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ASSESSMENT OF GEL-SPHERE-PAC FUEL FOR FAST BREEDER REACTORS*

Compiled by

W. J. Lackey and J. E. Selle

ABSTRACT

Recent interest in proliferation resistant fuel cycles for the Fast Breeder Reactor Program has focused attention on spiked plutonium and ^{233}U-Th fuels, which will require remote fabrication after reprocessing. For the gel-sphere-pac process all operations through rod loading deal with either liquids or spheres that are easily transferred by pneumatic methods in a relatively dust free fashion; fewer mechanically intensive steps are involved compared with pellet fabrication. For these reasons, the gel-sphere-pac process has advantages to consider for the remote operations that may be required for fabricating fast breeder reactor fuels. Therefore, an assessment of the state of the art for the gel-sphere-pac process was undertaken to provide a sound basis for further development of the technology.

Information is provided on sol preparation, sphere forming, drying, sintering, characterization, loading, fuel rod inspection, and irradiation performance. In addition, discussions are included on: evaluation of the potential for scale-up to production capacities, potential problems associated with remote operation, and future work required to further develop the technology.

Three techniques are available for microsphere production: (1) internal gelation, (2) external gelation, and (3) gelation by water extraction. Each has its own advantages and disadvantages; for example, internal gelation appears better suited to the preparation of large spheres than the other processes. Numerous advantages and disadvantages are discussed in detail. Scale-up or remote operation of these techniques appears achievable, although some would require less development than others.

Techniques have been developed for drying and sintering spheres. Extensive technology has been developed for sphere characterization, handling, and the loading and inspection of fuel pins.

Data available to date indicates that sphere-pac oxide fuel will perform similarly to pellet oxide fuels under fast breeder reactor operating conditions. Gel-sphere-pac technology also appears attractive for carbide fuels.

Considerable development work is required before the process can be accepted for breeder reactor fuel cycles. However, the flexibility of the gel-sphere-pac process coupled with the emphasis on advanced and alternative breeder reactor fuel cycles suggests that the process has potential for future application.

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*Work performed under DOE/RRT 189a OH145, Alternative Fuel Development.

1. INTRODUCTION

W. J. Lackey

The objective of this report is to provide an up-to-date, comprehensive assessment of U.S. and foreign gel-sphere-pac technology pertinent to breeder reactor oxide and carbide fuels. A similar report[1] has been prepared for light-water reactor fuels. The gel-sphere-pac route for fabrication of fuel rods is an alternate to the more conventional pellet approach. Gel-sphere-pac technology is not new but is currently receiving emphasis for a variety of reasons described later. In the gel-sphere-pac process, high-density fuel spheres of several sizes are produced, and these are subsequently loaded, with the assistance of vibration, into the fuel rod cladding.

The major steps in the process are shown schematically in Fig. 1.1. In the technology developed previously at Oak Ridge National Laboratory,[2] the first step in preparing fuel microspheres consisted of forming a sol (an aqueous suspension of extremely small actinide crystallites) and then gelation of sol droplets by withdrawing water — the so-called water extraction sol-gel process. More recent technology does not use a true sol but instead forms spheres by directly gelling the appropriate actinide nitrate solution, which, because of its organic additives, is sometimes called a broth. Because of this difference, the newer technology is referred to as gel-sphere-pac rather than sol-gel sphere-pac. After the sol or broth is prepared, gelation is accomplished by one of two methods: (1) ammonia gelation, in which the liquid droplet gels as a result of the precipitation of ammonium diuranate when the droplet is exposed to ammonia or (2) water extraction, in which the liquid droplet gels or becomes rigid as water is extracted from the droplet by contact with alcohol in a sphere-forming column. For ammonia gelation the ammonia may be supplied either externally, via ammonia gas and ammonium hydroxide, or internally via a chemical additive to the broth, which liberates ammonia as the droplet is heated by the liquid

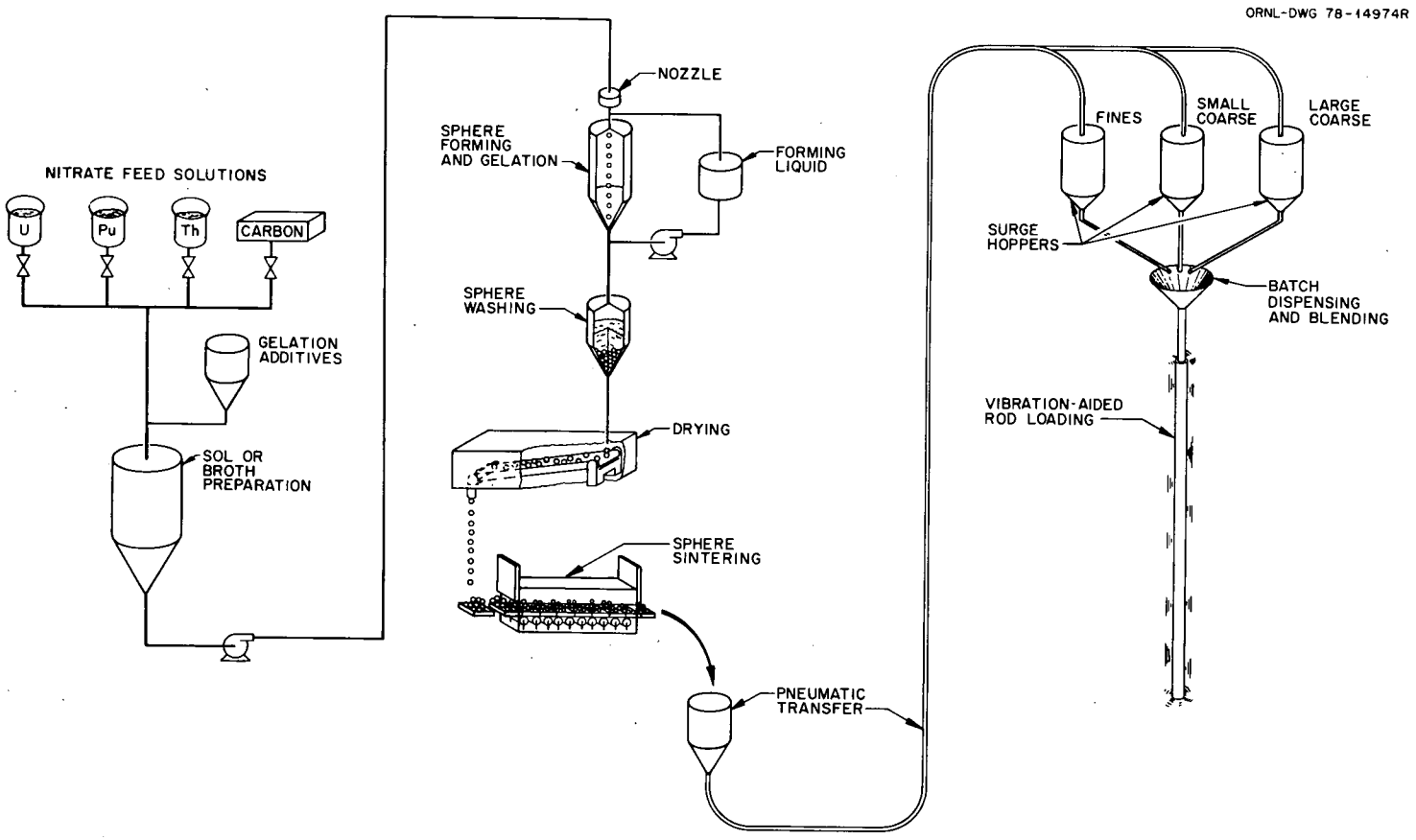

Fig. 1.1 Major Steps in the Gel-Sphere-Pac Process

in the sphere-forming column. When internal gelation is used, the gelation reaction is forced to completion by subsequent contact with ammonium hydroxide. After washing and drying, the spheres are sintered to high density.

With the sphere-pac process, two or three sizes of fuel spheres are vibratorily compacted into the cladding. Three sizes of spheres having diameter ratios of about 40:10:1 are required to achieve about 88% smear density. Thus, the maximum and minimum diameters are of the order of 1000 and 25 μm, respectively. When only two sizes are used, the maximum smear density is less than 85%. Several loading schemes can be visualized. Two important ones consist of either infiltrating the smallest size down through a bed of the remaining larger spheres or simultaneously loading all sizes into the cladding as a mixture. All the fissile material may be incorporated into the larger spheres; that is, the fines contain only fertile material. This so called fertile fines method is the preferred approach.

1.1 HISTORY

The sphere and sphere-pac concepts were originated in the U.S. almost 20 years ago. Sol-gel sphere-pac technology was vigorously pursued in the U.S. until June 30, 1972. At that time, the U.S. fast breeder reactor program concentrated on pellet fuel, and government support for microsphere fuel for breeder reactors was terminated. The state of the technology at that time was thoroughly reported.[2] Laboratory-scale capability existed for the fabrication and characterization of $(U,Pu)O_{2-x}$ fuel rods, and 60 rods were successfully irradiation tested. Since 1972, particulate fuel technology has been advanced on two fronts. First, sol-gel development of UO_2, $(Th,U)O_2$, and ThO_2 continued as a part of the U.S. and European efforts to develop spherical fuels for the High-Temperature Gas-Cooled Reactor.[3-5] Extensive progress was made regarding sphere formation processes, control of sphere size, and sphere handling, transport, and inspection. Also, breeder reactor and light-water reactor development efforts in England, Germany, Italy, Switzerland, and the Netherlands have contributed

significantly to gel-sphere-pac technology for both oxides and carbides. European achievements were most notable in three areas: use of hexavalent uranium, gel support via added organics, and chemical gelation by precipitation to produce large microspheres of UO_2.

1.2 JUSTIFICATION OF GEL-SPHERE-PAC

Continued development of gel-sphere-pac technology is justified for a variety of reasons. Recent interest in nonproliferation-type fuel cycles has focused attention on spiked plutonium and ^{233}U-Th fuels. These fuels will require remote refabrication following reprocessing, and the gel-sphere-pac processes and equipment appear amenable to remote operation because all operations deal with either liquids or spheres that are easily transferred by pneumatic methods in a relatively dust free fashion. In addition, the process requires fewer mechanically intensive steps than the pellet process. Also, the trend toward lower allowable radiation doses to operating personnel may lead to selection of a process for unspiked plutonium fuels having less dusting or to remote operation. In either event, the gel-sphere-pac approach is potentially attractive.

1.3 CONTENT OF REPORT

This report is organized into various technical areas in which development has occurred. These include sphere preparation, sintering and characterization, loading and inspection, and irradiation performance. Each step in the process is analyzed from the viewpoint of engineering evaluation and remotization. In addition, there are sections on the status of technology and future work required to further develop the technology.

1.4 REFERENCES

1. R. L. Beatty, R. E. Norman, and K. J. Notz, comps., *Gel-Sphere-Pac Fuel for Thermal Reactors — Assessment of Fabrication Technology and Irradiation Performance*, ORNL-5469 (in press).
2. A. L. Lotts, comp., *Fast Breeder Reactor Oxide Fuels Development — Final Report*, ORNL-4901 (November 1973).

3. P. R. Kasten, General Chairman, *Gas-Cooled Reactors: HTGR and GCFBR*, American Nuclear Society Topical Meeting, Gatlinburg, Tennessee, May 7-10, 1974, CONF-740501.
4. A. L. Lotts and P. R. Kasten, *Gas-Cooled Reactor Programs, Thorium Utilization Program Prog. Rep. July 1, 1975–Sept. 30, 1976*, ORNL-5266 (July 1977).
5. A. L. Lotts and P. R. Kasten, *Gas-Cooled Reactor Programs, HTGR Fuel Recycle Development Annu. Prog. Rep. Sept. 30, 1977*, ORNL-5423.

2. SPHERE FABRICATION

2.1 INTERNAL GELATION — J. M. Begovich

The internal gelation process, often termed the KEMA* process, will be discussed initially as it pertains to the production of UO_2 spheres.

