Formation of Liquid Drops with Uniform and Controlled Diameters at Rates of 10^3 to 10^5 Drops Per Minute

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The sol-gel processes developed at ORNL for preparing small thorium, uranium, and thorium-uranium oxide spheres are based on the conversion of colloidal oxide sol drops into gel spheres by extraction of water into an alcohol, usually 2-ethyl-1-hexanol (2EH) (Haas, 1969, 1972; Haas and Clinton, 1966). The sol drop contains the amount of oxide which will be present in the product sphere. The average drop diameter must be predictable and controllable so that fired spheres of a specified size can be produced from various sols, each having different properties. The size uniformity of these drops is important to the overall yield of product since oversized and undersized spheres constitute the principal off-specification material. Also, size uniformity is essential to the continuous operation of fluidized-bed sphere-forming columns (Haas, 1969).

In the study reported here, a procedure based on the operation of a two-fluid disperser with vibration was used to prepare batches of 10^6 to 10^8 ThO_2 spheres on a routine basis. Size distributions of the products were carefully measured by screen and radiographic analyses.

OPERATION OF TWO-FLUID DISPERSERS WITH VIBRATION

Thoria sol (Haas, 1972) containing 600 to 700 g of ThO_2 per liter and 2EH were fed to a two-fluid disperser coupled with a Derritron VP-2 vibrator-piston combination as shown in Figure 1. The sol was metered by displacement from a tank by 2EH metered by a small gear pump. The 2EH flow through the nozzle is required for separating and preventing coalescence of the freshly prepared drops. After a few seconds of aging, these drops are covered by a surface film, formed by surfactants in the 2EH (Haas, 1969), which minimizes coalescence. Vibration was imposed on the sol entering the capillaries or orifices of the disperser in order to promote the natural frequency of drop formation.

When sol drops are formed without vibration, the size of the sol drops depends on the flow rates of the sol and the drive fluid (that is, the 2EH) (Haas, 1969; Haas and Clinton, 1966). The natural frequency of breakup can be estimated, thus allowing selection of a suitable vibration frequency.

The procedure selected for applying the vibration was to vibrate a piston immersed in the sol at the entrance to the orifice or capillary from which the drops were formed. A typical equipment arrangement consisted of a 2.80 mm-diam. piston in a 3.3 mm-I.D. sol feed channel (Figure 1). The piston was coupled by a rod to the vibrator, which was driven by a sine-wave power supply rated at 0 to 25 V-A and 50 to 10,000 Hz. The coupling rod was sealed to the sol feed channel by a short section of thin-walled, 4.8-mm or 6.4 mm-I.D. rubber tubing. The difference between the diameter of the piston and that of the sol feed channel was kept small to reduce the loss of vibration input as a result of backflow by the piston. The coupling rod is relatively stiff, and the mechanical arrangement avoids undesirable structural resonances at normal operating frequencies. When this technique was used to promote natural frequencies of drop formation, favorable results were obtained with low power inputs over a complete range of high frequencies. In techniques using vibration alone, the high frequencies are difficult to apply and are commonly usable only with careful tuning to make use of resonance effects.

Most of the vibration-promoted drops were formed via a single two-fluid nozzle with Rayleigh or varicose-type breakup of sol after it left the feed capillary. The breakup of liquid jets at regular multiples of the jet diameter has been predicted theoretically and observed experimentally (Haas and Clinton, 1966; Perry and Chilton, 1973). For a two-fluid nozzle, the diameter of the sol jet may be varied by varying the flow rate of either the sol or the drive fluid. The sol is accelerated to the drive fluid velocity; then breakup into drops occurs in 2EH having a velocity equal to that of the sol stream.

