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Application of Gel Microsphere Processes to Preparation of Sphere-Pac Nuclear Fuel*

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ABSTRACT

Sphere-Pac fabrication of nuclear fuels using two or more sizes of oxide or carbide spheres is ideally suited to nonproliferation-fuel cycles and remote refabrication. The sizes and compositions of spheres necessary for such fuel cycles have not been commonly prepared; therefore, modifications of sol-gel processes to meet these requirements are being developed and demonstrated.

I. INTRODUCTION

The work reported here is part of a program to develop Sphere-Pac fabrication of nuclear reactor fuels. Although the initial emphasis is for light-water reactors, most of the technology can be extended to breeder reactor fuels. Nonproliferation fuel cycles impose new fabrication requirements but also present an opportunity to introduce Sphere-Pac technology, which has fabrication advantages and potential performance benefits. Processes of the sol-gel type appear to be the only practical methods for preparing the high-density ceramic spheres necessary for Sphere-Pac fabrication.

Our microsphere preparation studies have almost simultaneous requirements to select optimum processes and to prepare product samples for Sphere-Pac fabrication and irradiation tests. None of the basic gel microsphere or Sphere-Pac concepts are new; they have been demonstrated on a laboratory scale under a variety of conditions. However, preparation of the sizes and compositions of spheres required for optimum application

of Sphere-Pac fabrication either has not been demonstrated at all or the demonstrations have been so limited that the practicality of engineering operation and the irradiation performance are uncertain. In this paper, the particles necessary for the current Sphere-Pac program will be described first. Then the technology selected for our experimental tests will be reviewed and recent results will be summarized.

II. SPHERE-PAC REQUIREMENTS

The Sphere-Pac fabrication concept has been described previously;[1] details of studies are being reported at this meeting in a paper by Suchomel and Lackey.[2] The fabrication variables must be selected to give high and reproducible average densities. The procedures (including low-energy vibration), as illustrated in Fig. 1, and the sizes and amounts of spheres are the principal variables. The spherical shape is necessary if the particles are to assume a closely packed configuration.

Sphere-Pac fabrication might be applied to many types or compositions of nuclear fuels. Sol-gel processes can also satisfy these varied requirements. Our present development studies are primarily intended to prepare UO_2 spheres for light-water reactor (LWR) fuels according to the following criteria:

(1) The sintered UO_2 spheres must be of near-theoretical (>98%) density.

(2) About 60 wt % of the product shall be large coarse spheres of 800-μm diameter.

(3) About 20 wt % of the product shall be small coarse spheres of 200-μm diameter.

(4) About 20 wt % of the product shall be fines of about 30-μm average size.

(5) The uniformity of size and sphericity of the 800- and 200-μm particles must be very good, but a range of sizes and some degree of nonsphericity will be allowed for the fines.

III. SELECTED REVIEW OF SOL-GEL TECHNOLOGY

A large number of process variations have been developed to prepare spheres of many different compositions and sizes. Most of this information has been reported in four symposium proceedings.[3-6] Our review will be limited to the two processes that appeared to be most promising for the Sphere-Pac UO_2 particles. The selection is based on the reported suitability for the three desired sizes of UO_2 spheres (800, 200, and 30 μm) and the degree of demonstration or commercial-scale application of the processes. Processes developed at ORNL for U(IV) sols were not selected since they were not practical for 800-μm UO_2 spheres.

(1) Internal Gelation Using Hexamethylenetetramine

This process, sometimes identified as the KEMA process, was initially developed and reported by M. E. A. Hermans and others at KEMA, Arnhem, the Netherlands. The hydrolysis of hexamethylenetetramine $[(CH_2)_6N_4]$ in uranyl nitrate solution releases NH_4OH, which results in a rapid and uniform solidification of solution drops into gel spheres. The decomposition rate is strongly dependent on temperature and pH. At 0°C or less, the decomposition rate is low enough to allow mixing, pumping, and dispersion into drops over a period of hours. When the drops are heated to 60 to 95°C, usually in an organic liquid, solidification occurs in seconds.

The internal gelation conditions developed at KEMA were applied to the preparation of 500 kg of UO_2 spheres in a pilot plant. The basic flowsheet

operations (Fig. 2) are well described in KEMA reports[7,8] for UO_2 and have been applied with minor modifications to mixed oxide or carbide fuels elsewhere.

(2) External Gelation Using Ammonia

The external gelation technique has been called the gel support precipitation method. The original gel-support precipitation method was the SNAM process. Although developed in 1962, this method was not described in the open literature until 1970.[9,10] Its distinguishing feature is that a water-soluble organic polymer is added to the heavy-metal solution or sol. The polymer supports the particle spherical shape, while ammonia diffuses into the gel bead and precipitates the heavy metal. One of the most attractive features of the original method was that no pretreatment of uranium solutions was required. The necessary chemicals were simply added to the uranium solution and the microspheres gelled. The presence of the organic polymer makes the gelation results less dependent on the salt compositions of the feed solutions.

The SNAM process was developed in Italy; however, modified SNAM processes in Germany have been used or are being used at Hobeg, KFA, and Karlsruhe and at Harwell in Great Britain.[11-13] The general schematic flowsheet is applicable to all these modifications (Fig. 3). KEMA, in the Netherlands, also tested an external gelation method but had difficulty producing particles greater than 100 μm in diameter.[14] KEMA prefers their internal gelation process. In addition, KFA is working toward elimination of the water-soluble organic polymers. The largest pilot-plant operations are probably those at Hobeg and Harwell.