The formation of spheres by internal gelation uses a water-soluble chemical that when heated releases ammonia to precipitate the heavy metal to form a gel. Since the ammonia donor and the heavy metal ions are dissolved in the same solution, the gelation occurs rapidly and nearly uniformly throughout the drop. The rate depends on the solution concentrations and heat transfer into the drop from the hot immiscible liquid used to suspend the drops.

The internal gelation process generally requires the preparation of a broth containing an acid deficient solution of the heavy metal and an ammonia donor solution of urea and hexamethylenetetramine (HMTA). The broth is pumped through a dispersion device that forms spheres, which are then gelled in a hot organic medium. The organic medium is then washed off with a suitable solvent (e.g., CCl_4), and the spheres are washed with ammonia (NH_4OH) to remove HMTA, urea, and ammonium nitrate (NH_4NO_3). The spheres are then dried, calcined, and sintered in a reducing atmosphere to obtain spheres of 99% of theoretical density (T.D.).

2.1.1 Broth Preparation

The 3 *M* acid-deficient uranyl nitrate (ADUN) solution for the broth can be prepared[1] in a number of ways (the NO_3^-/U mole ratio should be 1.5):

1. adding UO_3 to a substoichiometric amount of nitric acid (HNO_3) or to a stoichiometric amount of uranyl nitrate.
2. adding U_3O_8 to a substoichiometric amount of HNO_3.
3. adding UO_2 to a substoichiometric amount of HNO_3.
4. amine extraction of acid from uranyl nitrate.

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*Keuring van Electrotechnische Materialen at Arnhem in the Netherlands.

For method (1), moderate heating can increase the dissolution rate, but too high a temperature should be avoided since $UO_3 \cdot 0.8H_2O$ can appear as a precipitate. ORNL experience indicates that 60°C is a reasonable temperature. For method (4), a 1 *M* uranyl nitrate solution should be used to minimize uranium losses. After the extraction, the 3 *M* ADUN solution is obtained by evaporation.

The broth is obtained by mixing 1 volume of the 3 *M* ADUN with 1.4 volumes of a solution that is 3 *M* in HMTA and urea. Under acid conditions, HMTA hydrolyzes to form ammonia and formaldehyde. To prevent premature gelation, two steps are taken:

1. maintaining the broth at a low temperature (-5 to 0°C) to reduce the decomposition rate of HMTA,
2. addition of urea to complex the uranyl ions (UO_2^{2+}) and "protect" it from the slowly decomposing HMTA.

At a temperature of -5°C, the broth is said to have a shelf life of 24 h. The shelf life is considerably shorter at higher temperatures (e.g., a few minutes at 15°C and a few seconds at 60°C). Our experience indicates that if a temperature greater than 5°C is allowed during mixing, premature solidification will occur in less than an hour even if the broth is subsequently cooled. Separately, the ADUN and ammonia donor solutions have indefinite shelf lives.

In one continuous process developed by KEMA and applied by ECN at Petten,[2] the urea and HMTA solution, kept at -5°C, was mixed with the ADUN solution, which was kept at about 2°C, in a volume (and molar) ratio of 1.4 to obtain a broth with a uranium molar concentration of 1.25 and a temperature of -3°C. To achieve theoretical density by use of this broth, the beads will have to linearly shrink by a factor of 3.2 from the diameter of the original gelled spheres. Thus, if final diameters of 800 μm are desired, the initial gel spheres must have diameters of 2550 μm. This initial bead diameter can be reduced if the broth has a higher uranium concentration.

Possible methods to achieve a higher uranium concentration in the broth include (1) adding solid urea to the ADUN such that the urea-to-uranium molar ratio is 1.4, and (2) adding solid HMTA to the ADUN such

that the HMTA-to-uranium molar ratio is 1.4, or (3) adding a slurry of HMTA and water to the ADUN. In the last option, just enough water is added to the HMTA to remove some of its heat of hydration (e.g., 0.5 liter to 1 kg HMTA). KEMA considered the last option but decided against it — most probably because of the difficulty in handling the HMTA slurry in a continuous process. Also, the entire heat of hydration is apparently not removed until enough water has been added to make the slurry a solution very nearly 3 *M* in HMTA.

The molar ratios of HMTA and urea to uranium can be varied[3-6] over a fairly wide range: 0.75 to 2.3. However, too low an HMTA concentration yields soft spheres, which have a tendency to repeptize, while too high an HMTA concentration can yield spheres with very small crystallite sizes, which present problems later in the washing and drying stages.

2.1.2 Sphere Forming and Gelation

The cold broth (-5 to +5°C) is pumped to a disperser, which forms drops of the required size in a hot organic liquid. Details of the drop formation process are described in Sect. 2.4. In the hot liquid, the rate of HMTA decomposition overcomes the urea-uranyl ion complex and causes the precipitation of ammonium diuranate, resulting in the gelation of the drops.[1] The role of the urea then changes, with a urea-formaldehyde polymer responsible for enhancing the HMTA decomposition rate and gelling the spheres. Various organic liquids and temperatures are used, depending on the desired sphere size.

2.1.2.1 Production of Large Spheres[1]

To produce dense 1000-μm-diam UO_2 spheres, KEMA used air pressure to force the broth through a capillary. Free formation of the drops in air was allowed, with the spheres then dropping into a paraffin oil-perchloroethylene (perc) mixture kept between 85 and 90°C. The organic mixture,[7] with a specific gravity of 1.4, was composed of Shell Ondira Oil No. 33 (20%) and perc (80%). A small amount of surfactant (0.02 vol %) was added to the organic mixture to help prevent drop clustering or sticking. The drop size uniformity was not

good, with the standard deviation being 65 μm. Using 12 nozzles achieved a production rate of 15 mol U/h. The drops gelled in a few seconds (<10 s) but after 2.5 min were still only softly gelled.

The choice of organic medium for the sphere-forming column is limited. A high liquid density is required to minimize the density difference between the sphere and the liquid so that true spheres are obtained, and the liquid must be nonvolatile enough to use at the gelation temperature. Although trichloroethylene (TCE) has a boiling point of 87°C, we have used it as the organic medium at temperatures ranging from 65 to 80°C. We have also used perc (bp = 121°C) as the organic medium. Both liquids gave good hard, smooth, spherical beads and a good sintered product. The best overall product was produced in TCE. Use of either is advantageous since they are volatile enough to be easily removed from the bead surface. A potential disadvantage may be possible chlorine contamination of the final product, although this has not been a problem in our work. A further disadvantage of the perc is its density — the uranium concentration of the broth must be greater than 1.55 *M* so that the spheres will not float on top of the organic.

Silicone oil at 85 to 95°C has been used at EIR, in Würenlingen, Switzerland, as the organic medium.[6] The particular brand, Dow Corning DC-200, 100 cS silicone oil, has a specific gravity of 0.9 and a viscosity of 36 mPa s (cP) at 90°C. The high viscosity of the liquid compensates for its low density and thus still allows the formation of true spheres. In fact, EIR suggests that as long as the sphere Reynolds number is less than 10, a true sphere can be formed. A disadvantage of the silicone oil is the possible silicon contamination of the final product.

2.1.2.2 Production of Medium-Size Spheres[1]

For the production of 100-μm-diam UO_2 spheres, KEMA used either spray nozzles or spinnerettes. The droplets, formed in air, were collected in a horizontally flowing stream of DOBANE PT 12 (a mixture of branched aliphatic, aryl-substituted hydrocarbons) at 80 to 99°C. When vibrated spray nozzles were used, the standard deviation was

40 μm, with a production rate up to 5 kg UO_2/h per nozzle. The standard deviation was reduced to 10 μm when the spinnerette was used.[7] A straight paraffin oil was used for this size fraction to give a low enough density to allow settling of the gelled particles.

The same system used for the large coarse fraction could also very likely be used for 200-μm-diam spheres. Multiple nozzles may be required to obtain the necessary production rate, but vibrated two-fluid nozzles should be able to form very uniformly the 640-μm-diam wet gelled spheres needed to obtain the final sintered diameter of 200 μm.

2.1.2.3 Production of Fines[1,2]

To produce 10-μm-diam fines, KEMA used an emulsion technique. The broth was stirred to disperse droplets in cold (0-5°C) Freon 113, which has a high enough density to float the spheres. The Freon was then warmed to 40°C, gelling the spheres. The mixture was then pumped into the bottom of a hot (60°C) NH_4OH (pH = 9.5) column, at which temperature the Freon (bp = 45°C) evaporated.

The disperser used was an ultrasonic vibrator. It gave the proper size but with a widely distributed size fraction. The solution, viscosity, and dispersion technique are all problems for the production of 10-μm-diam spheres. Using the volatile Freon 113 eliminates the problem of washing off the organic liquid; however, other problems still exist (i.e., washing of HMTA, urea, and NH_4NO_3, drying and sintering).

It is possible to produce the fines fraction by use of a turbulent shear nozzle to form the spheres and 2-ethylhexanol or trichloroethylene as the gelation liquid. Whatever method is used, the rate of production will likely be low if uniformity is to be achieved.

2.1.3 Washing

Washing is a critical step in the production of spheres. Improperly washed spheres will fail during drying or sintering. KEMA feels that only 5% of the HMTA decomposes during gelation and that the remaining 95% is recovered during washing, while the spheres complete their precipitation through reaction with NH_4OH.[2,7] The actual amount

of HMTA left unreacted in the spheres is probably lower than 95%, since some of the HMTA recovered in the washing step is reformed by the reaction between ammonia and the formaldehyde formed when the HMTA decomposed during gelation.

Under proper gelation conditions, the spheres produced are opaque.[7] Transparent spheres have too small a crystallite size and too high an osmotic pressure imbalance to wash out the excess ammonia, NH_4NO_3, urea, and HMTA. Such spheres crack during either drying or sintering. The opaque spheres have a large enough crystallite size to allow the urea, HMTA, and NH_4NO_3 to be easily washed out.

KEMA washed for 1 to 2 h at 40°C in two countercurrent washes of dilute ammonia (pH = 8.5) with a surfactant added to remove any organic phase present.[7] Alternatively, CCl_4 could be used to remove the organic before washing with NH_4OH, but then chlorine contamination of the beads is possible.[6] Enough NH_4OH was used[1] to keep the solution between spheres at or above a pH of 8.5. When the large spheres are washed, care must be taken to maintain the correct pH to avoid large osmotic pressure imbalances. The rate of washing of the large spheres appears to be limited by the mass transfer inside the spheres in that longer washing times are required as the particles get larger. Wash temperatures higher than 40°C should be avoided since higher temperatures degrade the product, allowing soft spheres to stick together. At EIR washing is monitored for completeness by conductivity measurements.[6]

When the fines are washed, care must be taken to eliminate channeling through the bed of spheres. At KEMA, the fines were washed in hot (60°C) NH_4OH at a pH of 9.5.[2] Then it was difficult to separate the fine spheres from the wash solution. The use of a centrifuge did not work well, as the spheres tended to be pressed together. An improved solids-liquid separator will clearly be needed for the large-scale production of fine spheres.

2.1.4 Drying

The spheres are dried in air at temperatures ranging from room temperature to 170°C. KEMA[1] dried its spheres at 70 to 80°C. In the

continuous process line at Petten, KEMA workers loaded the spheres, separated from the wash liquid, onto trays, which then were placed in a moving belt drier. The dried spheres had a porosity of 54% as measured with nitrogen adsorption and an average crystallite size of 10 to 15 nm. The linear shrinkage from the formed sphere to the dried sphere was a factor of approximately 1.6.

On a laboratory scale it is very convenient to dry in either of two ways: (1) overnight in an oven, or (2) overnight, using vacuum to pull air through the beads. If the spheres survive the drying stage, they will normally not crack during the remaining steps. The rate of drying must be limited to allow the water time to escape from the spheres without producing cracks.

