The Sol-Gel Process

Khalid Suliman Aboodh

Abstract: An increasingly important application of liquid jets is the disintegration of the jet to form droplets of liquid containing nuclear fuel. These droplets are then dried and sintered to form ceramic micro spheres for use in fuel elements in nuclear reactors. The total operations required to form the droplets, convert them to solids, and fire them to ceramic bodies comprise what are known as Sol-Gel processes (Reference [13]).

Keywords: sol-gel process ,jet breakup.

1 INTRODUCTION

The sol is an aqueous solution containing the metal (uranium or plutonium) to be as nuclear fuel. This solution is dispersed as droplets into an organic liquid drying agent (commonly 2-ethy1-1-hexanol or isoamyl alcohol) which removes the water from the sol, thus gelling the drops of sol into tiny spheres. The final step is to dry and fire the spheres. A number of techniques to form the sol droplets have been studied (Reference [5]). Figure 1 illustrates three of the more common techniques. With the shear nozzle, the sol issues from a capillary at right angles to the drive fluid column, where it is sheared from the capillary to form droplets. The major forces in this technique are shear and inertia. In the two-fluid nozzle system the sol, issuing from a capillary as a jet, is accelerated and finally broken up by a drive fluid. Interfacial tension, shear, and gravity are the major forces at play. In the vibrating capillary technique, the capillary from which the sol issue is vibrated while immersed in the drying agent. The drops of sol are essentially shaken off from the end of the capillary. The vibrating capillary technique has given good results, but only over a limited range of sol drop diameters. The shear nozzle technique is useful in producing micro spheres below the 200-micron-diameter range (Reference [6]), the lower end of the spectrum of useful micro sphere sizes, but the micro sphere size is not very uniform. The two-fluid nozzle, on the other hand, has been shown to produce the best uniformity in sphere sizes over the widest

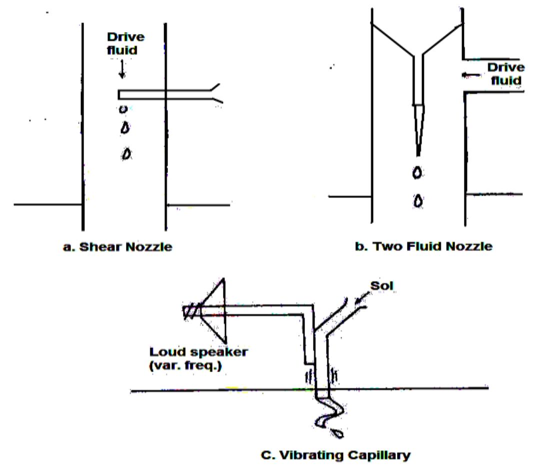

Fig 1 *Droplet Formation Techniques*

Range of sphere sizes. In the range of 200-to 2000-micron-diameter droplets, two fluid nozzles have given 90 percent by weight of the droplets within ± 15 percent of the mean diameter .modern developments incorporate a vibrator with the two fluid nozzle (Reference [7])for improved uniformity of drop size.

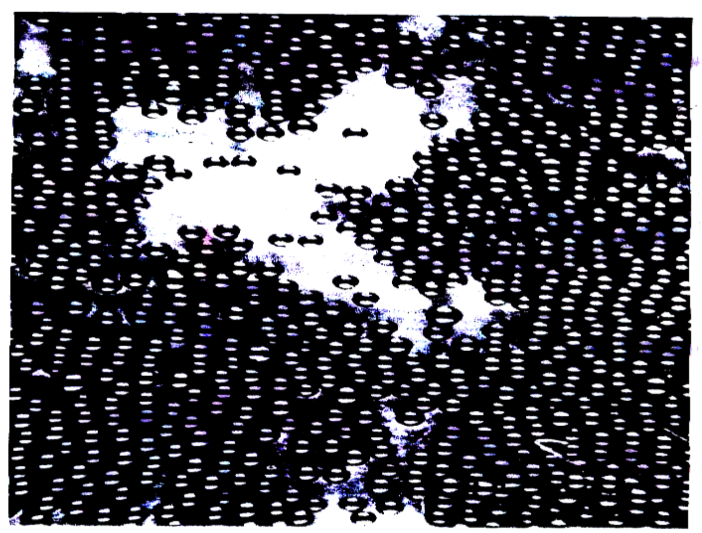

Fig 2. *fired Urania Microspheres from the Sol-Gel Process*

Figure 2 is a photograph of fired urania micro spheres formed by No turbulent operation of two nozzle system. The degree of sphericity is quite apparent. Note also the absence of satellites