IV. GEL MICROSPHERE STUDIES IN PROGRESS

The current series of Sphere-Pac development studies at the Oak Ridge National Laboratory was started near the end of 1977. These studies are part of the Department of Energy program for thermal reactor fuel refabrication. Much of the past sol-gel work at ORNL was performed for subsequent application to thorium fuel cycles. The initial program planning and assessment showed that UO_2 fuels for LWRs should receive first priority. Therefore, all results reported here are for preparation of UO_2 spheres, although many of the procedures or results would also be useful for other fuel compositions.

(1) Conditions for the Internal Gelation Process

Internal gelation results from chemical reactions of components of the broth or sol; therefore, mass transfer is not basic to the gelation process. This greatly minimizes difficulties from concentration gradients during mass transfer or from the lengthy periods required for mass transfer in large drops. For nuclear fuels, the only important internal gelation technique involves dissolving hexamethylenetetramine (HMTA) in nitrate solutions cooled to about 0°C and then heating drops of solution to decompose the HMTA to form NH_4OH and formaldehyde (Fig. 2). The rate of gelation depends on the concentrations in solution and heat transfer from the hot organic liquid used as a gelation medium.

The internal gelation process for nuclear fuels was developed in the Netherlands,[7,8] and we find that the broth or solution concentrations they recommend are useful for all sizes of Sphere-Pac fuels. Two solutions are mixed at 0 to -4°C to give the following final concentrations: 1.2 M uranium, 1.8 M NO_3^-, 1.5 M urea, and 1.5 M HMTA.

The acid-deficient uranyl nitrate (NO_3^-/U mole ratio of 1.5) and the HMTA must be chilled and mixed shortly before gelation; the urea can be present in either solution. The strength of the gel spheres can be increased significantly by the presence of organic polymers as described for external gelation. However, since adequate strength is possible without the polymers and their removal may complicate the firing conditions, we prefer to avoid polymer addition.

We are preparing the three sizes of UO_2 spheres needed for our Sphere-Pac fabrication studies by internal gelation in organic liquids. The large drops required for 800-μm spheres are gelled most effectively in chlorinated ethanes or ethylenes selected to have densities near, but less than, the aqueous-drop density. When the density difference is large, the drops become distorted and gel in nonspherical shapes. The two smaller sizes have been formed in the same organic liquids and in 2-ethyl-1-hexanol (2EH) partly saturated with water. Some dehydration of the gel spheres is desirable, but the amount must be controlled. Little or no dehydration results in a soft surface, while excessive dehydration gives a powdery surface which erodes during the washing steps. A surfactant[a] is helpful to prevent sticking or clustering of partially gelled drops.

We prefer to use the solution concentrations listed above, and gelation at 50 to 75°C to produce opaque yellow spheres with smooth, but not glassy, surfaces. Gelation, washing, and drying are less troublesome for products prepared under these conditions. Higher gelation temperatures

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[a]Span 80, an Atlas Powder Co. ester.

and/or higher HMTA/U ratios give more translucent or glossy spheres of an orange-yellow color. Such conditions are reported to yield smaller crystallite sizes.[15] The drop formation procedures are reviewed in a later section (Sect. 4.3). For all process operations other than drop formation, we are able to use the same simplified procedures to obtain all three sizes of Sphere-Pac UO_2 particles.

(2) Conditions for the External Gelation Process

The composition of the feed solution, or broth, is the controlling variable for external gelation processes. Of course, the gelation, washing, and drying conditions must be compatible with this composition. We have performed a series of experiments using the conditions most commonly recommended in sol-gel literature. In these experiments, large ThO_2 spheres were prepared from several different ThO_2 sols with widely different compositions. We have not been able to use external gelation for the preparation of 800-μm UO_2 spheres. The difficulties described appear to be inherent in the mass transfer necessary for external gelation and become more troublesome as the sphere diameter increases. Studies are continuing since the method offers advantages over external gelation; i.e., the stability of the feed broths and the elimination of organics would be advantages for remote operation.

External gelation occurs via diffusion of a gelating chemical (NH_3) into a sol or broth drop (Fig. 3). Chemicals are simply added to a uranyl nitrate solution to prepare the broth, which is very stable and can be stored for days or weeks. High acid and electrolyte concentrations are tolerated. Also, the wet gel beads are aged in aqueous NH_3 without need

for an organic removal step; however, the wet gel beads are often dehydrated with use of an organic extractant, thus introducing organic handling problems.

The gelation (i.e., conversion of the drops of broth into wel gel microspheres) process takes place in four steps, as follows:

(1) Formation of microspherical drops in an NH_3-free environment.

(2) Brief exposure to ammonia in the same phase to form a thin skin and fix the shape of the drop.

(3) Transfer of the partially gelled microsphere through an interface into the gelating solution (usually concentrated NH_4OH).

(4) Free fall through the gelating solution for several seconds and aging in this solution for several minutes or hours.

Two methods have been used to form the surface skin. In one, the drops are formed in air, followed by NH_3 gas, above concentrated NH_4OH. In the other, the drops are formed in an NH_3-free organic liquid (for example, methyl isobutyl ketone), followed by contact with the organic liquid containing NH_3 and then aqueous NH_4OH. The NH_3 quickly reacts with the surface of the drop to give a solidified skin or shell around a liquid core. Depending on composition of the broth, this outer shell may be thick, hard, and glassy or thin, soft, and pliable. The former usually results in a layered particle of nonuniform properties. A solid shell surrounds a fragile, macroporous core (these cores usually give hollows or voids after drying). The soft, pliable shell leads to a uniform gel throughout the microsphere that is also soft. These soft particles are easily deformed into nonspherical shapes. Both types of beads have shown evidences of splitting, which may be confined to superficial

surface fissures or may consist of large, deep cracks that sometimes result in two hemispherical particles. These splits appear to be caused by a volume change in the bead after the surface shell or skin has fixed the outer structure.

