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PREPARATION OF HIGH-DENSITY, SPHERICAL THORIUM OXIDE
PARTICLES WITH UP TO 10 ATOM PERCENT URANIUM

by

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PREPARATION OF HIGH-DENSITY, SPHERICAL THORIUM OXIDE PARTICLES WITH UP TO 10 ATOM PERCENT URANIUM

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In recent years, fairly extensive investigations of slurries for a variety of applications have been made. The possible use of aqueous suspensions of thorium oxide in a homogeneous reactor blanket⁽¹⁾ has received considerable attention. The material described here was designed for use as a fuel in a boiling water slurry reactor.⁽²⁾ Some of the important characteristics of the individual particles for this application were the shape of the particles, the size, the density, and the homogeneity of distribution of fissile atoms in the thoria matrix.

A relatively simple method has been evolved in which up to about 10 atom percent uranium may be homogeneously distributed throughout a spherical particle of thorium dioxide. The particle size can be varied from about one micron to fifty microns in diameter, and the final particle density is very close to the theoretical maximum of 10 gm/cm³. The fabrication process appears to be adaptable to large-scale production. About 100 lb of fired spherical material have been produced by this method.

Probably the most thoroughly tested and used method of fabricating thoria particles for slurries is via a controlled thorium oxalate precipitation.⁽³⁾ This method can be made to produce cubic platelets or pyramidal particles with an average size of one micron, and with only a very small fraction larger than five microns. Particles, with sharp-cornered shape, larger than approximately five microns usually erode almost any material seriously in circulating the slurry. Erosion, of course, is also a complex function of other variables, such as slurry concentration, circulation rates, and temperature. Spherical particles, in circulating through a system, are expected to cause much less erosion. At relatively low circulating velocities, this would permit average particle sizes considerably larger than five microns to be used. Particle size is expected to be an important variable in achieving clean steam separation from the slurry, in eliminating caking problems, in reducing flocculation, and in reducing non-Newtonian flow characteristics.

Laboratory Fabrication of Spherical Particles of ThO₂ and ThO₂-U₃O₈

The objective of the laboratory experiments was to prepare individual spherical particles of ThO₂ (5-50 microns in diameter) with ten weight percent uranium homogeneously distributed throughout the thoria matrix as a solid solution. This was accomplished as follows:

The thorium, as its nitrate, was dissolved in water, and reacted with ammonium hydroxide to give a nitrate-stabilized sol which was adjusted nearly to the gel point. Uranium as crystalline uranyl nitrate was added to and dissolved in the thorium sol immediately prior to spraying. The resultant solution contains colloidal thorium uniformly mixed with dissolved uranyl nitrate. This solution was then sprayed with a suitable spray nozzle so that droplets of the liquid can assume near-spherical shape in free fall. An ammonia-air mixture was used to cause the sol to gel. The uranium present in each droplet was simultaneously fixed as an insoluble compound uniformly distributed throughout the gel particle. The spherical particles so obtained were collected, washed, classified, dried, and fired. Figure 1 illustrates the method in operational steps. A detailed discussion of these steps is given below.

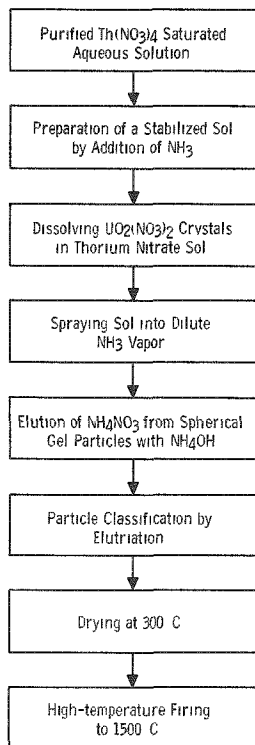


Figure 1

FABRICATION PROCESS FOR INDIVIDUAL SPHERICAL THORIA-URANIA PARTICLES FOR A SLURRY REACTOR

Thorium nitrate was dissolved in water to give approximately a 2.75 molar solution, of which a portion was retained for later use. The preparation of the nitrate-stabilized sol was accomplished by adding ammonium hydroxide with vigorous stirring in a large Waring Blender. Loss of water by evaporation due to the heat generated was prevented by using a closed container. Ammonium hydroxide was added until the solution suddenly gelled, at which time the addition was immediately discontinued. While the gel was still warm, fresh thorium nitrate solution was added and manually worked into the gelled mass, causing it to reliquefy. It has been the experience in this study that an addition of only 0.2% (of the volume of gel) of the 2.75 molar thorium nitrate solution will usually completely

liquefy the gelled mass. An additional 0.5% (of the volume of sol) of thorium nitrate solution was added to adjust the sol to a more stable condition. Since the sol will tend to precipitate at concentrations greater than about 2.7 molar, it was necessary to analyze the thorium concentration of the sol and to adjust the concentration with water before storing. The sol so prepared can then be stored for prolonged lengths of time in stoppered glass containers.