2.1.5 Calcining and Sintering

The available information on calcining is somewhat confusing. In 1970 KEMA mentioned no calcining step.[8] Air-dried spheres went directly into an oxygen-free, dry mixture of N_2–20% H_2 at 1400°C. In 1973, KEMA reported[1] calcining in air at 450°C to remove the volatile organics. The heating rate was 200 to 300°C/h. Then KEMA switched to a reducing atmosphere and heated at a rate of 10 to 65°C/min to a maximum temperature of 1600°C for 6 h.

Recent information indicates still another procedure in use at KEMA.[2,7] After drying, the spheres are heated to 500°C in a mixture of nitrogen and hydrogen. Then the spheres are sintered in the reducing atmosphere of nitrogen and hydrogen at 1600°C, although 1500°C may be high enough. During calcining it is important that U_3O_8 not be formed, since this leads to porous UO_2.

Although KEMA has apparently recently decided to go directly to a reducing atmosphere after drying, previous work on a continuous process at Petten used an air calcination step at 350°C after drying. During this calcination considerable organic material was driven off, giving UO_3 as the product. Reduction was then achieved by using a nitrogen-hydrogen atmosphere up to 1600°C. The large spheres required a gentle temperature gradient over the range 500 to 900°C. By this method, the

pilot plant produced 500 kg of the large spheres (∿1000 μm), with a design rate of 4 kg UO_2/h and 20 kg UO_2/shift.

It appears that the key to whether an air calcination step is required is whether all the organics have been removed during washing. If they have been removed, then an air calcination step is not necessary and in fact may be undesirable since the formation of U_3O_8 is to be avoided. However, if all the organics have not been removed during washing an air calcination step becomes necessary, and care must be taken during calcination to ensure that temperatures do not exceed 600°C to avoid the formation of U_3O_8. As a backup to the washing step, it may well prove desirable to include an air calcination step in the overall process.

2.1.6 Application to UO_2

KEMA produced smooth spherical particles that were 99% theoretically dense (T.D.).[1] The carbon and chlorine contents were each below 10 ppm, and metal impurities met accepted nuclear standards. The production rate per nozzle for the large spheres (1000 μm diam) was 340 g UO_2/h. A total of 500 kg of the large spheres was produced in the pilot plant at Petten. The total amount of the small coarse and fine fractions produced has not been disclosed; however, enough of each was produced to load fuel rods for irradiation testing.[2]

The Hydrolysis Process,[5,9,10] developed by the Institute for Reactor Materials at KFA, Jülich, differs in a few aspects from the KEMA process. Urea and HMTA are added as solids to a uranyl nitrate solution in molar ratios of 2.0 and 2.33, respectively. The reaction mixture is dispersed into droplets from a cooled two-fluid nozzle into paraffin oil at 90°C. The spheres are washed of paraffin oil with petroleum ether, which is followed by washing with NH_4OH for several hours to remove NH_4NO_3, urea, and HMTA. This last washing step and subsequent steps must be performed in a CO_2-free atmosphere to avoid the formation of soluble U(VI) carbonate complexes. After drying in air from room temperature to 70°C, the spheres are heated at a controlled rate to 1300°C in a flow of Ar-4% H_2 and sintered at 1300°C for 5 h. Spheres with diameters

between 100 and 900 μm were prepared in this manner, with a typical batch having the following properties: sphere diameters of 750 ± 50 μm, porosity of 0.7%, and 99% T.D. Intermediate sized spheres, 200 μm diam, were prepared in a pilot plant at the rate of 100 g UO_2/h per nozzle by use of six vibrated nozzles with diameters of 250 μm. These particles were sintered in hydrogen at 1200°C and then up to 1700°C and yielded spheres with diameters of 210 ± 30 μm and 98% T.D.

The Transuranium Institute at Karlsruhe has also made 100- to 1000-μm-diam UO_2 microspheres by the general KEMA process.[3-4] The reaction mixture was prepared by adding 3 *M* HMTA and urea solution to 3 *M* ADUN in molar ratios ranging from 0.75 to 1.25. If either the urea or HMTA was omitted or if the ratio of HMTA to urea differed appreciably from 1.0, the process failed. The broth was dispersed into a paraffin oil-perc mixture with a specific gravity of 1.4 at temperatures between 85 and 97°C. The spheres were washed first with CCl_4 to remove the oil and then with NH_4OH to remove the NH_4NO_3, urea, and HMTA. The beads were dried either in air at room temperature or under vacuum at elevated temperature; no difference in the final product was found. Then the spheres were reduced and sintered in a N_2-8% H_2 atmosphere, heated at a rate of 300°C/h to 1400°C, and held for 3 h. Densities of 99 to 100% T.D. were obtained with a carbon content of less than 200 ppm. If the spheres were sintered to only 1200°C, densities were only 96 to 98% T.D.

2.1.7 Application to Other Oxides

Apparently the internal gelation process has never been applied to ThO_2 and only briefly applied to $(Th,U)_2$ at KEMA. The KEMA work used the same recipe for the mixed oxide as for pure UO_2. Uranium contents up to 50% were studied. The process has also been applied to $(U,Pu)O_2$ at several places.

KEMA planned to use the same chemistry for uranium-plutonium mixtures that it used for pure urania.[2,7] Just enough work with plutonium was done at Petten to include it in patents. Plutonium was added to the ADUN used for the large coarse size fraction, making up about 6% of the solution. The spheres were produced in a small glove box at a maximum rate of 2.5 kg/d per nozzle. The only change in the process came in the calcination step, where the spheres were exposed

to air at 700°C to purposely encourage the formation of U_3O_8. Acceptable product was obtained when these spheres were then sintered at 1600°C in a nitrogen-hydrogen atmosphere.

The KFA hydrolysis process was modified[5] to produce $(U,Pu)O_2$ spheres over the size range of 100 to 1000 μm. The experimental work was actually performed at EIR in Würenlingen, Switzerland. The process was similar to that described[6] for EIR. The HMTA and urea were added as solids to a uranyl nitrate solution, which was then mixed with a plutonium nitrate solution to give final molar ratios of Pu/(U + Pu) = 0.1, urea/(U + Pu) = 2, and HMTA/(U + Pu) = 2.32. The reaction mixture was dispersed into silicone oil at 80 to 90°C. The spheres were allowed to age for 30 min in the hot oil before washing in water at 95°C followed by NH_4OH at 25°C. After drying in air at 70°C, they were calcined in argon at 450°C. Reduction and sintering were done in an argon-hydrogen atmosphere by heating at a rate of 210°C/h to 1460°C and holding for 5 h. High-density spheres were generally obtained with a single-phase structure. However, some spheres had single large spherical holes, which may have been caused either by incomplete degassing of the feed solutions or by radiolytic gas bubble formation during gelation.

Plutonium-uranium oxides have also been prepared at GWK,* KFZ, Karlsruhe.[11] Uranium and plutonium nitrate solutions are mixed in the ratio desired and denitrated by the addition of formaldehyde. After urea and HMTA are added, the broth was dispersed into perc at 90°C, causing the spheres to gel in a few seconds. The perc was then removed by evaporation, after which the NH_4NO_3, urea, and HMTA were washed out with dilute NH_4OH. The spheres were air dried at temperatures up to 170°C and then reduced and sintered in a nitrogen-hydrogen atmosphere at 1450°C. This last stage took 14 to 18 h, including the cooling period. The resultant spheres attained 99% T.D. with less than 2% being rejected for scrap. The standard deviation for the 1000 μm size was

*Gesellschaft für Wiederaufarbeitung von Kernbrennstoffen mbH, Kernforschungzentrum, Karlsruhe, Germany.

150 μm. The carbon content was less than 5 ppm, chlorine less than 25 ppm, fluorine less than 10 ppm, and water less than 2 ppm. The broth could be used either with or without nitrate deficiency.

The European Transuranium Institute at Karlsruhe adapted the KEMA process to the production of $(U,Pu)O_2$ spheres.[3] A 2.5 *M* PuO_2 sol was first prepared by precipitating $Pu(OH)_4$ from $Pu(NO_3)_4$ with NH_4OH. The hydroxide was washed and then dispersed in water and HNO_3 to obtain NO_3^-/Pu molar ratio of 1.5. After a few hours of heating at 90°C and stirring, a dark green sol was formed and could be concentrated to 2.5 *M*. This sol was then mixed with 3 *M* ADUN. Any precipitate formed redissolved after the addition of solid urea and HMTA. The reaction mixture was then dispersed into a paraffin oil and perc mixture at 70 to 75°C. Cluster formation of nonsolidified drops was a major problem, but the clusters were dispersed when washed with CCl_4 followed by dilute NH_4OH. The spheres were air dried at 110°C for 14 h, then reduced in a nitrogen-hydrogen atmosphere at 800°C. This heat treatment also produced a considerable amount of water and organic material, so that a good gas flow was necessary. The spheres were then sintered in the reducing atmosphere for 3 h at 1650°C. The densities of the final spheres ranged from 87 to 94% T.D., with carbon contents of about 40 ppm. The process was capable of producing spheres with diameters ranging from 60 to 1500 μm.

2.2 EXTERNAL GELATION — R. D. Spence

The external gelation technique has been called the gel-support precipitation technique. The original gel-support precipitation method was the Italian SNAM process. Though developed in 1962, this method was first published[12,13] in 1970. The distinguishing feature of this method 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 sphere 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 spheres gelled. A block diagram in Fig. 2.1 illustrates the different process steps in the SNAM process that are discussed in the following sections. Figure 2.2 illustrates the process flowsheet developed for continuous production using the SNAM process.

Although the Italians developed the SNAM process, HOBEG* and KFA-Jülich in Germany and Harwell in Great Britain use gel support precipitation processes.[2,7,10,14-16] Figures 2.3 and 2.4 illustrate the process flowsheets developed by KFA for continuous production of thorium-containing spheres. KEMA in the Netherlands also used an external gelation method, but had difficulty producing particles greater than 100 μm in diameter.[17-19] KEMA prefers its internal gelation process described in Sect. 2.1. In addition, KFA is working toward elimination of the water-soluble organic polymers.[2,7]

The SNAM-type process development status can be gleaned from the conclusions of a 1970 report.[13]

1. The main aspects which make the process particularly attractive are:
   a. The feed is a solution, which must be neither reduced nor denitrated.
   b. Spheres can be obtained with a nominal diameter chosen in a wide range (150–1100 μm) with low dimensional dispersion (±3%).
   c. The UO_2 product density can be controlled in a wide range (70–98% TD) and high crushing strength values and oxygen-to-metal ratios lower than 2.005 are obtained.
   d. The heavy metal losses in the different process steps are practically negligible.
2. The process has been successfully tested on a pilot plant scale basis to produce any combination of thorium, uranium and plutonium oxide mixtures.
3. A continuous production technique has been successfully established by direct and in glove-box operation of different pilot plants.
4. The pilot plant operation is automatically performed and only a minor surveillance is therefore required.
5. The know-how hitherto acquired on the pilot plant operation makes it possible to employ the process on an industrial scale basis.
6. At the present development status, the gel supported precipitation process is economically competitive in comparison with other processes.

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*Hochtemperaturreaktor-Brennelement Gesellschaft.