(3) Drop Formation and Sphere Size

The amount of metal oxide in a product sphere is equal to that present in the sol drop before gelation. The procedures used during formation of the sol drops is important to the yield since oversize and undersize spheres constitute the principal off-specification material. The average drop diameter must be predictable and controllable so that the specified fired-sphere size can be obtained from sols with different properties. The capacities needed for development systems and production plants are generally in the range of 0.1 to 10 kg of product spheres per hour. Table 1 gives the corresponding sphere preparation rates for a typical product density of 10 g/cm^3. All the sol-gel processes for sphere preparation require similar capabilities with regard to liquid drop preparation, independent of the gelation technique. All of the drop-formation procedures start with flow of the sol through small orifices or capillaries.

A liquid jet discharged from a small opening at viscous or laminar flow conditions will tend to break up into short lengths which, in turn, form spherical drops. The cause of this behavior is surface energy as represented by interfacial tension. The most common drop diameter is about two times the jet diameter and is formed from a length of jet about five times the diameter. This type of breakup persists to high velocities if the jet is protected from other disturbances.

Optimum application of this jet breakup to sol-gel sphere preparation requires procedures to minimize several problems. One effective technique is to impose a regular vibration on the liquid jet to control the breakup. This may be done by moving the jet opening or by pulsing the liquid flow to the jet. Frequencies of drop formation near the natural frequency of breakup described above can be imposed by small energy inputs of vibration; however, frequencies different from the natural frequency by a factor of 2 or more are difficult to impose. The use of vibration is very helpful in that it greatly improves the uniformity of the drop size, promotes the formation of drops from more viscous fluids, and permits adjustments to be made in the average drop diameter without changing the capillary or orifice size. Another effective technique is to use a two-fluid nozzle with a drive fluid in an annulus around the jet. The velocity of the smaller jet will quickly change and become equal to that of the drive fluid, but the drive fluid and the jet should not have large differences in velocities. The use of a drive fluid is very helpful since it allows drops to be formed in a liquid without coalescence or effects from velocity differences. The drive fluid must be laminar or viscous since the disturbances from turbulent flow would disrupt the jet.

The drop formation techniques described above have been applied by using many different configurations of equipment. The sol (or broth) jet is fed through a centered orifice or thin-wall capillary with a drive or blanket fluid flowing in an annulus around the jet. The vibration is produced by an electronic system. A sine wave of controlled frequency

is amplified and supplied to an electronic vibrator which has a moving element similar to a loudspeaker coil. The movement of the vibrator can be mechanically applied to the jet capillary or to the liquid feed stream to the jet. The effects of the vibration are observed by using a stroboscopic light of the same frequency. The arrangement, shown in Fig. 4a, is used at ORNL for operation with vibration and a drive fluid.[16] A simpler nozzle for forming drops in gas without a drive fluid is shown in Fig. 5. It is possible for a single vibrator or a single drive fluid flow to serve multiple jets. On the other hand, the jets are usually supplied by individually metered flows of sol or broth as an unequal division of flow; therefore, nonuniform drop sizes nearly always result when orifices in parallel are supplied by a single feed stream. The vibration can also be effectively applied in other ways, such as:

(1) Pulsing a diaphragm in the feed line near the nozzle.

(2) Applying the vibration to a rubber or plastic feed line held between a fixed anvil and the vibrator.

(3) Moving the entire nozzle shown in Fig. 5 by coupling it rigidly to the vibrator (axial motion).

(4) Moving the capillary from which the jet discharges side-to-side (90° to the axis).

(5) Applying an a.c. electrostatic potential to the jet.

All of these can provide a uniform breakup at frequencies near the natural frequency of jet breakup, but become less effective as the difference from the natural frequency increases. The arrangement shown in Fig. 4a is believed to be less sensitive to resonances in the apparatus than the

other mechanical arrangements and is effective at very low power inputs. Long periods of operation show uniform size distributions with standard deviations of <1% of the average diameter.[16]

The natural frequency of breakup for a laminar jet of sol or broth can be calculated from the volume flow rate and the diameter. The diameter of a jet in gas (Fig. 5) is equal to the diameter of the capillary tip. For a liquid drive fluid (Fig. 4a), the jet is accelerated to the drive fluid velocity and the effective diameter is calculated from this velocity and the sol flow rate. The center-line velocity for laminar flow is twice the average velocity. The natural frequency of breakup corresponds to jet lengths of about five times the jet diameter; the frequency, then, is the jet velocity divided by five times the diameter. From these relationships, the drop diameter using a two-fluid nozzle is $1.4\ ID\ (R)^{0.5}$, where ID is the inside diameter of the drive fluid channel and R is the ratio of sol to drive fluid flow. From a simple volume balance, the rate of drop formation multiplied by the drop volume must equal the sol flow rate.

Practical capacities for small spheres require very high rates of drop formation (Table I), and the laminar jet breakup and drop weight mechanism are not practical for production use. A range of sphere sizes for the fines in Sphere-Pac fabrication is probably acceptable and may even be preferred; however, the range should be limited since the two tails of the size distributions are troublesome. If an excessive amount of material is present in the tail on the large end, it will have to be separated and recycled. The finest spheres cause difficulties with respect

to collection, washing, solids handling, spread of contamination, and perhaps clustering during calcining.