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in this particular case. These appear as the operation becomes turbulent. (See for example, Reference [5]). Consider the case of the driven jet as in figure 1, in which the shear forces ominate. The shearing of the sol jet stream by the drive fluid may be approximated by equation

$$\tau_{rz}\ |_{r=a} = \frac{-\mu_1 w_0}{a} \text{ As } \tau_0(z) \cong \frac{\mu_D W_0}{t(z)} \qquad (1)$$

When this shear stress principally determines the sol jet surface velocity, we have, from equation

$$w_0(z) = w(r,z)|_{r=t} = \frac{\tau_0 t}{4\mu} + \frac{q}{\pi\rho t^2} \quad w_0(z) \cong \frac{\tau_0(z)t(z)}{4\mu_s} \qquad (2)$$

Where μ_s is the viscosity of the sol. Substituting equation (1) into (2) Gives

$$w_0(z) = \left(\frac{\mu_D}{\mu_s}\right)\frac{W_0}{4} \qquad (3)$$

Neglecting radial velocity gradients in the sol stream, the volumetric flow rate of the sol is given as

$$F = \frac{q}{\rho_s} = \pi t^2(z) w_0(z) = \left(\frac{\mu_D}{\mu_s}\right)\frac{W_0 \pi t^2(z)}{4} \qquad (4)$$

When $t(z) = t_c$, the jet radius at breakup, equation (4) yields

$$t_c = \left(\frac{\mu_s}{\mu_D}\right)^{1/2} \sqrt{\frac{4F}{\pi W_0}} \qquad (5)$$

From simple conservation of pressure in the sol stream, to a first approximation the radius of the (spherical) droplet formed is

$$R_0 \cong 2t_c = 2\left(\frac{\mu_s}{\mu_D}\right)^{1/2} \sqrt{\frac{4F}{\pi W_0}} \qquad (6)$$

Table 1: Physical Quantities Involved in Determining Drop Size

Property	Symbol	Units	Fundamental Units
1. Droplet radius	R_0	m	L
2.Sol absolute viscosity	μ_s	$kg/(m)(\sec)$	M/LT
3.Drive fluid absolute viscosity	μ_D	$kg/(m)(\sec)$	M/LT
4.Sol volumetric flow rate	F	$m^3/\sec$	L^3/T
5.Velocity of drive fluid	W_0	$m/\sec$	L/T

A simpler, but less satisfying, approach to such a relationship as equation (6) is to assume that by the time of breakup, the sol stream velocity has essentially attained the drive fluid velocity W_0. Then equation (4) becomes

$$F \cong \pi t_0^2 W_0 \qquad (7)$$

So that $R_0 = 2t_c = \sqrt{\frac{4F}{\pi W_0}} \qquad (8)$

For the case in which the sol viscosity is similar to that of the drive fluid equations (6) and (8) appear to bracket the experimental results, given by an early correlation (Reference [9])

$$R_0 = 1.2\sqrt{\frac{4F}{\pi W_0}} \qquad (9)$$

Obviously an exact theoretical treatment of the two-fluid nozzle for the Sol-Gel process is indeed a complex one. However, as for jet breakup length, the relationship between the variables may be explored by use of dimensional analysis. Consider the droplet size to depend on the variables given in equation (6). One may then make the following tabulation of the number of physical quantities involved is $n = 5$. These depend on only three fundamental units: M , L, T ,so that $r = 3$. We may therefore expect $(n-r) = 2$ Dimensionless grouping (π terms). The problem is assumed to Be of the form

$$f(R_0, \mu_s, \mu_D, F, W_0) = 0 \qquad (10)$$

And $\phi(\pi_1, \pi_2) = 0 \qquad (11)$

Where $\pi = R_0^a \mu_s^b \mu_D^c F^d W_o^e \qquad (12)$

Or hence $\pi = L^a \left(\frac{M}{LT}\right)^b \left(\frac{M}{LT}\right)^c \left(\frac{L^3}{T}\right)^d \left(\frac{L}{T}\right)^e$

$$= L^{a-b-c+3d+e} M^{b+c} T^{-b-c-d-e} \qquad (13)$$

Since π is a dimensionless quantity, the exponents must be zero. Hence

$$\begin{aligned} a-b-c+3d+e&=0\\ b+c&=0 \qquad (14)\\ b+c+d+e&=0 \end{aligned}$$