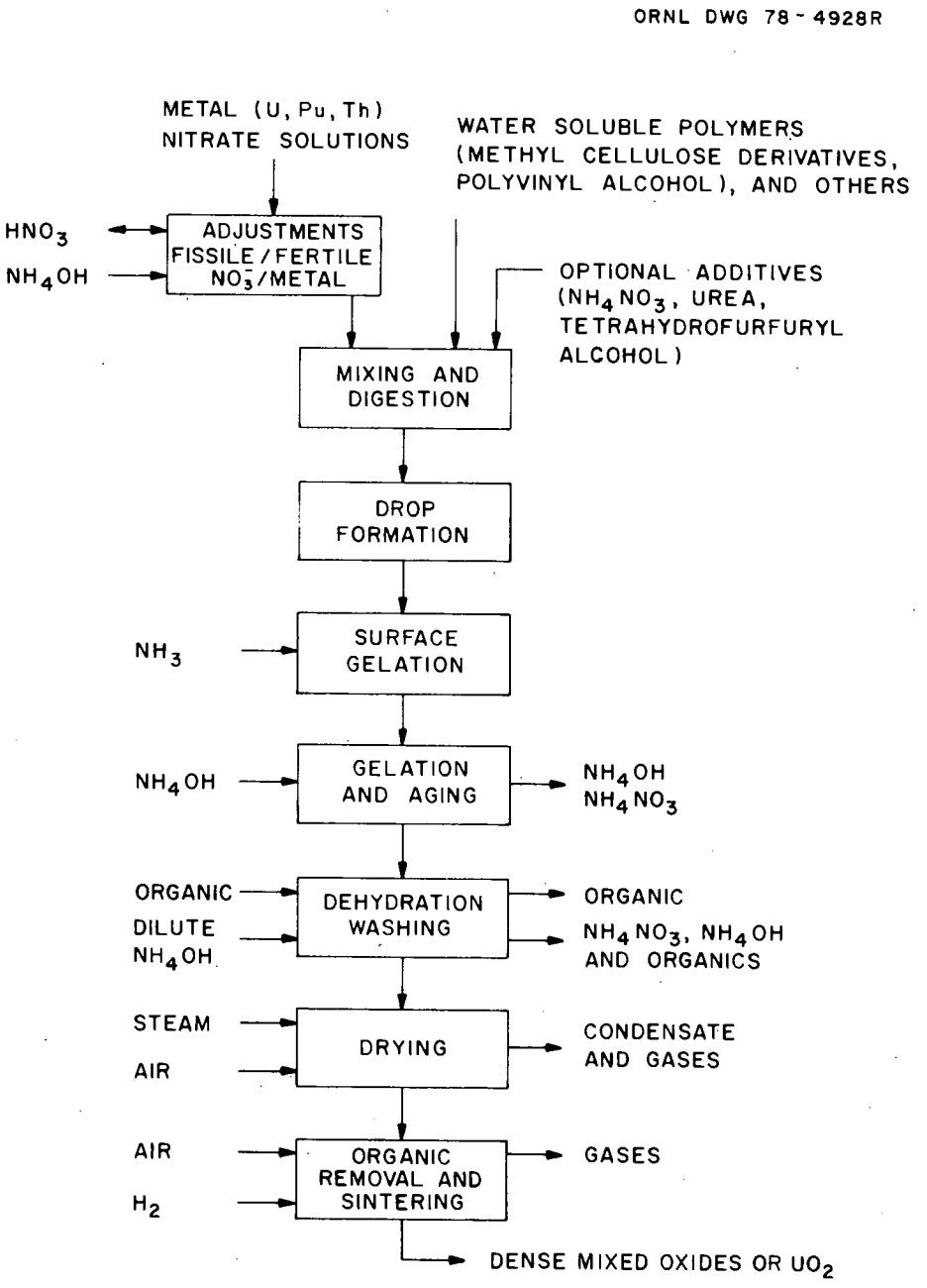

Fig. 2.1. Sphere Preparation by External Gelation.

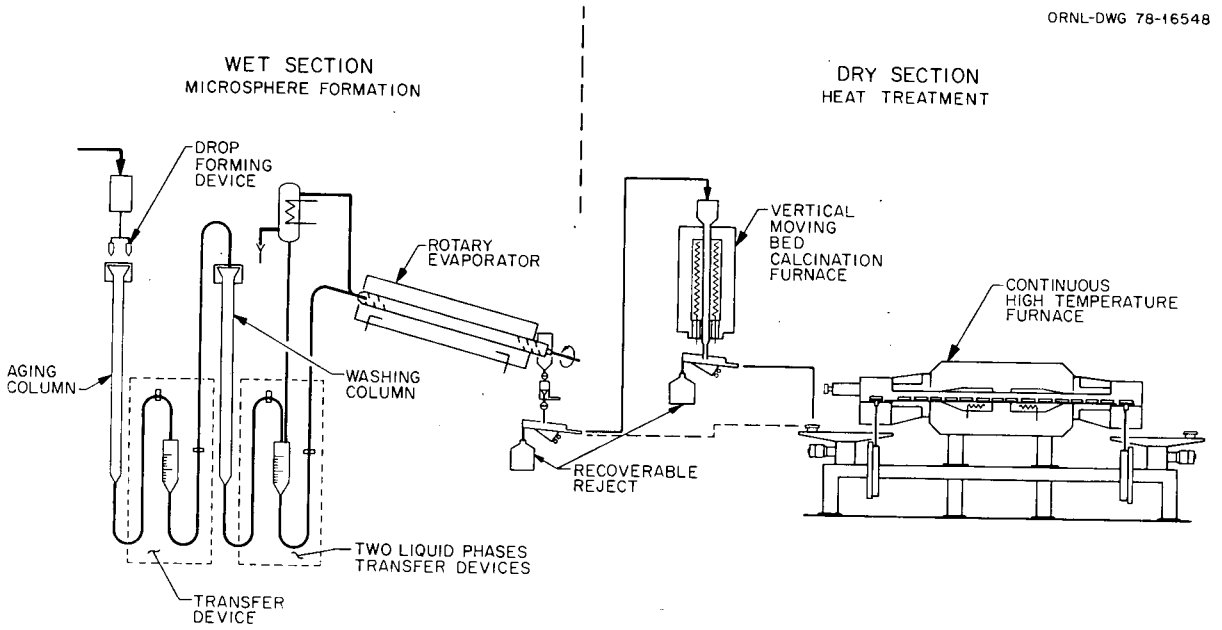

Fig. 2.2. Flowsheet of the SNAM Process. Based on G. Brambilla et al., pp. 191–209 in *Symposium on Sol-Gel Processes and Reactor Fuel Cycles*, CONF-700502 (May 1970).

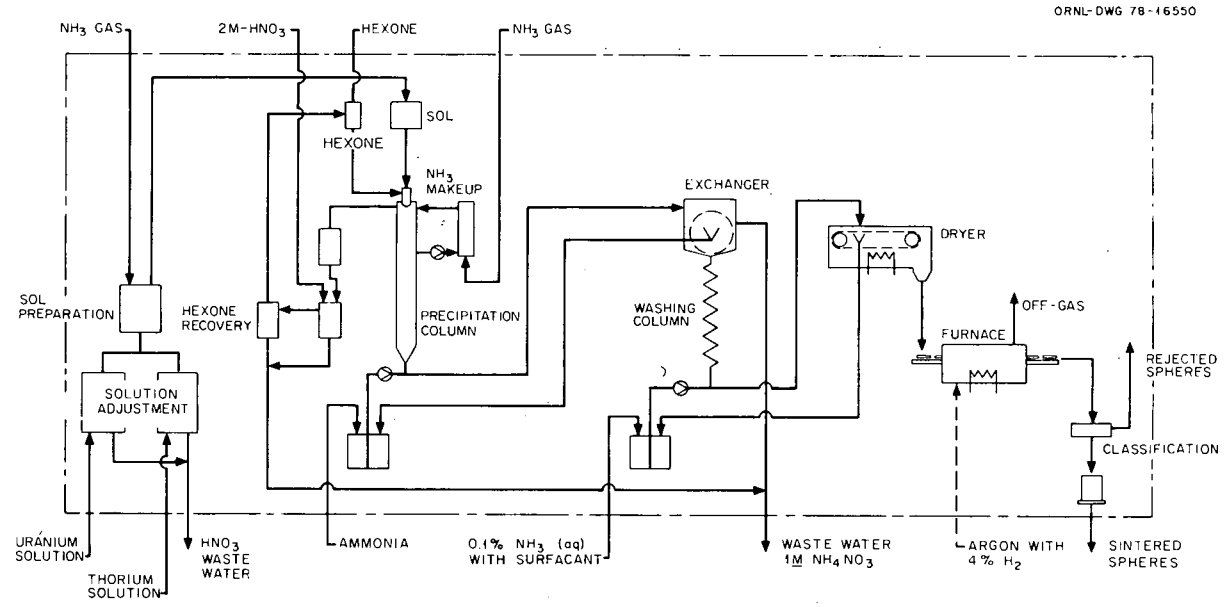

Fig. 2.3. Flow Sheet of the KFA Precipitation Process Using Hexone. Based on E. Zimmer et al., *Trans. Am. Nucl. Soc.* 20: 591-93 (1975).

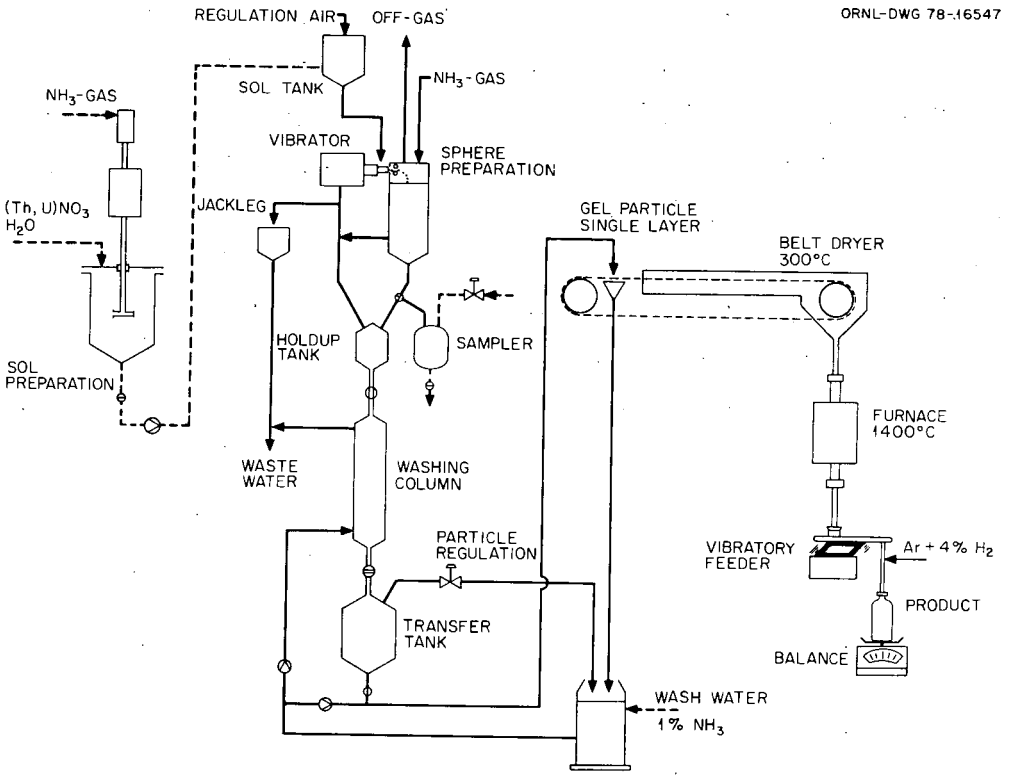

Fig. 2.4. Flowsheet of the KFA Precipitation Process Without Hexone. Based on H. D. Ringel and E. Zimmer, *Trans. Am. Nucl. Soc.* 27: 292-93 (1977).

The spherical shape is formed by dripping the sol or broth from a capillary or by flowing the sol or broth through a vibrating nozzle into air or organic liquid. Spherical drops form from the effect of surface tension before exposure to the precipitating chemical. Deformation may occur at the gas-liquid interface or liquid-liquid interface. This problem has been handled successfully by exposing the droplet to ammonia gas or dissolved ammonia, thereby strengthening the surface of the sphere. The British have even developed a foam technique.[20] The foam is formed by bubbling ammonia gas into ammonium hydroxide and cushions the impact as well as helping harden the sphere.