A drop-formation mechanism based on turbulent flow of drive fluid in a two-fluid nozzle is useful for Sphere-Pac fines. The sol or broth stream is dispersed into drops whose average diameter depends on the size of the turbulences (i.e., the inside diameter of the channel and the Reynolds number of the drive fluid). The average diameter is controlled by controlling the drive fluid flow rate. The turbulent nozzle gives a narrower range of size, in particular a smaller quantity of fines, than mechanical mixers or spray nozzles. The drops are formed in the organic medium, which is an advantage as compared with spray nozzles or spinning disk atomizers in gas. Our experimental data can be adequately correlated by Eq. (1), which is derived from dimensional analyses:

$$\frac{D_s}{ID} = 180 \left(\frac{G}{F}\right)^{0.1} Re^{-1.3} \left(\frac{\mu_s}{\mu_o}\right)^{1.3} \left(\frac{\rho_o}{\rho_s - \rho_o}\right)^{0.5}, \qquad (1)$$

where

D_s = average diameter of the sol drops,

ID = diameter of the organic flow channel,

G = flow rate of the organic forming medium,

F = broth or sol flow rate,

Re = Reynolds number of the organic,

μ_s = viscosity of the broth or sol,

μ_o = viscosity of the organic,

ρ_s = density of the broth or sol,

ρ_o = density of the organic.

The range of variables was limited in our studies, and Eq. (1) should not be applied for low interfacial tensions between the organic and broth or for low values of $\rho_s - \rho_o$. Equation (1) was found to be valid for Re >600 for the right-angle sol inlet capillary (Fig. 4b) and for Re >2000 for the concentric sol capillary (Fig. 4a). Since streamline flow usually exists for Reynolds numbers <2000, the "turbulent" dispersion for Re <2000 is probably the result of promoted turbulence and/or shear at the sol inlet. All of the experimental tests were made with O/F >30, that is, <3 vol % of sol drops in the total flow.

The most important advantage of operating with the two-fluid nozzle under turbulent flow conditions is that only small amounts of very small spheres are produced. Other dispersers give much higher yields of such small spheres. Large representative samples of product obtained during operation with two-fluid nozzles under turbulent flow conditions were generally 60 wt % within 0.7 d_{50} and $d_{50}/0.7$.

In summary, the practicality of drop formation is as follows:

(1) Large spheres (diameters >600 μm) are produced at practical rates from the breakup of sol fed through 0.5- to 2-mm-ID capillaries. Maximum capacities per nozzle exceed 1000 g of uranium per hour for drops formed in air or 2EH and exceed 100 g of uranium per hour in chlorinated organic liquids.

(2) The uniformity of drops from capillary breakup can be greatly improved and controlled by imposing a vibration on the liquid jet.

(3) The techniques indicated in (1) and (2) become increasingly less practical as the product diameter decreases below 300 μm because of reduced capacity and the plugging of small capillaries. Although laboratory preparation of uniform 100-μm-diam product is practical, production-scale operation is not. The calculated capacities per nozzle are 7 to 150 g of uranium per hour for 150-μm spheres.

(4) The uniformity of the product using vibration can exceed 98 wt % between $0.9d_{50}$ and $1.1d_{50}$, where d_{50} is the average diameter.

(5) For a turbulent nozzle, the typical result is a product yield of 60 wt % between $d_{50}/1.3$ and $1.3d_{50}$ and <3 wt % smaller than $0.2d_{50}$.

(6) Turbulent nozzles easily meet the capacity requirements for production operation. Calculated capacities per nozzle for 38-μm spheres and laminar flow jet breakup are too small to be practical (1 to 26 g of uranium per hour).

(4) Gel Sphere Washing, Drying, and Calcining

The wet gel spheres contain about 25 wt % UO_3. Soluble components (NH_4NO_3, urea, HMTA, and formaldehyde) that can be removed by washing with dilute NH_4OH solution also make up about 25 wt % of the gel. Most of the water is removed by a drying step. The weight loss during sintering (UO_3 to UO_2 and small amounts of all other constituents) is less than 2% of the original gel weight, but the densification depends on the calcining conditions.

Washing of the gel spheres serves three purposes: (1) it physically displaces the forming medium, (2) it leaches NH_4NO_3 and other soluble constituents from the gel, and (3) it allows additional reaction with NH_4OH to give an improved composition and structure for drying and sintering. When the forming medium is a high-density organic, it can be displaced by the downflow of gas or NH_4OH solution. When the forming medium has a high viscosity or boiling point (e.g., PERC, 2EH, or silicone oils), a preliminary wash with a more volatile organic (CCl_4 for PERC, isopropyl alcohol for 2EH, CCl_4 or hexane for silicone oils) is desirable. The principal part of the washing is accomplished by using 0.1 to 0.5 M NH_4OH solutions. For slow wash rates, the total wash volumes required are those necessary to dilute the NH_4NO_3, urea, and HMTA by a factor of ~1000, or about seven volumes per volume of gel. For 2000-μm-diam gel spheres, the minimum time required at high wash flow rates is about 1 hr. Countercurrent washing will be used for scaled-up operations to reduce the wash solution/gel volume ratio.