We have three equations in five unknowns, so that two unknowns may be chosen arbitrarily provided that they are independent of the others. As mentioned previously, the independency is established if the determinant of the coefficients of the remaining terms dose not vanish.

First solution

Since we desire R_0 to appear as a function of the other variables, it is logical to choose $a=1$ As agues also choose $b=0$. Then equations (14) become

$$\begin{aligned} -c+3d+e&=1\\ c&=0 \qquad (15)\\ c+d+e&=0 \end{aligned}$$

Which has solution $c=0$, $d=-1/2$ and $e=1/2$. To check for validity of the assumptions on the exponents, we must have the determinant is

$$\begin{vmatrix} -1 & 3 & 1\\ 1 & 0 & 0\\ 1 & 1 & 1 \end{vmatrix} = -2 \neq 0$$

Hence our assumptions are valid. The first dimensionless grouping π_1 is thus established from equation (12) as

$$\pi_1 = R_0^1 \mu_s^0 \mu_D^0 F^{-1/2} W_0^{1/2} = R_0 \sqrt{\frac{W_0}{F}} \qquad (16)$$

Second solution

If viscosities are to appear at all, then we must try $b=1$. Since π_1 contains R_0 already, it is logical to take $a=0$ for the second solution. Then equations (14) become

$$\begin{aligned} -c+3d+e&=1\\ c&=-1\\ c+d+e&=-1 \end{aligned}$$

Which has solution $c=-1$, $d=0$ and $e=0$. The second dimensionless grouping is thus established from equation (12)

$$\pi_2 = R_0^0 \mu_s^1 \mu_D^{-1} F^0 W_0^0 = \left(\frac{\mu_s}{\mu_D}\right) \qquad (17)$$

Thus from equation (11)

$$\phi\left[\left(R_o\sqrt{\frac{W_0}{F}}\right), \left(\frac{\mu_s}{\mu_D}\right)\right] = 0 \qquad (18)$$

The simplest functional relationship one might assume is

$$R_0\sqrt{\frac{W_0}{F}} = k\left(\frac{\mu_s}{\mu_D}\right)^x \qquad (19)$$

Where k and x are constants to be determined experimentally. Rearranging equation (19)

$$R_0 = k\left(\frac{\mu_s}{\mu_D}\right)^x = \sqrt{\frac{F}{W_0}} \qquad (20)$$

We obtain the form of equation (6) where $k = 4/\sqrt{\pi}$ and $x = \frac{1}{2}$.

A more general relationship than equation (19) may be obtained by including additional variables such as the densities of the sol and drive fluids, ρ_s and ρ_D respectively, and the geometry of the drive fluid flow channel. The results (Reference [5]) may be expressed in the form

$$\left(\frac{R_0}{R}\right) = k\left(\frac{G}{F}\right)^x \left(\frac{\mu_s}{\mu_D}\right)^y \left(\frac{\rho_s}{\rho_D}\right)^z \mathrm{Re}_s^a\, \mathrm{Re}_D^b \qquad (21)$$

Where R is the radius of the drive-fluid flow channel, G is the volumetric flow rate of the drive fluid, and Re_s and Re_D are the Reynolds numbers for the sol and for the drive fluid, $\mathrm{Re}_i = (D_i V_i \rho_i / \mu_i)$, where D_i is the diameter of the ith fluid stream and V_i is its velocity. From experimental data, equation (21) has been evaluated as (Reference [5])

$$\left(\frac{R_0}{R}\right)=1600\left(\frac{G}{F}\right)^{0.1}\left(\frac{\mu_s}{\mu_D}\right)^{0.5}\mathrm{Re}_D^{-1.5} \qquad (22)$$

Where $a = z \cong 0$. This correlation is valid for $\mathrm{Re}_D \geq 1000$ and for laminar flow. Note the recovery of the theoretically derived exponent for the dependency on viscosities.

