viscosity, which is typically ~1000 to 2000 centipoise (cP) at an approximate shear rate of 10^4 s^{-1} . To minimize the viscosity, the surface charge on the particles at the slipping plane, or the ZP, may usually be altered by appropriate pH adjustment as shown above. Usually, the *minimum* viscosity occurs near the *maximum* ZP.

We have measured the viscosity of various slurries using a Haake RS-1 Rheometer/Viscometer. This instrument has a Peltier cooling plate to maintain temperatures below the ambient temperature so as to minimize evaporation during measurement, which is a serious problem for dense slurries.

Urania/thoria slurries of 50/50 mol. ratio, were prepared with 25% solids loading and ball-milled for 24h. The pH of the ball-milled slurry was found to be about 7.9. After making viscosity measurements a small sample of that slurry was drawn and it's pH was adjusted to 3.0 using HCl. Another such sample's pH was adjusted to 10.0 using KOH. All viscosity measurements were made using the 35mm/5° cone/plate sensor assembly with *increasing* applied shear rates.

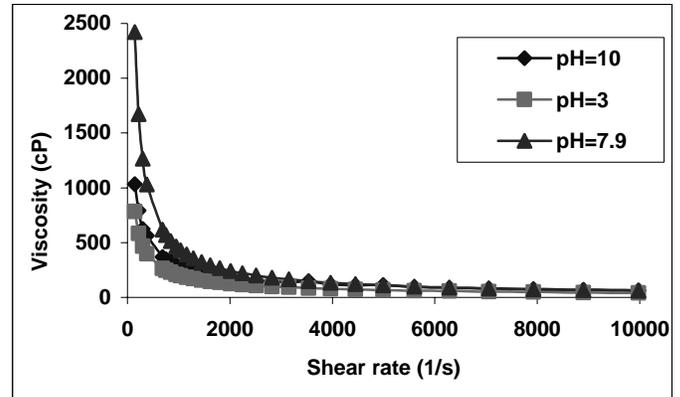


Fig. 11 Viscosity vs. Shear rate for $(U_{0.5} Th_{0.5}) O_2$ slurries at 25% solids loading.

Figure 11 shows the variation of viscosity with increasing shear rate with no additives. The viscosity at all values of pH shows shear thinning behavior, with the viscosity falling off exponentially with the shear rate, which is consistent with the reports in literature [7]. For any given shear rate, the lowest viscosity was measured at pH=3, then at pH=10 and finally at pH=7.9. This is consistent with the Zeta Potentials measured above. The viscosities at Spray Drying shear rates of $\sim 10^4 \text{ s}^{-1}$ were found to be: 41.44, 65.06 and 60.65 cP for the three values of pH which are quite reasonable for spray drying and may allow still higher solids loading. It was also found that all the above samples showed lower viscosities when the tests were repeated on the same sample, which may result from an increase in temperature during the course of the test in spite of the Peltier plate. Some hysteresis in the viscosity curves were also observed for *decreasing* shear rates.

When 0.5 vol % of TEA was added to the ball-milled slurry, similar shear thinning behavior and slightly reduced viscosities were observed, Fig. 12, but in this case the highest viscosity was for pH=3.

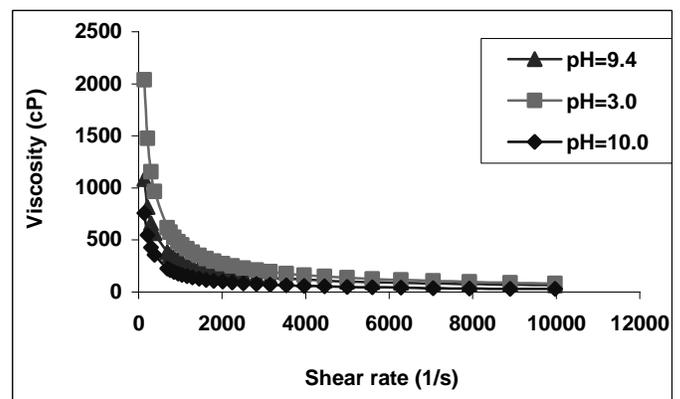


Fig. 12 Viscosity vs. Shear rate for $(U_{0.5} Th_{0.5}) O_2$ slurries at 25% solid loading and ball-milled for 24hrs. and 0.5% (wt.) of Tri Ethanol Amine (TEA) added.

Spray Drying System

The spray drying system, shown schematically in Fig. 13, is a commercial, laboratory-scale spray dryer made by Niro Inc. It consists of a funnel-shaped chamber approximately 1m 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. 14. 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 exiting “fines” are fed to a collection sump with a deflector array that is intended to trap the larger particles, then 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.



Fig. 14 Photograph of the Spray Drying System Showing the Chamber and HEPA Filtration System.