During drying, most of the water is removed as vapor and the uranium concentration increases from about 0.3 g/cm^3 to >1 g/cm^3. As compared with other sol-gel processes, the washed gels we have prepared via the internal gelation route are very easy to dry. Beds of drained particles up to 8 cm thick and 22 cm in diameter are heated overnight in ovens at 220°C. The water vapor escapes from the gel without difficulty; the rate of drying is determined by the rate of heat transfer. The gel can also be dried by large air flows at lower temperatures (i.e., down to room temperature).

Studies of the effects of sintering conditions are continuing.[2] The literature information is confusing and somewhat contradictory. Since our washed gel particles from internal gelation have low carbon contents, the O_2 or CO_2 atmospheres below 500°C to remove carbon are not necessary. Our highest-density products are obtained by sintering in a reducing atmosphere which may convert UO_3 to UO_2 without formation of U_3O_8. Sintering of internal-gelation UO_3 spheres of low carbon content (no organic polymer additives) in Ar-H_2 at 1450°C gives sphere densities of $\geq$10.8 g/cm^3.

VI. SUMMARY

Processes of the sol-gel type are being applied to prepare microspheres for Sphere-Pac fabrication of nuclear fuels. The present emphasis is on high-density UO_2 spheres of 800-, 200-, and 30-μm average diameter for LWR fuels. Published results indicate that the external gelation and internal gelation of acid-deficient uranyl nitrate solutions are simpler than processes using U(IV) solutions or sols. For internal gelation, uranyl nitrate solution containing HMTA at 0°C is formed into drops which are solidified by decomposition of the amine into NH_3 and formaldehyde at 60 to 75°C. For external gelation, solution drops containing water-soluble organic polymers are solidified by exposure to NH_3 gas and/or NH_4OH solutions with mass transfer into the drop. The concentration gradients associated with the mass transfer during external gelation result in

nonhomogeneous particles and difficulties during washing and drying. We are presently preparing the three desired sizes of UO_2 spheres by internal gelation. Vibration imposed on the breakup of laminar jets gives controlled, uniform drop diameters (~2600 and 650 μm) for the 800- and 200-μm UO_2 spheres. A turbulent two-fluid nozzle gives the average drop diameters required for the UO_2 fines. The procedures used for washing in dilute NH_4OH solutions and drying are simple and trouble-free. Sintering of internal gelation spheres without organic polymer additives in $Ar-H_2$ at 1450°C yields final products with densities of >10.8 g/cm^3.

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Table I. Rates of Drop Formation

Product sphere diameter (μm)	Sphere weight (μg)	Drop formation rate (drops/s)	
		For product at 0.1 kg/h	For product at 10 kg/h
900	3820	7.3	7.3×10^2
300	141	2×10^2	2×10^4
100	5.24	5.3×10^3	5.3×10^5
33	0.194	1.4×10^5	1.4×10^7

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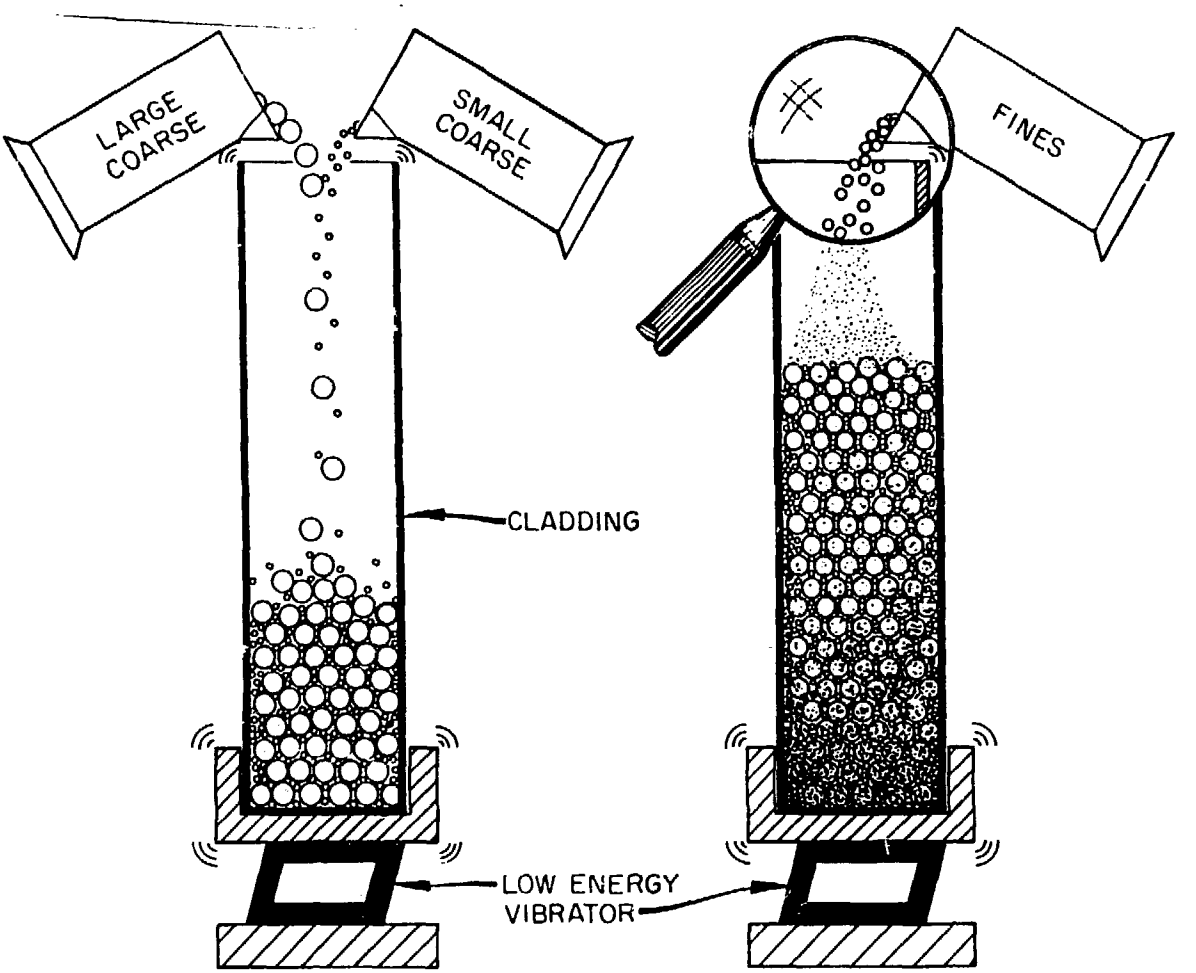