Immediately prior to spraying, a weighed amount of uranyl nitrate was dissolved with vigorous stirring in the prepared sol. If the mixed solution was allowed to stand several hours, a yellow precipitate began to form.

The sol-uranium solution mixture was fed through an atomizing nozzle into a large chamber with a dilute ammonia-air atmosphere. The correct ammonia-air concentration ratio was maintained by bleeding anhydrous ammonia gas into the process chamber. The sol droplets falling through the ammonia-air atmosphere quickly assume a nearly spherical shape, and almost immediately gel to soft, spherical particles. These were allowed to collect in the bottom of the chamber and were drawn off periodically through a valve. The diameter of the chamber used was one foot, with 5 feet straight height constructed of Lucite and a conical stainless steel bottom. The conical bottom was provided with an angled entry which was connected through a glass wool filter to the area ventilation ductwork.

Occasional fouling of the atomizer by accumulated fines collected about the nozzle could be readily detected and corrected. Two types of atomizers have been used - two-fluid and single-fluid. The solution orifice diameter of the atomizer used can be varied to give different ranges of particle size. Pressure feeding of the solution was used with both atomizer types. A 40-mil ID orifice was the largest used with the two-fluid style, and a 25-mil ID orifice was used with the single-fluid style. Variation of air pressure in the two-fluid atomizer also varied particle sizes obtained.

The soft, spherical particles were washed with several volumes of 7 molar ammonium hydroxide to remove ammonium nitrate. Concurrently with the washing, the ammonium hydroxide can also be used to classify the particles by elutriation as an optional operation. Gravity flow through a sintered stainless steel filter device was used in most cases. After the final wash, the material was allowed to drain until it appeared to have formed a relatively dry cake. One or two washings with ethyl alcohol served to hasten drying.

The material was transferred to shallow containers and dried by heating slowly to about 250C. The dry slurry was finally transferred to a furnace and fired by raising the temperature slowly to 1500C. All firing was done in an air atmosphere. An optional operation was to prefire to a minimum of 900C for stable storage of the particles, and transfer was made later to a high-temperature furnace for firing at 1400-1500C. Firing time should be at least one hour at the maximum temperature.

Discussion

It has been recognized for many years that thorium hydroxide can be readily suspended in aqueous solution as a positively charged colloid. Thorium hydroxide boiled with thorium nitrate,^(4,5) uranyl nitrate, and many other salts or acids⁽⁶⁾ will stabilize a colloid of thorium hydroxide to relatively high concentrations. Both the preparation and the stability of thorium and mixed thorium-uranium sols have been studied recently at Ionics, Inc.,⁽⁷⁾ with the object of using the sol itself in an aqueous homogeneous reactor.

Several properties of the sol were important in achieving a successful spray operation. Either of two undesirable situations was possible. First, there was the failure of the sol to gel into a soft, but solid, sphere before impingement on a container surface, and second, there was the possibility of an extremely rapid gel formation resulting in rounded but nonspherical shapes.

The first situation is the result of too small a free flight path of the sol droplets after spraying. Improper sol preparation can easily require droplet flight paths for solidification that exceed the dimensions of any ordinary equipment. It was possible, however, to obtain spherical particles in equipment which was relatively small, e.g., 12 in. from the spray nozzle to the nearest container surface.

The gel rate on spraying can be made so fast that a large fraction of the material solidified in nonspherical shapes as shown in the very fast gel rate of Figure 2 and a somewhat slower rate in Figure 3. Optimum operating conditions yielded virtually all spherical particles, as shown in Figure 4. The gel rate was a direct function of the thorium concentration of the sol, pH of the sol, and ammonia gas concentration.

The viscosity of a sol increases with higher thorium concentration, and also as the gel point is approached in adding ammonium hydroxide. The more viscous sol could be sprayed into higher concentrations of ammonia in air (i.e., to give faster gel rates), yet it still produced spherical particles.