The SNAM process originally had some problems with sphericity, twinning, and satellites,[2,21,22] but the Italians[21] practically eliminated the latter two and improved their product sphericity to typical values of 1.03.

Another problem common to the SNAM-type processes was the presence of organic compounds in the wet gel spheres. The organic compounds caused sticking during drying and cracking during calcining. The problem was handled by use of surfactants during washing and dehydrating,[23,24] special calcining to decompose the organic compounds (porosity is essential for escape of decomposition gases),[2,7,10,13,14,16,25-28] dissolution of these compounds during washing,[7] or as mentioned above elimination of the organic compounds from the feed.[2,7]

Although other users have produced fines with their variation of the SNAM process, the Italians used the CNEN method to produce fines.[15,29-31] The CNEN method uses a nitrate-extracting organic in the gelation step to gel the sphere while removing the nitrate species. After evaluating both processes the Italians decided to try to develop the SNAM process to produce both coarse and fine particles.[29-31]

2.2.1 Sol and Broth Preparation

As mentioned above, no pretreatment was required for preparing the uranium broth used in the SNAM process. However, the thorium was supplied as a sol and the plutonium as Pu(IV) polymer, though for low plutonium content the monomeric form is acceptable. Pretreatment to achieve the desired state involves denitration of thorium or plutonium nitrate. Several denitration methods are available and no preference is cited for one method over another.

In general, the starting solution was the heavy metal nitrate. If necessary, the nitrate solution is pretreated to form a sol. Next, the organic polymer and other additives are added, often as another solution. These additives provide pH adjustment, viscosity adjustment, and filler. Besides the polymer a modifier is added to help adjust the viscosity and protect the polymer from acid attack. The British reported[32] investigating a number of polymers (not named) and that each polymer has a modifier associated with it. According to the literature any polysaccharide was suitable. Four prerequisites were required for accepting a polymer. The polymer must:

1. be water soluble and compatible with the high ionic content of the sol or broth;

2. thicken the sol or broth along with the modifier to enhance drop formation, but leave the sol or broth fluid enough to achieve reasonable flow rates through the nozzles;
3. quickly form a gel structure to withstand impact at the aqueous interface;
4. form a gel structure strong enough to support the heavy metal in the spherical shape until the heavy metal solidifies, then be capable of debonding without damaging the inorganic structure.

The polymers that have been used include hydroxypropyl methyl cellulose (Methocel), polyvinyl alcohol (PVA), dextran, natural gums, and starch derivatives (Wisprofloc). The modifiers and additives include tetrahydrofurfuryl alcohol (TFA), formamide, urea, ammoniun nitrate, dioxane, acetamide, and glycine. Three combinations of polymer and modifier seem to have enjoyed the most success. The original SNAM recipe used Methocel and TFA, the Germans have done most of their work using PVA and various additives including urea and TFA, and the British have settled on a proprietary polymer and modifier.

There are two exceptions to the above general description. One, the Germans are working to eliminate the organic additives. They use a large excess of urea and ammonium nitrate and preneutralize by heating to decompose the urea into ammonia and carbon dioxide. Viscosity and pH of the solution are very important parameters. Two, the British have used uranium fluoride (which must be converted to uranyl fluoride) as a starting solution.[13,14,33]

2.2.2 Sphere Forming and Gelation

Drop formation was accomplished by dripping from a capillary or needle, by natural stream breakup, or with a vibrating nozzle. The details of drop formation are covered in Sect. 2.4. The original SNAM process used a two-fluid nozzle with air and sol or broth as the two fluids.[12] The air flow rate along with the nozzle diameter controlled the drop diameter. Also, the air flow kept ammonia from gelling the solution on the nozzle and clogging the nozzle tip. The drop formed its spherical shape in air, then passed through an ammonia gas layer, which hardened the surface into the final shape. The drop then impacted the aqueous ammonia surface, the hardened surface retaining

its shape. The drop quickly gelled as it settled to the bottom of the vessel in the gelation solution (concentrated ammonium hydroxide) for aging. All the versions of the SNAM process follow this basic sequence, drop formation, surface hardening, interface impact, and gel formation and aging in aqueous ammonia. Although the British do not use a two-fluid nozzle, they still form the drops in air, followed by ammonia gas and concentrated ammonium hydroxide.[2,20] In addition, they have developed a foam mentioned above to soften the impact and enhance surface hardening. The foam is formed by bubbling ammonia gas into concentrated ammonium hydroxide that contains a surfactant.

The Germans developed a process that differed in detail from the original SNAM process. Rather than a gaseous layer over the aqueous ammonia, an organic compound (methyl isobutyl ketone was used) containing ammonia (typically 0.15 *M*) was used.[2,10,23,24,34] Going through the familiar SNAM sequence, the drops are formed from a two-fluid nozzle (vibration was not used) in ammonia-free ketone, pass into ammonia-containing ketone, where the surface hardens, impact the aqueous interface, and quickly gel in the aqueous ammonia. The Germans also developed a continuous process using a horizontal vibrating nozzle.[2,7,28] The drops form in air, followed by an ammonia gas layer, and drop a short vertical distance (30 mm) to a 1% aqueous ammonia solution.

2.2.3 Aging, Washing, and Dehydrating

The aging solution was generally the same solution as the gelation medium, aqueous ammonia (1-30%). The aging time varied from several minutes to overnight. Generally, when large-scale or continuous production was being considered a time of 10 to 30 min has been considered long enough.

To prevent cracking on drying, the salts (generally ammonium nitrate) were washed from the wet gel beads. Usually a dilute ammonia solution was used to keep the heavy metals from repeptizing, although distilled water has been used. The latest report[28] from the Germans indicates that they use 1% ammonia in the gelation stage as well as during washing. A surfactant was introduced in the washing stage.[23,24,34]

The HOBEG and NUKEM* (Germany) processes used an isopropanol wash, which not only washed out the salts and the PVA (eliminating the need for thermal removal), but also dehydrated the wet gel beads.[2,10,16]

The Italians used azeotropic distillation to dehydrate the spheres after washing with water.[12,13] Carbon tetrachloride was recommended because of its nonflammability. This method of dehydrating was also designed for continuous production on pilot plants with capacities up to 30 kg/d.[13,35] The Italians preferred this method because it gave the beads a more open porous structure, important in calcining. Also, no sticking occurred during dehydrating in an organic liquid. Other methods they found successful were air drying (at 100-120°C) and vacuum drying.

2.2.4 Drying

In the original SNAM method, no details are given on drying the organic liquid from the azeotropic distillation before calcination, although the beads are clearly "let free" of the organic.[13] Most likely the carbon tetrachloride does not wet the spheres very well; so draining, brief exposure to air, and good ventilation during the initial stages of heat treatment are sufficient. (It is important to remember that carbon tetrachloride decomposes to form phosgene. Therefore, carbon tetrachloride should be removed before high temperatures are achieved.) As mentioned in the previous section, the Italians indicated air drying and vacuum drying were satisfactory for combining dehydration and drying.

KFA has developed a belt drier for continuously drying the beads in a monolayer in air at 250 to 300°C.[2,7,10,23,24,28,34] Before drying, the spheres were washed with a surfactant. The atmosphere in the dryer is kept at a minimum humidity level to ensure controlled drying; otherwise, drying would be so rapid that cracking would occur. Even so, drying is very rapid, taking only about 10 min. Drying is so rapid that spheres may absorb water and burst on cooling. Therefore, the water content of the spheres must be equilibrated at 160°C with that present at room temperature. The continuous process designed by the Germans has the spheres going directly to a furnace from the belt drier, eliminating the bursting problem.

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*Nukem Gmbh, Germany

The HOBEG and NUKEM processes, which dehydrated with isopropanol, used vacuum [53 kPa (400 torr) for HOBEG, 67 kPa (500 torr) for NUKEM] at elevated temperatures (80°C for HOBEG, 100°C for NUKEM) to remove the isopropanol, which could be recycled.[2,10,16] The NUKEM method took several hours to dry the isopropanol from the spheres.

2.2.5 Calcining and Sintering

Heat treatment at temperatures around 500°C eliminates the organics still present in the dry gel particles and converts the metals to oxide. The Italians calcined at 450 to 550°C in air.[12,13,25,26] Harwell calcined in CO_2 at 50°C/h to 800 to 850°C (held for 4 h).[14,33] HOBEG calcined in air at 300°C. The NUKEM process calcined at 300°C in air for 5 h. The KFA belt drier combines dehydration, drying, and precalcination at 250°C in 10 to 15 min.

Sintering was performed in a reducing atmosphere at high temperatures. Generally, the particles were sintered for a few hours in hydrogen or Ar-4% H_2 at temperatures ranging from 1200°C to 2500°C. The heating rates used ranged from 100 to 400°C/h. These sintering conditions led to greater than 95% T.D. for the particles.

Both SNAM and NUKEM processes used air in sintering thoria particles.[10,12] The KFA spheres could achieve 99% T.D. in 10 min at 1000°C but were sintered at 1300°C for several hours to produce a more stable product.[23,24,28]

2.2.6 Application to ThO_2

All the processes start with $Th(NO_3)_4$ solution. The SNAM process preneutralizes 70 to 80% to $Th(OH)_4$ by NH_4OH addition. The resulting sol is boiled 15 min, cooled, and mixed with the Methocel solution.[12,35] The final sol has 0.5 to 0.7 *M* Th and 5 to 10 kg/m^3 Methocel. This sol is used to make ThO_2 spheres by the SNAM process described above. The ThO_2 spheres are sintered in air or an inert gas to 1300 to 1350°C at 150 to 200°C/h to a density of 96-98%.[12] Narrow size ranges of ±3% are obtained[12,13,25] for average diameters of 150 to 1100 μm. Batches of kilogram size have been produced in laboratory studies, while several hundred kilograms have been produced in a continuous pilot plant.[19,35]

Shape separation is done after drying and after sintering in the continuous sytem, with less than 1% rejects in each case.[13]

Harwell reported[27] work on ThO_2 several years ago. A viscous solution was formed by adding an organic polymer (usually Dextran) to a $Th(NO_3)_4$ solution. This solution was then formed into drops and precipitated with ammonium or sodium hydroxide. The Dextran was removed by heating to 250°C under vacuum. Details given for thorium-uranium spheres will be presented in Sect. 2.2.8.

The Thorium sol for the KFA process is prepared by treating $Th(NO_3)_4$ with ammonia gas.[2,7,10,24,28,34] The resulting precipitate is stirred and heated to form the sol with 1 *M* Th. The gel spheres are formed by use of the two-fluid nozzle with a ketone overlayer described above. The spheres are washed with 0.5 *M* ammonia containing a small amount of surfactant and dried in air at a controlled humidity (e.g., 40°C dew point) at 200°C. The dried spheres could be immediately sintered at 1200 to 1300°C (several hours) to produce 200 to 600-μm-diam ThO_2 spheres of 99% density. The laboratory-scale unit using this process produced 250 drops/second or 0.5 kg Th/h (based on 475-μm-diam kernels).

In the process developed later by KFA, the sol is formed in much the same way. However, 2 to 3 *M* Th sol is used, and viscosity is a critical parameter. The ketone overlayer has been eliminated, and drops are formed in air with a horizontal vibrating nozzle as described in Sect. 2.2.2. A one-nozzle laboratory facility processed 0.5 to 1.0 kg/h of heavy metal. The sphere diameters produced were 200 to 600 μm, with narrow distributions (400 ± 3 μm) and good sphericity (1.01).

The HOBEG process for producing ThO_2 spheres is the same as that for producing $(Th,U)O_2$ spheres. The details are given for the mixed oxide in Sect. 2.2.8. About 2 Mg of ThO_2 spheres with diameters of either 500 or 600 μm and 97 to 99% T.D. have been produced.

The General Atomic Company has extensive experience in the preparation of ThO_2 by external gelation. A pilot plant has produced several tons of ThO_2 spheres at the rate of 10 kg/h. Details of the process are proprietary.