Experimental results have shown that the diameters of the sol drops D_I are about 2.1 times the diameter of the jet. Thus, the sol flow rate F is related to the 2EH velocity V_{max} by

$$F = \frac{\pi}{4}\left(\frac{D_I}{2.1}\right)^2 V_{max} \tag{1}$$

For a cylindrical flow channel and laminar flow, V_{max} at the center of the channel is twice the average velocity. Then

$$D_I = 1.70d\sqrt{\frac{F}{f}} \tag{2}$$

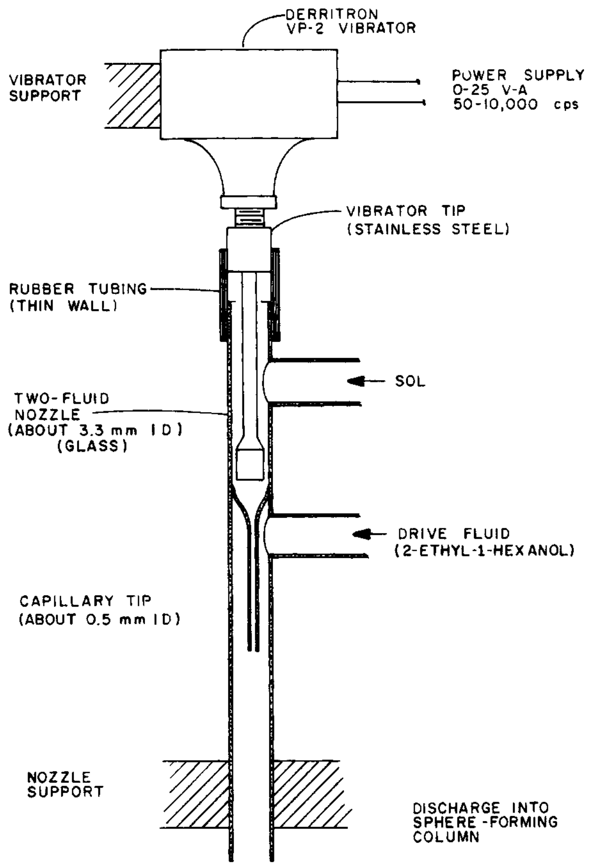

Fig. 1. Equipment arrangement for using the two-fluid nozzle with vibration.

where F and f are the sol and the drive fluid flow rates, respectively, and d is the inside diameter of the 2EH channel. From a simple volume balance, the rate of drop formation n is

$$n = \left(\frac{6}{\pi D_I^3} \right) F \tag{3}$$

The shrinkage during gelation and firing is determined by the initial sol concentration. In the case of a typical sol containing 680 g of ThO_2 per liter, the sol drop diameter is $(10{,}000/680)^{1/3} = 2.45$ times the ThO_2 sphere diameter (density = 10.0 g/cm^3).

Jet breakup was promoted and made more regular by using vibration. When observed with a stroboscopic light, operation to form approximately thirty thousand 980-μm-diam drops/min. gave a jet 2 to 5 cm long prior to breakup when 500-Hz vibration was applied, as compared with a 7- to 10-cm jet when no vibration was used. Without vibration, the drops were blurred and the formation of nodes in the jet was not sufficiently regular to be stopped by the stroboscopic light. When vibration was employed, the breakup was easily and completely stopped by the stroboscopic light. The spheres made using the vibration technique were more uniform as shown by the size distribution data presented in the next section.

When the natural frequency of drop formation was matched to that of the vibration, the beneficial effects of the vibration were obtained for a very wide range of power inputs or vibration amplitudes. Under the conditions of the example (above), any input available from the power supply (0.2 to 3.0 A) was effective with a small change in jet length before breakup when the power was varied over this range. The lower power inputs were not effective when frequencies were >600 Hz, when the drive fluid flow was not matched to the frequency, or when the inside diameter of the sol feed capillary was very different from $D_I/2$. Any one of these three unfavorable factors can usually be overcome by increasing the power, but realization of effective operation is unlikely if two of them are unfavorable. While all results reported here were obtained using 2EH as the drive fluid, the same behavior would be expected if a gas were used for this purpose.

The capacity of a single nozzle is limited by the necessity for laminar flow of the drive fluid and by the excessive pressure drops required for high flow rates. The allowable V_{max} for 2EH is about 15,000 cm/min., since changes in cross section in the nozzle tend to cause turbulences. For large drops (1500 μm) and a sol jet of 0.0750 cm, this corresponds to about 60 cc of sol/min. and about 35,000 drops/min. For small drops ($\sim$500 μm) and a sol jet of 0.0250 cm, this V_{max} corresponds to about 7 cc of sol/min. and about 100,000 drops/min. The uniformity of the drops was better for V_{max} values below 10,000 cm/min. than for the 10,000- to 15,000-cm/min. range.