The effects of various types of spray nozzles available were not investigated systematically. Both single-fluid and pneumatic atomizing nozzles of the siphon type were used.

One important feature of this approach to fabricating thoria microspheres is that it is possible to dissolve a wide variety of metal salts in the thorium sol prior to spraying. This ensures a virtually homogeneous distribution of the additive in the final thoria matrix. This would undoubtedly be an important variable in optimizing the characteristics of the microspheres for a particular application. Other methods have been (1) the autoclaving of oxides or salts onto porous low-fired thoria particles in aqueous medium, or, for larger pellets, (2) mechanically mixing the oxides before firing.

Figure 2

THORIUM OXIDE SOL SPRAYED UNDER VERY RAPID GEL
RATE CONDITIONS
(High Sol Thorium Concentration 2.7 Molar, pH 3.8, 1:1
by Volume Ammonia Gas-Air Atmosphere)



Figure 3

THORIUM OXIDE SOL SPRAYED UNDER MODERATELY
RAPID GEL RATE CONDITIONS
(Sol Concentration 2.7 Molar Thorium, pH 2.7, 1:10
by Volume Ammonia Gas-Air Atmosphere)

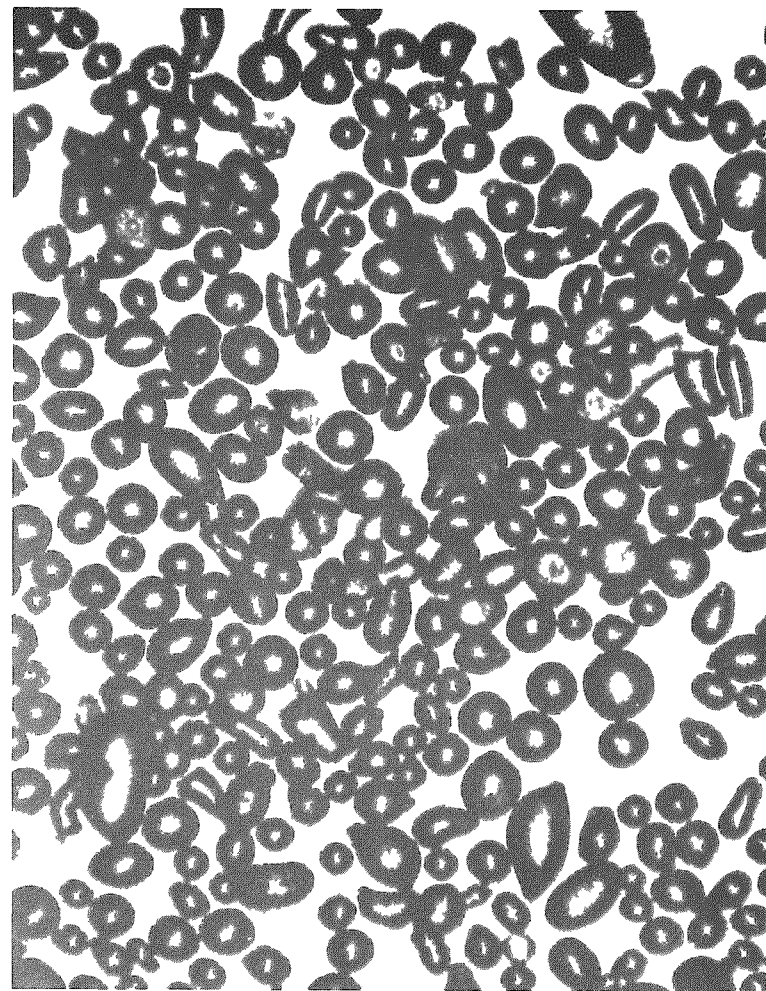
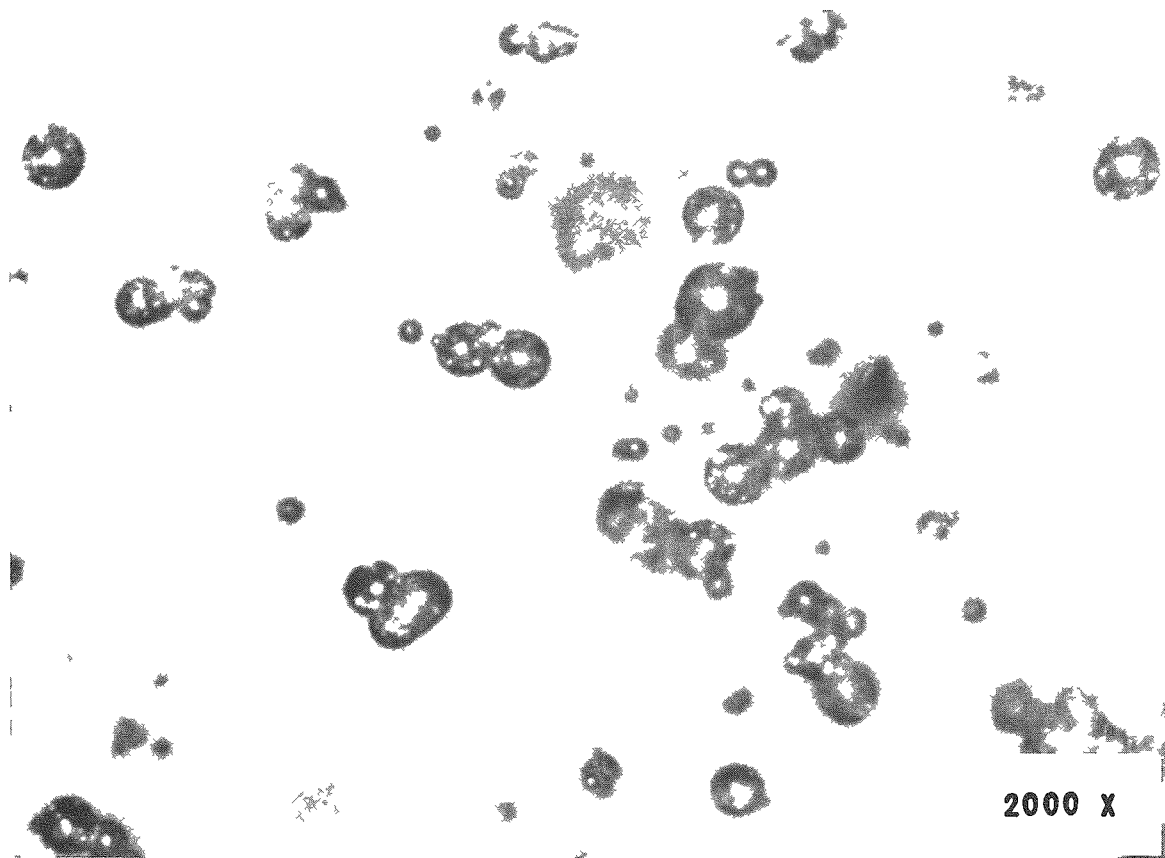