Fig. 1. Sphere-Pac fabrication concept.

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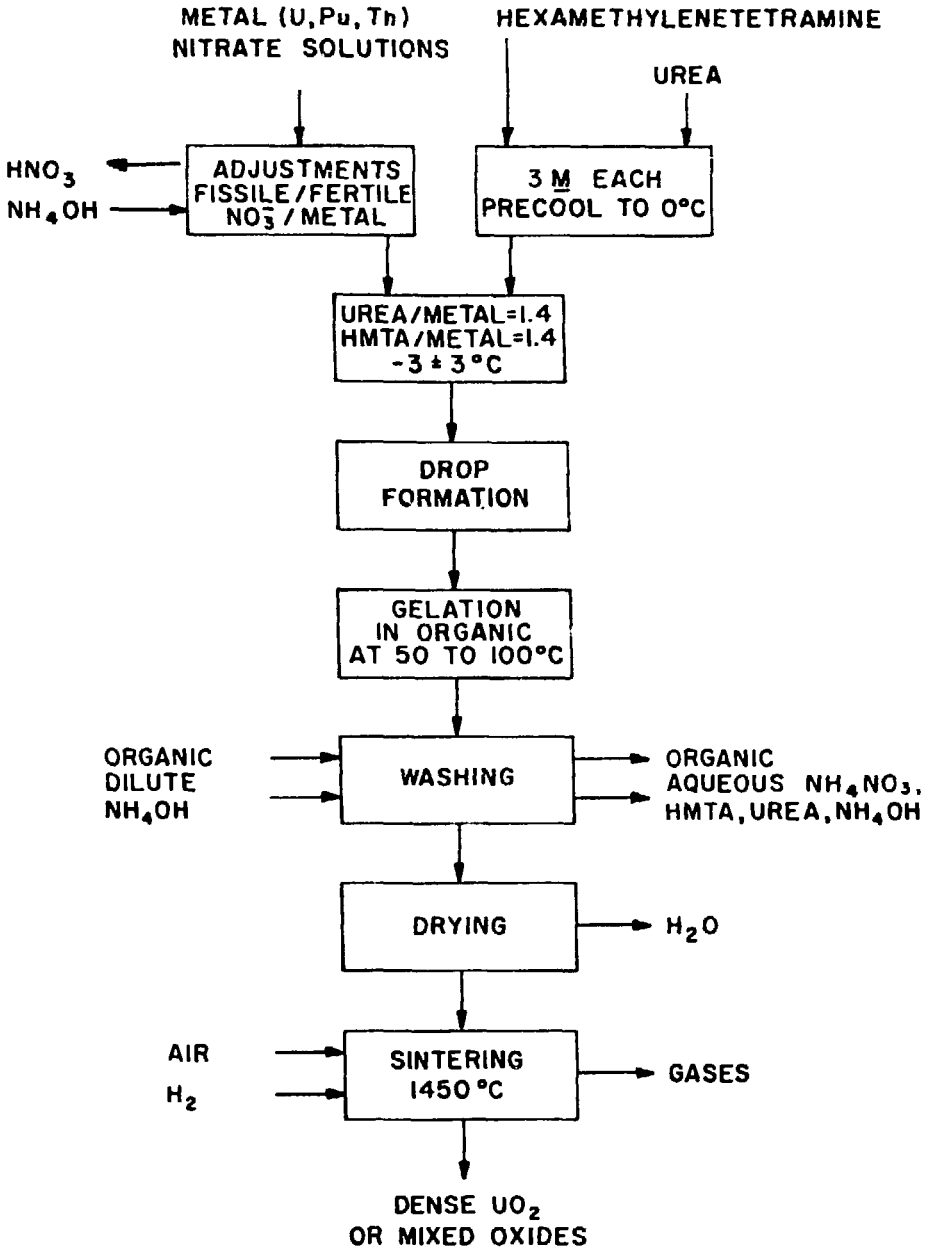

Fig. 2. Microsphere preparation by internal gelation.