SIZE MEASUREMENT PROCEDURES

The kernel diameters in each batch of ThO_2 microspheres were determined both by screen analysis and by radiographic measurements. In the case of the screen measurements, the entire batch of spheres was analyzed. New 8-in. diam. micromesh screens reported to be accurate to $\pm$ 2 μm were used with 350-g quantities of spheres. After screening, each size fraction was passed over a shape separator to remove any nonspherical or broken particles.

Samples consisting of about 2000 spheres to be used for the radiographic measurement of diameter were riffled from each batch of spheres prior to screening or shape separation. For each resulting radiograph, the diameters of 200 randomly selected spheres were measured at a magnification of 100X using a microscope equipped with a calibrated split-image eyepiece. The standard deviation of the radiographic measurement was determined to be 1.2 μm by repeatedly measuring the diameter of a single sphere. This error was removed from the reported particle diameter standard deviation s by an accepted statistical technique.

SIZE MEASUREMENT RESULTS

Results of the screen analysis for one of the batches of spheres (J-146) are given in Table 1. Yields for each size fraction both before and after shape separation are reported; in each case, they were based on the initial batch weight. The excellent quality of the product is evidenced by the fact that 98.6 wt. % of the as-formed material was spherical and in the size range 360 to 390 μm. Note that the amount of material rejected during shape separation was only 1.1 wt. %.

A more precise measure of the quality of this material was obtained from the radiographic measurements. Histograms constructed from the radiographic data (see Figure 2) indicate that the spheres made with the technique

TABLE 1. SCREEN ANALYSIS OF ThO_2 BATCH J-146

Total rejected by shape separation = 1.1%

Spherical material in size range 350-400 μm = 98.8%

Spherical material in size range 360-390 μm = 98.6%

Particle size, μm	Yield before shape separation, wt %	Yield after shape separation, wt %
<350	0.09	0.03
350-360	0.05	0.05
360-370	0.79	0.78
370-380	91.42	90.58
380-390	7.26	7.22
390-400	0.14	0.13
>400	0.24	0.14

TABLE 2. TYPICAL TEST CONDITIONS AND SIZE DISTRIBUTION RESULTS

	Batch number					
	146	147	149	172	310	311
Sol volume, cm^3	3,450	6,400	4,000	—	5,100	—
Time, min.	283	538	377	—	329	—
Sol flow rate, F, cm^3/min.	12.2	11.9	10.6	15.5	15.5	18.3
Sol conc., g ThO_2/liter	670	670	670	676	675	615
Nozzle I.D., d, cm	0.335	0.335	0.335	0.325	0.330	0.335
2EH flow rate, cm^3/min.	265	265	563	193	215	150
Sol Capillary ID, μ	430	430	450	600	710	600
Drops/min., n	28,800	28,800	60,000	15,900	9,500	6,600
Calculated drop diameter, μ	932	926	696	1,228	1,465	1,740
Calculated sphere diameter, μ	378	376	283	501	595	690
Batch weight, kg	2.2	4.2	2.6	13.2	3.0	5.3
Average diameter, μ[a]	378.0	379	283	500	594	695
Standard deviation, μ[b]	2.5	3.7	5.0	3.6	3.1	5.4

[a] The 95% confidence intervals were $\pm$ 0.3 to $\pm$ 0.7, assuming that the size distribution is normal.

[b] The 95% confidence intervals were $\pm$ 0.3 to $\pm$ 0.8, assuming that the size distribution is normal.