Figure 4

THORIUM OXIDE SOL SPRAYED UNDER SLOW GEL RATE CONDITIONS
(Sol Concentration 2.7 Molar Thorium, pH 2.0, 1:25
by Volume Ammonia Gas-Air Atmosphere)



Microspheres of pure, high-surface-area thoria were prepared by spraying the sol and firing to 650C. Uranium trioxide to 7.5 atom percent was then autoclaved onto the thoria microspheres in aqueous medium at 250-300C for twenty-four hours. The resulting material was fired for one hour in small batches to 1000C, 1100C, and 1200C. Sintering occurred at 1100C and 1200C, making the material useless for slurry applications. When material with the same atom content, however, was prepared by dissolving uranium nitrate in the sol prior to spraying, no appreciable sintering was observed up to 1750C. This was apparently a result of the homogeneous distribution of uranium in the thoria matrix, achieved in using the latter fabrication method, compared to a uranium-rich surface obtained by the autoclaving method.

Material in the size range of 5-25 microns fired at 1500C for one hour in air showed an individual particle density (pycnometric: organic and aqueous) which was approximately equal to the theoretical density of thorium oxide, 10 g/cc. The measured room-temperature emanation rates of

Rn^{220} from the material did not reach a minimum value until after approximately 2-hr periods of firing at 1500C in air. X-ray diffraction patterns showed an increasing crystallinity with increasing firing temperature.