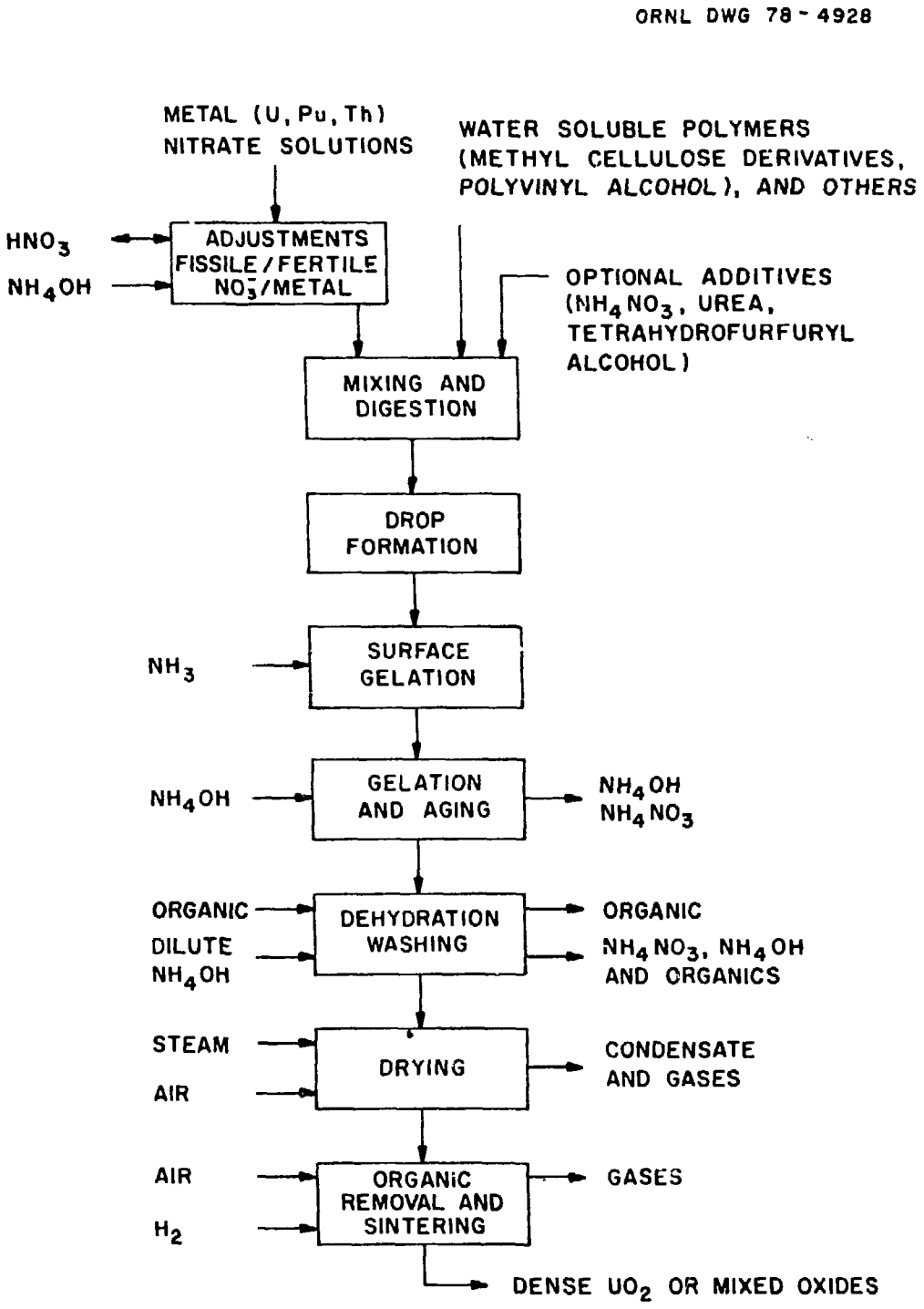

Fig. 3. Microsphere preparation by external gelation.