The NUKEM process is described in detail for the $(Th,U)O_2$ spheres in Sect. 2.2.8 and is the same for ThO_2 spheres. The pilot plant for

ThO_2 spheres includes a vibrating nozzle holder with 12 nozzles. A batch consists of 55 liters of broth containing 180 kg Th/m^3. From this, 90 liters of wet gel spheres are formed, and after washing, drying, and calcining the spheres are sintered to 97 to 99% T.D. at 1250°C in air. The facility produces 500-μm-diam spheres at 0.5 kg Th/h per nozzle or 600-μm-diam spheres at 0.8 kg Th/h per nozzle (a total rate of around 10 kg ThO_2 spheres per day). Sieving yields of 95 to 98% for 450 to 550 μm and 550 to 630 μm were cited.

2.2.7 Application to UO_2

The SNAM process starts with uranyl nitrate solution. No pretreatment of the solution is required; excess acid and salts are tolerated. The organic polymer and other additives are simply mixed with the uranyl nitrate before the wet gel spheres are formed. The final broth is composed of 0.5 to 0.8 *M* U, 50 to 300 kg/m^3 TFA, 5 to 10 kg/m^3 Methocel, and 0.2 to 1 *M* HNO_3 (free).[12,13,25,35] The TFA increases the solution viscosity, enhances the gelation, and protects the polymer from acid attack. The other details of the process are covered in the previous sections. The process differs from that for the ThO_2 spheres only in the sintering rate. The UO_2 spheres are sintered in a hydrogen or Ar–4% H_2 atmosphere at a rate of 200 to 300°C/h to 1300 to 1350°C and held for 1 h to produce particles of 96% T.D. Particles of 98.5% T.D. were achieved at 1600°C. The production quantities and shape separation results are similar to those described for ThO_2 spheres above.

The Harwell process using Dextran mentioned above for ThO_2 and described below for $(Th,U)O_2$ applies as well for UO_2. Harwell has extended its work far beyond these initial tests with Dextran in developing a process for plutonium or plutonium-uranium (see Sect. 2.2.9). A British patent[33] gave the following two examples for producing UO_2 spheres. A broth was made containing 63 g $UO_2(NO_3)_2$, 4 ml glacial acetic acid, and 84 g of a polymer solution. The polymer solution was made up as 150 ml containing 15 g Wisprofloc P. The broth was added dropwise to NH_4OH solution, aged for 1 h, washed with water, dried in trays at room temperature, calcined in CO_2 to 850°C (50°C/h), and

sintered in H_2 to 1450°C (100°C/h). Dense UO_2 spheres were produced with extensive surface cracking. The other example starts with 25 ml (1 g UO_2F_2/ml); 3.75 g Wisprofloc W and 10 ml formamide are added, and the final volume made up to 45 ml. The broth was added dropwise to ammonia. The wet gel spheres were washed and boiled in water and dried in trays in air at room temperature.

The KFA process originally used PVA in the broth recipe and a ketone layer over the gelation solution. The broth composition reported was 502 U, 160 NH_4NO_3, 240 urea, 3 surfactant (Atlas G 1554), and 25 PVA (kg/m^3). The Germans are attempting to eliminate PVA from the recipe. The recipe developed so far[2] is 1.5 *M* U, 1.1 kg urea/kg U, and 550 g NH_4NO_3/kg U. This solution is gently heated to decompose the urea, and the final pH is adjusted to 3.6. The drops are gelled in an ammonia bath and aged in 7 *M* NH_4OH at 60°C for 10 min. The dry spheres are calcined at 600 to 700°C and sintered at 1800 to 2500°C to produce 200- to 300-μm UO_2 kernels.

The HOBEG broth was composed of uranyl nitrate, PVA, other additives (including TFA)[2,7,16] and water. The broth was formed into droplets at the rate of 1000 to 2000/min with a vibrating device. The droplets fell 0.2 to 0.3 m through ammonia gas and were collected in NH_4OH. The wet gel spheres were washed with aqueous ammonia, dehydrated with isopropanol, and vacuum dried at 80°C. The dry spheres were calcined at 300°C in air, then sintered in hydrogen at 1700°C to produce 200-μm-diam (std dev 10 μm) UO_2 spheres with greater than 95% T.D.

2.2.8 Application to $(Th,U)O_2$

The thorium sol and uranium broth used in the SNAM process to produce the pure heavy metal spheres (see the two preceding sections) are simply mixed, and the resulting mixture is used in the same process discussed previously. A reducing atmosphere is used for sintering since uranium is present.

The Harwell process using Dextran is described in more detail in the following for mixed-oxide spheres.[27] "In a typical preparation of ThO_2-UO_2 spheres, 2 g Dextran was added to 10 ml of 2 *M* nitric acid

containing 100 g U(VI)/liter and 100 g Th/liter as metal nitrates; precipitation of drops through a 1-mm diameter jet with ammonium hydroxide gave 3-4 mm diameter transparent amber gel spheres, which were washed, dried and calcined." The KFA process for the mixed oxide is a repetition of the process for ThO_2. Uranyl nitrate is added to the thorium sol to give a minimum Th/U ratio of 4.

The sol for the NUKEM process was prepared by mixing $Th(NO_3)_4$ preneutralized with ammonia gas (to a pH of 3.5), uranyl nitrate, PVA, and water.[10] The Th/U ratio was 5.0 or 10.76, and heavy metal concentration was 100 to 240 kg/m^3. Drops of this broth were formed in air by vibrating nozzles (three facilities of six nozzles each) followed by ammonia gas. A gelation solution of NH_4OH was used. The wet gel spheres were washed and dehydrated in isopropanol and dried 4 h at 100°C under a slight vacuum [67 kPa (500 torr)]. The dry spheres were calcined 5 h in air at 300°C and sintered in hydrogen at 1700°C (4 kg heavy metal/h). The dense $(Th,U)O_2$ kernels were continuously screened (354 to 425 μm desired diameter) and shape separated for a 96 to 98% yield. The throughput based on 400-μm spheres is 0.23 kg/h per nozzle (a total of 4.2 kg/h). Full capacity was 60 to 100 kg spheres per day.

The HOBEG process used a sol made from uranyl nitrate, $Th(NO_3)_4$ with the pH adjusted to 3.5-4.0, PVA, other additives, and water.[2,16] The sol went through the familiar sequence of vibrating nozzle, air, ammonia gas, and NH_4OH solution. The wet gel spheres were washed in an NH_4OH solution, dehydrated in isopropanol, and vacuum dried at 53 kPa (400 torr). The dried spheres were calcined in air at 300°C and sintered in hydrogen to 1600-1700°C to 97-99% T.D. The dense spheres were screened and shape separated with less than 1% rejects. The process has produced 10 Mg $(Th,U)O_2$ spheres with varying compositions (Th/U ratios from 4 to 40) and diameters (200, 400, 500, 600, 800 μm). The capacity of the facility was 18 kg/d with 95 to 98% yields.

2.2.9 Application to $(U,Pu)O_2$

In the SNAM process the heavy metals were prepared in solutions independently then mixed. The process steps from drop formation to

sintering were the same as those already described for particles containing uranium (see Sects. 2.2.7 and 2.2.8). The plutonium was prepared in the polymeric form by denitrating $Pu(NO_3)_4$ by solvent extraction.[12,31,35] The polymeric plutonium forms with as much as 0.1 *M* free acid still in solution. The stock solution was concentrated to 2 *M* Pu. If only a few percent of plutonium was required, monomeric $Pu(NO_3)_4$ was added to the uranium solution. As with the other oxides, kilogram batches of PuO_2 spheres were prepared in the laboratory by the SNAM process. In addition, a pilot plant with a capacity of 3 to 6 kg/d at CNEN, Casaccia, Italy, has also been used to prepare kilogram batches.[13,26]

The SNAM process has been reported to have problems with making good sintered spheres containing plutonium.[2,7,21] The sintered spheres have shown a tendency to crack and signs of surface roughening. After a few days the resistance to cracking is practically zero. These problems have been associated with water absorption; consequently the sintered particles must be stored in a dry atmosphere.

The Harwell process blends acidic $Pu(NO_3)_4$ (300 kg Pu/m^3 5 *M* HNO_3), $UO_2(NO_3)_2$ solution, the organic polymer (a proprietary agent), and modifier together. The resulting mixture is formed into drops (3-mm drops give 800-μm product) at the rate of 60/s into the NH_3-NH_4OH-surfactant foam system described earlier. This foam system is not used in producing fines. The spheres are collected and aged in concentrated NH_4OH for 30 min and washed with water. The dehydrating step is critical because the spheres shrink appreciably. The wet gel spheres are dehydrated carefully at room temperature (2-3 h for a batch of 700 g heavy metal). The spheres are heated to 800°C in CO_2 at a rate of 50°C/h and held for 4 h. The calcined spheres (90% T.D.) are then sintered by heating to 1450°C in Ar-5% H_2 at 100°C/h to give dense $(U,Pu)O_2$ at 98 ± 2% T.D. The final product is mostly spherical, with the major deformation being a slight pear shape. The laboratory work has been on a batch basis because of criticality. However, the pilot plant described in Sect. 2.2.10 is planned to be continuous. The Harwell facility is capable of producing large amounts of material to

demanding specifications. Campaigns of 50 to 100 kg have been handled, producing fines of 80 μm diam (std dev 2 μm) and coarse particles of 800 to 1100 μm.

2.2.10 Pilot Plants

Although designs for pilot plants up to 30 kg/d using the SNAM process were commissioned, indications are that some of these ambitious plans were not carried through and little development work is being carried on in Italy at present. The KFA and Harwell processes have developed to the level of design and construction of continuous pilot plants, with further development being vigorously pursued. The NUKEM process was developed for ThO_2 and $(Th,U)O_2$ production, although the KFA process has supplanted NUKEM for $(Th,U)O_2$. HOBEG developed its version of the SNAM process to production level.

The facilities and capacities are given in Table 2.1.

Table 2.1. Pilot Plants

Process	Site	Kernel Composition	Capacity (kg/d)	Ref.
SNAM	San Donato Milanese Milan, Agip Nucleare	UO_2, ThO_2, $(Th,U)O_2$	10	26
SNAM	Casaccia, Rome, CNEN	PuO_2, $(U,Pu)O_2$	3	26
SNAM	Springfields, BNFL	UO_2	20	26
KFA	KFA, Jülich	ThO_2, $(Th,U)O_2$	12	28
Harwell	Harwell, Berks. AERE	UO_2, PuO_2, $(U,Pu)O_2$	17	7
HOBEG	HOBEG, Hanover	UO_2, ThO_2, $(Th,U)O_2$	18	16
NUKEM		ThO_2, $(Th,U)O_2$	60-100	10

2.3 GELATION BY WATER EXTRACTION — P. A. Haas

For this type of sol-gel process, the liquid drops are converted to solid spheres by extraction of water by an organic liquid. The

colloidal particles of the sol are concentrated until they become unstable and gel. The water extraction processes have been described in detail.[36,37] Water is removed by mass transfer across the phase boundary, and the rate of gelation is determined by the rate of mass transfer. Since external gelation requires mass transfer of chemicals (usually NH_3 or NH_4^+), external gelation and the water extraction process share similarities and problems that do not occur for internal gelation, which does not depend on mass transfer.

In general terms, the water extraction sol-gel processes for preparing high-density oxide spheres require the following three principal operations:

1. preparing an aqueous oxide sol;
2. dispersing the sol as drops into an organic fluid, usually 2-ethyl-1-hexanol (2EH), which extracts water from these drops to give solid gel particles;
3. drying and sintering at controlled conditions to remove volatiles, promote densification, and reduce or convert chemically as necessary.

A continuous sol preparation process was developed for $(Th,U)O_2$, but other sol preparation processes were batch operations. Gel spheres were formed in continuous column systems. Sphere drying and sintering were batch processes.