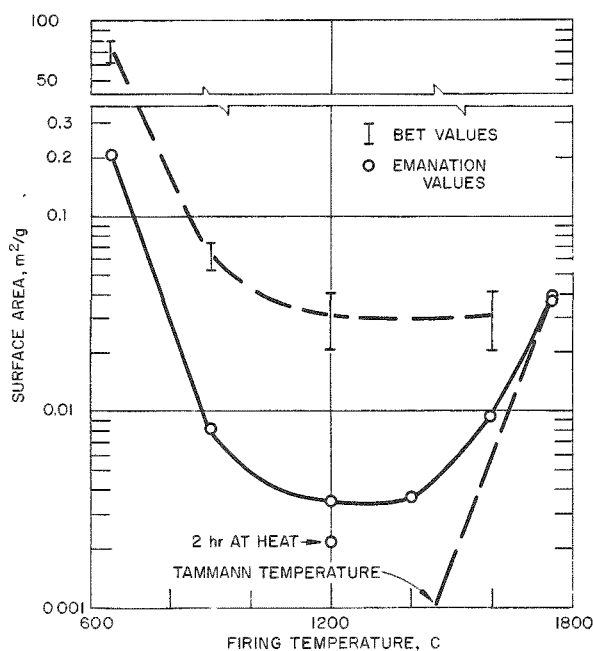
Firing at temperatures above 1500C for one hour in air, however, produced a marked increase in the emanation rates of the material observed

after cooling to room temperature, as shown in Figure 5. Chemical

analysis of this material also showed increasing losses of uranium oxide with the firing temperatures above 1500C. Samples, for example, fired at 1750C in air for one hour showed a loss of about 38 percent of the uranium

(7.30 weight percent uranium to 4.50 weight percent). G. Tammann(8) predicted for metal oxides that a lattice loosening should occur at about one-half the absolute melting point. At the lattice-loosening temperature, lattice positions are expected to be fairly rapidly exchanged, and solid state reactions become operative. This would also be expected to facilitate evaporation of volatile material out of the thorium oxide matrix. The sharp increase in emanation power observed in this material begins at a firing temperature of 0.55 times the absolute melting point of thorium oxide. The

Figure 5
SURFACE AREA CHANGE AS A FUNCTION OF FIRING TEMPERATURE FOR ThO_2-UO_2 SYSTEM (Firing Time: 1 hr)



lattice-loosening effect and the evaporation of U_3O_8 out of the particles probably combine to produce the increased emanation rates in the material which are observed at room temperature after a one-hour firing at high temperature.

Analysis of the oxygen/uranium atomic ratios on material fired at 1500C indicated that the uranium oxide was approximately the mixed oxide composition of $2UO_3 \cdot UO_2$, with the UO_2 factor generally slightly greater than unity.

In the fabrication of spherical thoria and thoria-urania microspheres, two phenomena were observed. First, the microspheres, when partially dried between 100C and approximately 200C and stored, may lose their spherical shape. The spheres, as observed in several batches under a

microscope, acquired irregular protrusions which could be discerned as the sharp corners of crystals growing in the spheres. Finally, the spheres shattered into crystalline fragments. Several attempts to repeat this phenomenon were unsuccessful. Secondly, when microspheres were fired at 650C and cooled, several batches, upon reaching room temperature, were observed to explode or pop into fragments slowly and spontaneously. This effect could be seen on a microscope slide. In one case, a slide was viewed periodically for 36 hours until, in a field of several thousand spheres originally, almost all were shattered. Additional samples of the total batch of several hundred grams of thorium oxide viewed under the microscope verified the fact that more than ninety percent of the spheres had shattered within 36 hours after cooling.

The first effect, therefore, is the result of the growth of a crystalline compound of thorium, and may possibly have been the result of incomplete elution of the nitrate out of the particles. The second effect is probably the result of physical strains left in the glassy thoria microspheres. Both difficulties were avoided by drying at 300C, then immediately prefiring to 900C before storing.