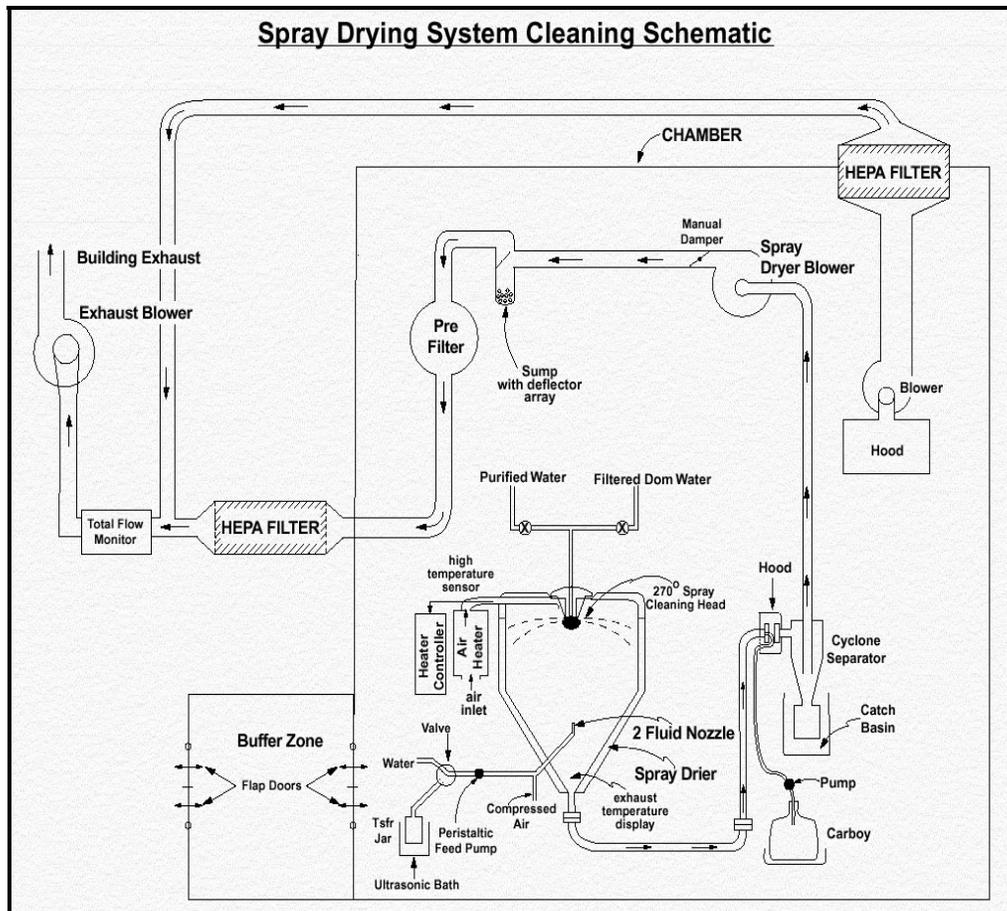


Fig. 13. Spray Drying System Schematic.



Fig. 15 Photograph of the Two-Fluid Nozzle Assembly.

The two fluid nozzle assembly is shown in Fig. 15. The slurry is propelled as it is being fed by the peristaltic pump by compressed air at ~40 psi. Spray-dried spheres are separated in the Cyclone Separator and collected in the Sampling Jar. The material trapped in the Sump and even in the prefilter can be recovered and recycled with no further chemical 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. 13, inlet air passes through a 6 KVA heater; then enters the vessel at the top and is eventually exhausted out the bottom with the dried spheres. Initially, the droplets experience counter flow, which produces rapid drying and long residence times which lead to larger particles.

The allowed Derived Air Concentration or DAC for thorium in ThO_2 is $5\text{E-}13 \mu\text{Ci/ml}$ compared to that for uranium in UO_2 of $2\text{E-}11 \mu\text{Ci/ml}$. Therefore special steps were taken to limit the spread of airborne thoria 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, Fig.13. The hood was fabricated to aid in cleaning operations especially for the two-fluid nozzle.

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. 13, the chamber is cleaned by a special tank-cleaning spray head that is first fed ~6 gal filtered domestic water at 40 psi, then ~1 gal of DI or distilled rinse water using a diaphragm pump. After each wash, the water that collects at the bottom of the vessel is pumped into a carboy using a rubber hose that is fed to the bottom of the vessel exhaust line, Fig. 13.

Results of Spray Drying (U,Th)O₂

For our initial spray drying run, a slurry of (U,Th)O₂ was prepared by ball-milling 30 mol.% urania and 70 mol.% thoria and 0.5 vol.% triethanolamine for 24 hours. Hydrochloric acid was used to adjust the pH of the slurry to 3. The total volume of

the slurry was about 50 ml. The Spray Dryer was run at 200 °C inlet temperature, and 100°C outlet temperature at a feed rate of 25 ml/min. Sintering was carried out at 1650°C for 10h in flowing Ar-5%H₂. The sintered spheres are shown in Fig. 16. The size distribution included spheres as large as 300 μm, and the surface is not smooth.

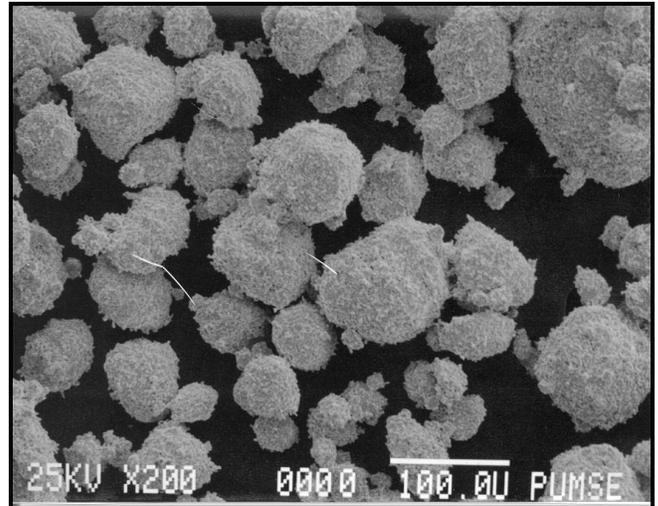


Fig. 16. SEM micrograph of sintered U,ThO₂ spray-dried spheres.

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