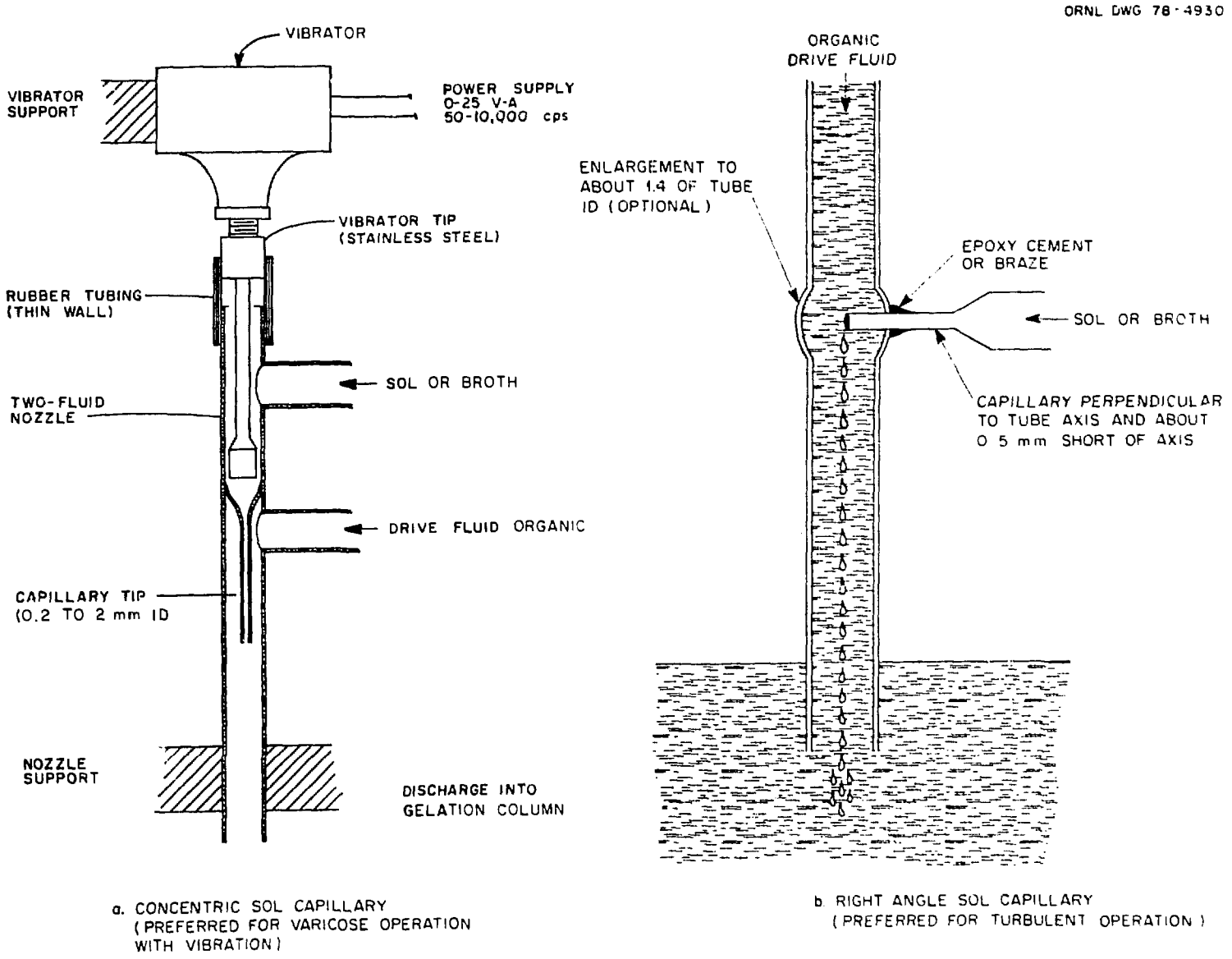

Fig. 4. Two-fluid nozzle configurations.

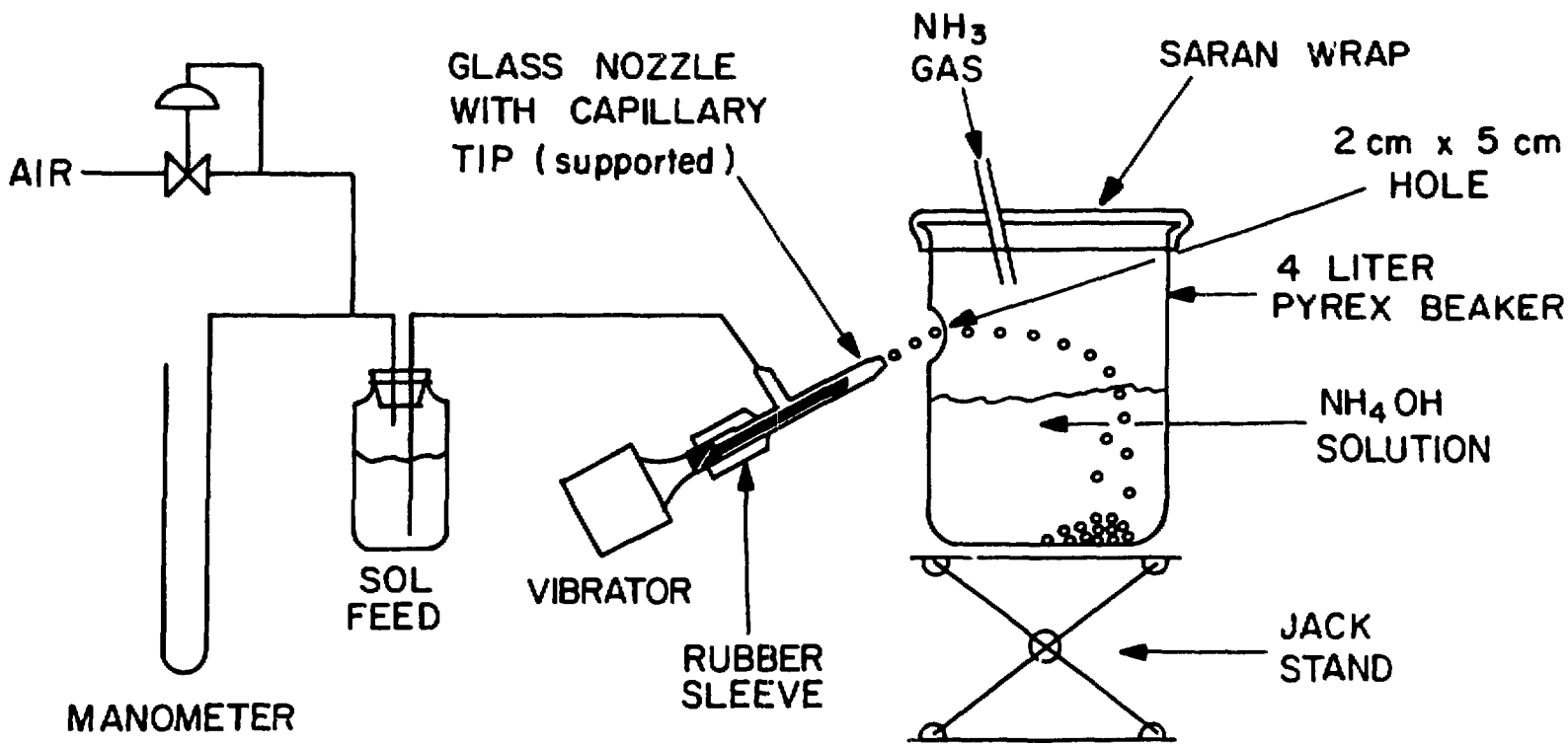

Fig. 5. Nozzle with vibration for external gelation.