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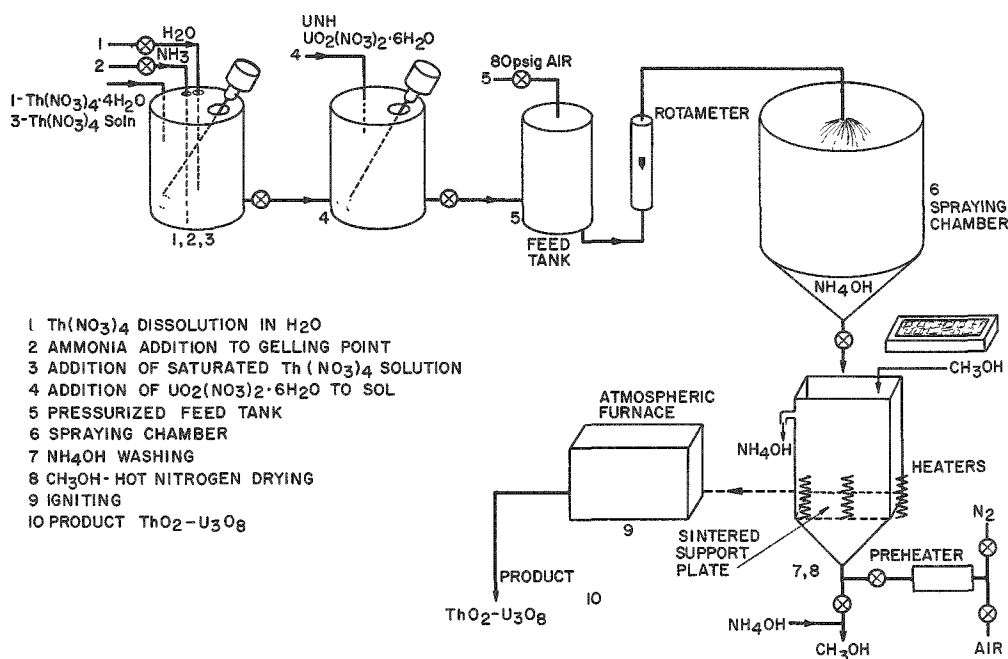
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Appendix: Semi-works Production of Spherical Particles of $\text{ThO}_2\text{-U}_3\text{O}_8$

For a study of the boiling slurry concept in a reactor test loop (one-half full scale), a program was undertaken to produce approximately 500 lb of the thorium oxide-uranium oxide spheres. Because of the urgency of the requirements, the production was undertaken in existing equipment, which, in most instances, was not particularly well suited to the specific operation performed. A schematic diagram of the equipment used is shown in Figure 6.

Figure 6

PILOT PLANT EQUIPMENT FOR THE FABRICATION OF INDIVIDUAL SPHERICAL THORIA-URANIA PARTICLES FOR A SLURRY REACTOR



A step-wise procedural account follows:

1. Dissolution of Thorium Nitrate in Water

Thorium nitrate was dissolved in water to form a nearly saturated solution. At room temperature the limit of solubility proved to be about 630 g Th /liter (2.71 M). From a consideration of the size of the available equipment (a covered stainless steel tank, 18 in. in dia and 24 in. high), the dissolution was carried out in only 30-liter batches. Because of the highly endothermic nature of the dissolution, 1500-watt tubular heaters were employed in conjunction with a $\frac{1}{3}$ -hp agitator in order to effect dissolution.

2. Preparation of Gel

Following the dissolution, anhydrous ammonia gas was introduced through a sparge line at the bottom of the tank. (As additional equipment became available, this step was performed in a covered 55-liter tank fitted with an agitator, in order to permit use of the first tank solely for dissolution.) Extremely vigorous agitation was necessary to prevent the localized formation of the extremely hard, white, opaque hydroxide which was not susceptible to ready dissolution. The exothermic nature of the reaction required that the reaction vessel be covered during this operation to reduce the loss of water as steam.

The ammonia addition was continued until such time as the entire tank contents suddenly gelled. This point was determined visually. Cursory experiments conducted to determine this gelling point by instrumentation were not successful. Production requirements precluded any extended tests which would develop the required degree of sensitivity to establish automatic control.

3. Preparation of the Sol

After the gel state had been reached and the ammonia introduction halted, thorium nitrate solution was added to the gelled mass (preferably while still warm) and manually worked into the gel with a rod. Reliquefaction was in general accomplished with surprisingly little work. The amount of thorium nitrate solution that was added in this step was approximately 2 ml/liter of gel. Because of a tendency of the sol to precipitate, about the same amount of additional thorium nitrate solution was added to stabilize the sol for extended storage. Sols prepared in this fashion were kept in covered tanks for greater than two-week periods with no precipitation occurring. The ultimate storage life under these conditions was not determined. Analyses of the sol showed a pH of the order of 3.8 and a thorium concentration of about 2.7 M.

4. Preparation of the Thorium Sol-Uranyl Nitrate Feed

Immediately prior to use, a measured quantity of uranyl nitrate hexahydrate was added to the thorium sol and dissolved by vigorous stirring with a mechanical agitator. The amount of uranyl nitrate hexahydrate added was, of course, dependent upon the desired weight percent of uranium in the final product. Upon standing at room temperature for several hours, a yellow-orange precipitate forms. This behavior dictated that (in the existing equipment) the subsequent treatment of the feed be batchwise and be limited to a process duration of about $1\frac{1}{2}$ hours.