It is important to recognize that the characteristics of a sol or gel depend on the conditions used to prepare it and that the effects of a change of conditions are difficult to predict. Sols and gels are *not* at thermodynamic equilibrium, and their properties are not fixed by a combination of conditions that would fix a system at equilibrium. As a result of the nonequilibrium states, the process requirements must be given in the form of recipes that are dependable for producing the desired products.

The second of the general sol-gel process operations, the formation of gel spheres, may be further divided as follows:

1. dispersion of the sol into drops, each of which contains the amount of oxide that will be present in a sintered sphere;
2. suspension of the sol drop in an organic liquid, usually 2EH, while water is extracted to cause gelation;

3. separation of gel spheres from the forming liquid;
4. recovery of the organic liquid for reuse.

These four parts of gel sphere formation are carried out in continuous column systems. The first and third operations are similar for all sol-gel processes for preparation of spheres. The formation of liquid drops is reviewed separately (Sect. 2.4), and the separation of gel spheres will be mentioned briefly as part of specific sphere formation or drying procedures. Recovery of the organic liquid for recycle will be mentioned separately for each sol composition.

2.3.1 Sol Preparation

The sol is the most important variable for operation of any sol-gel process. A sol is thermodynamically unstable and cannot be uniquely specified by any practical combination of chemical and physical measurements. Therefore, any generalized discussion of the effects of sol variables is qualitative. With these qualifications, the discussion in this section considers the generalized effects important to understanding the sol-gel process including limitations and problems. Detailed or specific preparation procedures are reviewed later in the specific sections for each composition of product.

Gelation by extraction of water requires that the sols be stable aqueous dispersions of well-crystallized oxides. Low concentrations of nitrate peptize all the nuclear fuel materials. Most feed purification or fuel reprocessing processes give nitrate solutions as the products, and nitrate in the gel spheres decomposes during high-temperature sintering without leaving any undesirable residues.

All the sol preparation processes reported in the following sections start with nitrate solutions. Uranium and plutonium can require adjustments to the optimum valence, while thorium is only tetravalent. The true sols result from growth and dispersion of colloidal oxide crystallites. All the true sols are basically four-valent; that is, ThO_2, PuO_2, and UO_2 dispersions. The procedures for conversion of the nitrate solutions to colloidal oxide sols are of the types listed below. All these have been applied to thorium, plutonium, and U(IV) unless otherwise noted.

1. precipitation of hydroxides with NH_4OH, washing out NH_4NO_3, and peptizing with HNO_3;
2. extraction of HNO_3 with liquid amines and hot digestion to grow crystallites;
3. hydrothermal denitration to oxide, then peptization of the oxide mixed with H_2O by residual or added HNO_3 (This is not practical for U(IV) as it oxidizes to U(VI).);
4. slow addition (partial neutralization) of NH_4OH with digestion to grow oxide crystallites dispersed at pH of 2 to 4. While stable sols can be prepared with the NH_4NO_3 present, gelation by extraction of water is practical only for low NH_4NO_3 concentrations.

Each sol preparation procedure has advantages and disadvantages. The precipitation processes are simplest on a laboratory scale, but are difficult to scale up. The solvent extraction of HNO_3 involves liquids throughout without any handling of precipitates, solids, or slurries. The hydrothermal denitration gives a usable nitrate waste (HNO_3 solution). The pH adjustment with ammonia gives no waste and is a simple process, but the subsequent removal of the NH_4NO_3 is troublesome and produces a waste product. The solvent extraction and the pH adjustment procedures can start with $Th(NO_3)_4$-$UO_2(NO_3)_2$ solutions (and probably Th-Pu or U-Pu nitrate solutions) to give mixed sols, while the other two procedures cannot. Individually prepared sols can be simply mixed to give mixed oxide sols if both the colloidal dispersions remain stable at the mixed conditions.

2.3.2 Sphere Forming and Gelation

After a sol drop is formed, it must remain suspended until sufficient water is extracted to produce a relatively dry, gelled sphere. A gel surface that is in equilibrium with unsaturated 2EH (not saturated with H_2O) is generally smooth and nonsticking; thus the gel spheres can be drained, dried, or handled. The settling velocity of the spheres increases as the water is extracted. Settling is affected more by the densification of the gel particles than by the decrease in size due to removal of H_2O. In the continuous operation of a fluidized gelation column, the higher settling velocity is used to preferentially remove gelled product spheres from the column.

Problems related to fluidization are encountered when sol drops or incompletely gelled spheres (1) coalesce to give large drops, (2) stick to the column and cause large accumulations on the walls or subsequent releases of large clumps, or (3) cluster into clumps without coalescing. Large drops or clumps that are formed as a result of these problems have higher settling velocities than the usual product gel spheres and, consequently, will fall out of the column before gelation is complete.

Another fluidization problem involves the failure of the sol drop to remain in the column until gelation is complete. Perfect fluidization is not possible; thus the conditions that allow discharge of the gel product spheres also occasionally allow discharge of incompletely gelled spheres. Since the settling velocity depends partially on the diameter of the drop, and the average residence time required for gelation varies inversely with its size, a disperser that forms sol drops of uniform size should be selected. The discharge of a small quantity of incompletely gelled particles can be tolerated. If the surface of a particle is gelled, any water remaining in the core may diffuse to the 2EH and, in turn, to drier gel particles. If the incompletely gelled particles contain sufficient water to reform a sol drop or to give a sticky surface, they will adhere to and ruin adjacent particles.

The mass transfer of the water in the organic liquid outside the drop must be controlling and therefore must be slower than the mass transfer of water in the sol drop. If the mass transfer is too rapid, the outside of the drop will gel quickly and then crack or distort as water is extracted from the liquid core. Organics that have a high solubility for water tend to have low interfacial tensions with the sol and thus allow distortions of the sol drop. Surface-active compounds in the organic can greatly reduce the coalescence or sticking of sol drops, but they lower the interfacial tensions.

The gelation by extraction of water generally requires well-crystallized sols of low nitrate-to-metal ratio. High nitrate concentrations in the sols consistently increase distortion, clustering, and sticking problems and also increase cracking during drying and sintering of the gel spheres. Sols that are less well crystallized appear to gel at lower concentration and then crack as removal of water continues.

2.3.3 Drying and Sintering

After the extraction of water is completed, the gel spheres wet with 2EH (or other organic) must be dried and sintered. The weight loss is less than 0.2 g per gram of metal oxide (PuO_2, UO_2, ThO_2), and most of this material (alcohol, H_2O, NO_3^-) is removed by volatilization below 220°C. The chemical gelation processes, such as the internal and external gelation processes described in Sects. 2.1 and 2.2, give gel spheres with over 10 times as much material to remove, and some components (NH_4NO_3, organic polymers) cannot be removed by drying.

The treatment of spheres following water extraction consists primarily of slowly heating from room temperature to 1150 to 1550°C, depending on composition, with a purge gas to remove fumes and vapors; densification is then completed during several hours at the peak temperature. In practice, the required conditions are more complex and must meet one or more of the following requirements:

1. Gels containing U(IV) must be protected from oxidation by an inert atmosphere until densification is completed.

2. Gels formed in 2EH should be dried in a steam atmosphere to 220°C to promote removal of 2EH. If this treatment is omitted, the chemically bound 2EH can cause rapid heating and cracking if burned out with air or give excessive carbon in the product if not burned out.

3. Since the gel is not washed to remove nitrate, high nitrate in the sol can result in rapid heat generation and cracking of the gel. The presence of both U(VI) and organic material in the gel makes drying of high-nitrate gels very difficult.

4. Carbon remaining in the calcined product can result in incomplete densification. For PuO_2, UO_3-U_3O_8, or ThO_2, the carbon can be burned out by use of an air purge above 220°C. For U(IV) sols and UO_2 gels, steam and/or CO_2 will aid removal of carbon without excessive oxidation of the uranium.

2.3.4 Application to ThO_2

Thoria gives the most stable sols, the strongest gels, and the simplest process chemistry since Th(IV) is the only significant valence.

Therefore, most of the sol-gel process variations can be applied to thoria. Thoria sols have been prepared by the four procedures listed in Sect. 2.3.1. Another process used was precipitation of thorium oxalate, washing, thermal decomposition, and peptization of the ThO_2 with HNO_3. Any of the ThO_2 sols with low nitrate content can be formed into gel spheres by extraction of water.

The processes developed to prepare ThO_2 spheres for High-Temperature Gas-Cooled Reactor fuels use hydrothermal denitration for sol preparation. The process conditions have been described[38] and equipment drawings are available.[39] The conversion of thorium nitrate to a dispersible ThO_2 powder must be carried out under conditions that minimize the decomposition of nitrate into nitrogen oxides. The desired overall reaction is:

$$Th(NO_3)_4 + 2H_2O \rightarrow ThO_2 + 4HNO_3 \ .$$

When this hydrothermal denitration is continued until the residual nitrate in the ThO_2 is less than 0.1 mol per mole of thorium, the ThO_2 can be almost completely dispersed (more than 99%, often 99.9%). When improper conditions are used, a large fraction of the ThO_2 cannot be dispersed, *even though chemical analyses and common physical measurements are identical with those of the dispersible* ThO_2.

The following three requirements are critical in the preparation of dispersible ThO_2:

1. Local overheating and the thermal decomposition of thorium nitrate must be carefully avoided.

2. Superheated steam must be supplied throughout the temperature range 200 to 400°C to favor the hydrothermal reaction. Denitration with a deficiency of water gives an undispersible ThO_2 product.

3. The denitration conditions should favor desirable types of N-O-Th bonding; the presence of O_2 (or air) for temperatures up to 250°C appears to favor the preferred bonding.

2.3.4.1 Fluidized-Bed Denitration

Fluidized-bed denitration appears to be an excellent method for avoiding local overheating and for providing good contact with superheated steam plus air. A 0.25-m-diam (10-in.) fluidized-bed denitrator was operated[40] to produce dispersible ThO_2 at the rate of 45 kg/h (100 lb/h).[5] The ThO_2 product was carried out of the reactor with the gases and collected on a filter. This product, which was dispersed by agitation with hot water, was excellent for the preparation of high-density ThO_2 fragments. However, the residual NO_3^-/Th ratios were higher than the optimum mole ratio (0.11) for a sol prepared from a hydrothermal denitration product. The ThO_2 sol produced from a sample of fluidized-bed product was not suitable for preparation of spheres; the gel spheres cracked into fragments, as frequently occurs with high-nitrate sols. Higher temperatures and/or longer residence times in the fluidized bed would probably yield a product having a lower NO_3^-/Th mole ratio and hence more desirable for use in preparing spheres. Other process variations, such as holding the thorium nitrate feed at the boiling point and using some air with the fluidizing or atomizing gas, might be favorable since such variations could affect the N-O-Th bonding.

2.3.4.2 Formation of Gel Spheres

Only the process conditions receive detailed discussion here. The design and operation of the fluidized-bed sphere-forming columns have been reported elsewhere.[41]

Surfactants are added to the gelation column to prevent coalescence of drops, clustering, or sticking of the gel spheres to the column walls. Although Span 80 is more effective than Ethomeen S/15, Span 80 alone or in high concentrations tends to cause a wrinkling or raisin type[6] of distortion.[41] High Ethomeen S/15 concentrations, although less objectionable, may cause a dimple distortion or contribute to drying difficulties. The overall approach for ThO_2 spheres is to add Ethomeen S/15 and Span 80 in weight ratios of at least 4 to prevent clustering or coalescence and to avoid the distortions attributed to Span 80 alone.

The water content of the 2EH affects the rate of gelation. A low water content requires high flows of 2EH through the still to remove water. We generally use still flow rates that are 100 to 150 times the flow rate of the sol so that the steady-state water concentration of the 2EH is between 1.0 and 1.5 vol %.