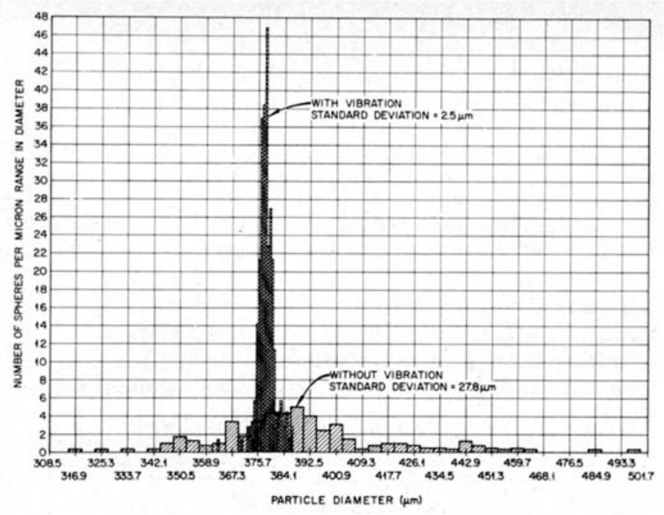

Fig. 2. Comparison of size distribution of ThO_2 microspheres made with and without vibration.

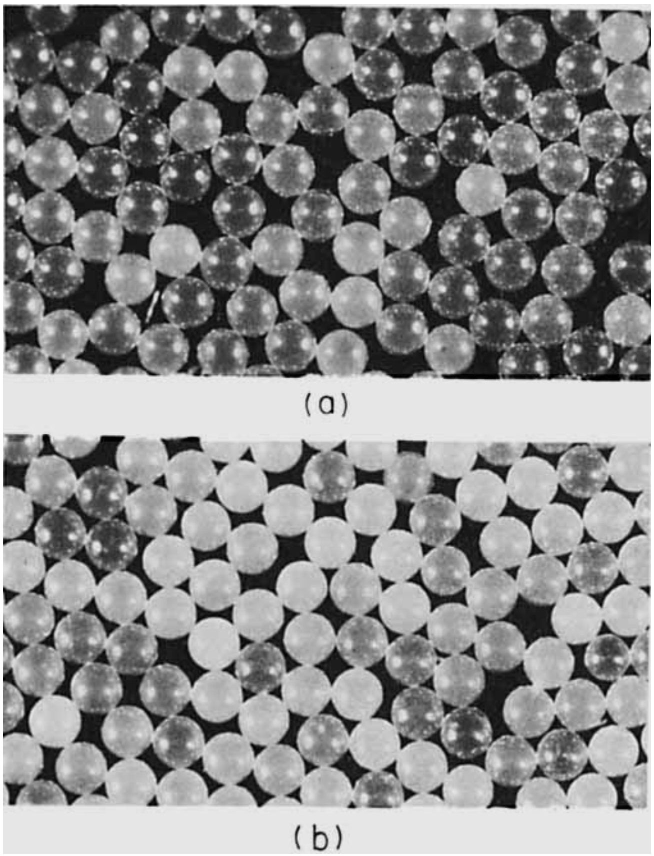

Fig. 3. Photomicrographs of samples riffled from (a) Batch J-146 and (b) Batch J-147.

employing vibration were extremely uniform in size. The standard deviation of the particle diameter was 2.5 μm, compared with 27.8 μm for spheres made without vibration. Typical test conditions and results for other batches are tabulated in Table 2.

The densities of the spheres comprising four of the batches (J-146, -147, -148, and -149) were determined by mercury pycnometry. In each of these batches, the spheres were found to be theoretically dense to within the accuracy of the technique (0.1 g/cm^3). Photographs of riffled samples from two batches are shown in Figure 3.

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Laminar Two-Dimensional Non-Newtonian Jets

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Laminar Newtonian jets have been studied extensively and a full account of all significant theoretical and experimental work is given by Schlichting (1968). The boundary layer theory and the similarity solutions given by Schlichting have also been extended to laminar non-Newtonian jets. Lemieux and Unny (1968) and Atkinson (1972) developed similarity solutions for the two-dimensional jet and Rotem (1964) for the axisymmetric jet of a power-law fluid issuing into a mass of the same fluid. Laminar non-Newtonian jets are perhaps more realistic than Newtonian. Many non-Newtonian fluids, such as polymer solutions and melts, have large apparent viscosities and laminar flow persists under usual processing conditions. A study of jets of such fluids is of basic interest in polymer mixing, extru-