5. Feed Processing (Spherical Particle Production)

Feed prepared as above was next transferred to a 20-liter elevated feed tank. Air at a pressure of 80 psig was applied to the tank and the feed was thereby pressured through an atomizing nozzle of the single-fluid pressure type (Spraying System Co. $\frac{1}{4}$ LN-3). The feed was maintained at a constant flow rate by means of a Moore Flow Controller at 250 ml/min. The spraying was done into the top of a closed tank, 3 ft in diameter and 4 ft high, with a conical bottom and containing an ammonia atmosphere. The ammonia atmosphere was provided by charging the vessel with ~45 liters of 12 M ammonium hydroxide solution. Operations were viewed through a Lucite window in the side of the vessel.

With sol made as described above, this arrangement provided in the 28-cu ft (free volume) tank sufficient ammonia vapor to complete the gelling of the individually produced atomized particles and sufficient free-board to insure their continued sphericity after contact with the vessel wall. It should be mentioned that too much ammonia vapor in the tank invariably caused nozzle plugging; too little ammonia vapor was insufficient to cause gelling of particles individually, and a coalesced conglomeration resulted. The properly gelled particles collected in the conical bottom, falling through the ammonium hydroxide in the process. This served to partially wash excess ammonium nitrate from the particles and also to exclude air from them. (It was found that upon exposure to air, the particles would undergo drastic degradation.) The collected particles in the bottom of the process tank were withdrawn periodically by opening a 1 $\frac{1}{2}$ -in. plug valve in the discharge line from the tank.

If temporary storage was required before further processing, the particles were stored in polyethylene bags under a dilute ammonium hydroxide solution. Particles so stored maintained their integrity and sphericity for as long as two weeks although, in general, further processing was performed within a day or two of the initial production.

6. Washing and Drying Procedure

The particles were next transferred to a four-sided container (1 ft sq) which served as a washing and drying facility. A sintered metal section was welded inside the unit to serve as a support plate for the particles. This plate was about 18 in. from the top and above a tapered pyramidal section at the bottom. A pipe nipple welded through a wall at a point about 2 in. from the top acted as a liquid overflow pipe. A covering top was fabricated incorporating a sintered metal section about ten inches square. Two 1000-watt band heaters were fastened around the vessel above the support plate to supply heat for drying.

Dilute ammonium hydroxide solution was introduced slowly through the bottom of the vessel to wash the solids by upflow. Approximately

8 volumes of dilute hydroxide solution were used in backwashing the spherical particles. Because the spheres were still extremely delicate during this operation, gentle hand manipulation was used to agitate the solution and suspend the particles momentarily during the backwashing, thereby insuring excellent washing of the individual particles. In addition, by careful control of the hydroxide flow, minute particles were elutriated from the product before further processing.

Following the backwashing step, the supernatant hydroxide was siphoned from the container and the residual hydroxide removed by gravity. During this step, the particles became quite tightly packed, and it was found expedient to force air alternately through the bed from the bottom and then allow hydroxide to flow out. Vacuum removal of the hydroxide from the bottom was found to distort the particles and was not used.

Methanol, added from the top, was used as a rinse for the ammonium hydroxide. Approximately four volumes were used, the first of which was discarded after use - the others being recycled in order in succeeding runs. The final rinse was thus with fresh methanol in each run.

The overflow outlet was next capped and the cover placed on the vessel. As a safety precaution, flexible ventilation ductwork was extended over the vessel prior to the next step. Heat was then applied to the vessel by means of the bond heaters and preheated nitrogen (to preclude explosive mixtures of air and alcohol) was forced through the bed from the bottom at ~110C. This phase of the drying operation took about seven hours per batch (~6 kg).

7. Igniting

As soon as possible, the spheres were removed from the tank and transferred to an atmospheric furnace where the spheres were placed in shallow trays and slowly fired* to 1500C.

8. Sizing

A Fisher Sub-Sieve Sizer was used to determine the diameter of the fired spheres. The average diameter was determined in a series of tests to lie between 14 and 23 microns. The spheres before firing average about 60 microns. Optical observations of the fired spheres showed that the bulk of the particles retained their spherical shape.

*Work performed under J. H. Handwerk of Metallurgy Division, ANL.