The general solution of (14)

Let $b = k$, $a = \lambda$

$$-c + 3d + e = k - \lambda$$

$$c + 0 + 0 = -k$$

$$c + d + e = -k$$

Then

$$c - 3d - e = -k + \lambda$$

$$c + 0 + 0 = -k$$

$$c + d + e = -k$$

$$\begin{vmatrix} 1 & -3 & -1 \\ 1 & 0 & 0 \\ 1 & 1 & 1 \end{vmatrix} = 0 - 3 - 1 = -4 \neq 0$$

Then $b = k$,$c = -k$

Conclusion

In the dimensional analysis. A general solution of equation (14) was obtained showing all the possible solutions of the dimensional analysis method

References

[1] J.N.ANNO, The Mechanics Of Liquid Jets, Lexington Book, Massachusetts, 1977.

[2] W.BICKLEY, The plane jet.phil.mag .ser . 7,23,727-731(1939).

[3] P.W.Bridgman, Dimensional Analysis, (Yale University Press, New Haven Conn., 1931)

[4] N.CURLE and H.JDAVIES, MODERN FLUIDDYNAMICS, OLUME1: INCOPRESSIBLE FLOW, STUDENTS PAPERBACK EDITION, Massachusetts

[5] P.A.Haas, Preparation of Sol-Gel Spheres Smaller Than 200 Microns Without Fluidation, Nuclear Technology, 10,283-292, March (1971)

[6] P.A.Haas, F.G.Kitts, and H.Beutler, Preparation of Reactor Fuels by Sol- Gel Processes, Chemical Engineering Progress Symposium Series, 63,16-27(1967).

[7] P.A.Hass and W.J.Lackey, Improved Size Uniformity of Sol-Gel Spheres by Imposing a Vibration on the Sol in Dispersion Nozzles, Report ORNL-TM-4094,Oak Ridge National Laboratory, Oak Ridge, Tennessee,(May 1973).

[8] Dr.HERMANN SCHLICHTING, Boundary-Layer Theory, sixth Edition, Massachusetts, 1968.

[9] P.A.Hass and S.D.Clinton, Preparation of Thoria and Mixed Oxide Microspheres,

[10] Lord Raleigh, On the Instability of Jets, Proceedings of the London Mathematical society, 10, 4(1879).

[11] Lord Raleigh, The Theory of Sound (Dover Publications, New York,1945), Vol.2,pp.351-359.

[12] P.D.McCormack, L.Crane, and S. Birch, An Experimental and Theoretical Analysis of Cylindrical Liquid Jets Subjected to Vibration, British Journal of Applied Physics, 16, 395 (1965).

[13] Proceedings of the Symposium on Sol-Gel Processes and Reactor Fuel Cycles, Gatlinburg, Tenn., May 4-7,1970.Oak Ridge National Laboratory Publication CONF-700502.

[14] H.SCHLICHTING, Laminare stranhlenausbreitung .ZAMM13, 260-263(1933).

[15] C.Weber, Zeitschrift F r Anegewardte Mathematik Und Mechanik, 2,136(1931).

[16] C.Weber,Zum Zerfall eines Flussig keitsstrahles, (Dis-integration of a liquid Jet),Zeitschrift Fur Angewandte Mathematik Und Mechanik, 11,136 (1931).

[17] E.H.ZARANTONELLO, JETS,WAKES, AND CAVITIES, CAMBRIDGE, MASSA CHUSETTS, 1957.

[18] L. PRANDTL, Uber Flussigkeits bewe gung bei sehr kleiner Reibung. Proc. Of the Third intern. Mat. Congr. Heidelberg 1904.Reprinted in Vier Abhdl. Zur Hydro- und Aerodynamik Gottingen 1927; NACA Tm 452 (1928); see also collected works (Gesammelte Abhand-lungen), Vol.II, PP.575-584(1961).