2.3.4.3 Sphere Drying and Sintering

Drying and sintering of ThO_2 spheres involve some complex physical and chemical changes. The densities of the gel spheres are less than 40% of that of the sintered spheres; they must lose up to 15% of their weight after discharge from the sphere-forming column. Energy changes are detected by differential thermal analyses of gel spheres as endothermic peaks.[42] The volatile constituents include water, nitrate, 2EH, and surfactants. As a preliminary treatment to drying with heat, air may be blown (or drawn by vacuum) through the bed of gel spheres to remove much of the 2EH and perhaps some water.

The overall drying-sintering schedule, starting with gel spheres from which gross amounts of 2EH had been removed, was as follows:

Drying:

1. argon flow from 25 to 100°C for 1 to 16 h
2. argon plus steam flow from 110 to 220°C for 6 to 24 h
3. argon plus steam flow at 220°C to give a total of 20 to 30 h with steam

Sintering:

1. air atmosphere to 500°C at 100°C/h
2. air atmosphere from 500 to 1150°C at 300°C/h
3. air atmosphere at 1150°C for 4 h
4. cooldown in air at rates of 0.5 to 20°C/min.

The purpose of the drying operation is to remove volatiles (1) at rates that do not cause cracking during drying, and (2) completely enough that burning in air during the sintering of ThO_2 does not cause cracking of spheres. The argon atmosphere is necessary since the partially dried gels can ignite at surprisingly low temperatures (as low as 150°C for pure ThO_2 gels, and 110°C for other compositions). A

high nitrate content in the sol and/or the presence of U(VI) lowers the autoignition temperatures and acts as oxidizing agents, which can cause exothermic reactions even in the absence of air. The ThO_2 spheres that are prepared from hydrothermally denitrated ThO_2 powder are the least troublesome of sol-gel spheres to dry and sinter; spheres smaller than 300 μm can be dried and sintered without the use of steam. As the sphere diameter increases, the use of steam at the higher temperatures becomes more essential if cracking is to be avoided. Sintering in air burns out the remaining carbon so that low carbon contents do not depend on the steam stripping.

Most of the drying and sintering times given above were selected to allow heat and mass transfer through beds of spheres and are much longer than the requirement for a single sphere or a thin layer of spheres. The short times were determined for 1 kg of ThO_2 in small glass dryers, while the long times were for 15 to 30 kg in larger dryers. Sintering was performed in alumina crucibles containing up to 5 kg of ThO_2 each.

2.3.5 Application to UO_2

Since neither U(VI) nor UO_3 gives stable oxide sols, the initial step for preparing low-nitrate uranium sols is reduction to U(IV). At least five flowsheets were used to convert the uranous [U(IV)] nitrate solutions to UO_2 sols based on both the precipitation with ammonia and the extraction of HNO_3 by liquid amines. Three problems are common to all the flowsheets:

1. The U(IV) is oxidized to U(VI) by O_2, nitrate, or other mild oxidizing agents, and the sol properties become poor as the fraction of uranium present as U(IV) is reduced to 0.8 or less.

2. Digestion is required to grow amorphous UO_2 to more crystallized UO_2, which is necessary for higher uranium concentrations and lower NO_3^- concentrations in a fluid, stable sol.

3. Troublesome properties occur during intermediate stages of the sol preparation. Very poor settling and filtering behavior cause difficulties for the NH_4OH precipitation and washing. Thixotropic gels

can be formed at intermediate nitrate concentrations for the amine extraction of HNO_3.

The first difficulty is minimized by the combination of three procedures: (1) adding formic acid to complex the U(IV) and make it less sensitive to oxidation by nitrate, (2) blanketing all process operations with argon or nitrogen to eliminate oxygen, and (3) limiting the temperatures and times for digestion. As a result of the second difficulty, batch processes gave much better UO_2 sols than continuous processes. The batch process conditions can be controlled to give a complex sequence of conditions that are not practical for a continuous process. The batch processes also allowed selection of process conditions to minimize the third problem. The final versions of both the precipitation and the amine extraction processes gave good UO_2 sols. The amine extraction process appeared to be much more practical for scale-up to larger capacities and for remote operations, and therefore only the batch amine extraction process is described in detail.

The engineering-scale demonstration of preparation of UO_2 spheres by water extraction was limited to nonfluidized column operation only. Larger UO_2 spheres were prepared in fluidized-bed columns as described for ThO_2 spheres, but long-term recycle of 2EH was not practical. Therefore, about 200-μm UO_2 spheres (sintered diameter) was the largest practical size.

2.3.5.1 Preparation of Sols

To describe the preparation of UO_2 spheres, two one-week demonstration runs will be discussed.[43] The 1 *M* urania sols used in the demonstration runs were prepared by the Concentrated Urania Sol Preparation (CUSP) process, in which a 1.0 to 1.4 *M* crystalline urania sol is produced directly by solvent extraction. The handling of solids, which was required in some earlier urania sol processes, is avoided, while the sol concentration step inherent in the earlier solvent extraction process for the preparation of dilute sols[44,45] is eliminated or minimized. Further, this process lends itself to closer control than can be imposed easily on the previous processes. In general, sols

prepared by the CUSP process show greater reproducibility and have longer shelf life than urania sols prepared by other solvent extraction methods.

Sol preparation time, which varies from 3.5 to 4 h, is independent of batch size since nitrate must be extracted for prescribed periods of time. Various precautions must be taken during sol preparation. For example, the first nitrate extraction should require a minimum of 90 min, to allow time for the proper release of nitrate; otherwise, the NO_3^-/U mole ratio of the sol product will be too high, even though the conductivity is in the proper range. However, care must be taken not to prolong the first nitrate extraction excessively since thickening or possibly gelation can result from overextraction. During the second extraction, favorable oxidizing conditions are present (elevated temperature and release of NO); consequently, to minimize the oxidation of U(IV) to U(VI), this extraction, while sufficiently long to ensure complete crystallization, should not be unnecessarily extended.

Following sol preparation, the sol and solvent are drained separately and the equipment is washed out successively with dilute HNO_3 ($\sim$3 *M*) and with water. Some solids accumulate at the solvent-sol interface, primarily during the crystallization phase. These solids tend to cling to the equipment during draining, resulting in a loss of uraniun to the equipment wash solution equivalent to approximately 2 to 4% of the uranium in the feed solution, and a loss to the solvent wash (dilute HNO_3) of approximately 0.5%. The uranium can be recovered from these acidic wash solutions.

Some uranium is lost to the solvent, primarily during the first and second nitrate extractions. This loss, which amounts to approximately 0.5% of the uranium in the feed, is in the form of entrained sol and is present as a colloidal suspension. The particles are well dispersed, carry a slight negative charge, cannot be removed by filtration or adsorption on silica gel or activated carbon, and are not effectively removed by the standard solvent treatments.

2.3.5.2 Preparation of Spheres

Compared with earlier demonstrations, the major differences in the week-long demonstrations of UO_2 sphere preparation were the use of sol prepared by the CUSP process and the formation of spheres in a nonfluidized column. In addition, the column height was 8.5 m (28 ft) vs the 3-m (10-ft) column of earlier work,[46] and the temperature of the 2EH was 50 to 80°C in the nonfluidized column (vs 25 to 35°C for the fluidized columns). Our initial experience with CUSP sols showed that recycle of 2EH was very troublesome. Therefore, recycle of the 2EH was a principal point to be demonstrated. In the week-long runs, 2EH was successfully recycled.

The principal limitation with regard to the nonfluidized preparation of microspheres is that the sol drops introduced into a nonfluidized column must be small enough to gel before they settle to the bottom. The required column heights depend on mass transfer and on the settling velocity. Clinton[47] has investigated and correlated mass transfer as a function of sol drop size and organic liquid variables. The settling velocities may be calculated with Stokes' equation or a drag coefficient. Both the sol drop size and the density vary with time. Thus, mass transfer and the settling velocity also vary with time, and analytical solutions are not possible. However, the time and free-fall distance as a function of sol drop variables and alcohol variables can be conveniently calculated with a computer program.[48]

2.3.5.3 Drying and Sintering

The overall drying-sintering program, starting with gel spheres that are wet with 2EH, was as follows:

Drying:

1. argon flow, from 25 to 110°C, for 1 to 2 h;
2. argon plus steam flow, at 110 to 180°C, for about 4 h;
3. argon plus steam flow, at 180°C overnight;

Sintering:

1. to 500°C at 100°C/h in argon;
2. over the range 500 to 1150°C at 300°C/h in argon;

3. at 1150°C for 4 h in Ar-4% H_2;
4. over the range 1150°C to <100°C for >36 h in argon.

The purpose of the steam was to promote removal of organic substances and thus avoid leaving excessive carbon in the sintered spheres. We used 0.5 to 1 g of steam per gram of UO_2. Although the higher temperatures with steam are more effective for carbon removal, they tend to make the UO_2 gel become more reactive and more sensitive to oxidation. Therefore, 180°C was chosen as the maximum temperature, so that we would have less difficulty with oxidation during the transfer from the drying equipment to the sintering furnace. The Ar-4% H_2 reduces uranium oxides to UO_2 for the temperatures employed. The long cool-down is characteristic of our furnace; however, faster cooling, as high as 20°C/min or higher, would not affect the spheres. Use of an oxygen-free atmosphere is necessary during cooling because any O_2 present would oxidize the UO_2. The dense UO_2 spheres *are not* reactive with air below 100°C.

The drying and sintering equipment consisted of small, laboratory-scale batch units. The product collectors and dryers were Pyrex vessels fabricated from 600-ml filter funnels with coarse-porosity filter frits. These dryers were placed in a laboratory oven and connected both with an argon supply and with steam from a distillation flask. Sintering was performed in alumina crucibles in a commercial muffle furnace that had been modified to allow improved atmospheric control.

2.3.5.4 Results and Material Balances

The size distributions of the calcined spheres produced during a demonstration run are shown in Table 2.2. The nonfluidized sphere-forming column was operated continuously. The production rate for the run was approximately 2.9 kg UO_2/d.

Some of the chemical and physical properties of the calcined microspheres are as follows: density, 97 to 100% T.D.; O/U ratio, 2.003 to 2.005; roundness ratio (D_{max}/D_{min}), 1.02 to 1.03; carbon content, 24 to 60 ppm; and iron content, 12 to 46 ppm. The size control was good for a nonvibrating nozzle. The standard deviation

Table 2.2. Size Distribution of UO_2 Spheres Produced During Nonfluidized Column Demonstration Run[a]

	Proportion, %, in Each Size Range (μm)					
Batch	<125	125–149	149–177	177–210	210–250	>250
1	11.8	6.7	75.8	5.7	0.07	0.03
2	14.7	7.1	73.4	4.5	0.09	0.09
3	14.4	7.4	68.5	9.3	0.3	0.15
4	15.3	9.0	67.5	8.1	0.1	
5	17.9	8.6	65.6	7.6	0.2	0.09
6	10.1	5.4	74.2	10.2	0.1	
7	10.3	7.2	71.6	10.6	0.2	0.07
8	13.3	7.6	67.7	10.3	0.6	0.4
9	11.7	6.6	71.3	9.9	0.5	0.1
10	9.7	7.1	64.6	16.3	0.7	1.6
11	12.4	6.6	70.7	9.8	0.3	0.2
12	14.7	13.5	67.1	4.4	0.1	0.1
13	9.7	7.1	79.1	4.0		
14	10.8	19.1	55.9	13.3	0.8	0.1
Total weight, g	1542.4	1020.2	8356.2	1066.5	35.8	25.2
% of grand total	12.8	8.5	69.4	8.9	0.3	0.2
			86.8			

[a]One glass two-fluid nozzle [0.33-mm-ID (0.013-in.) sol feed capillaries] was used; sol flow rate, about 7.3 cm^3/min. No vibration.

for run 2 was about 10%. There was very little surface porosity, as indicated by the small surface area (8 to 400 m^2/kg) and the low gas release (∿4 cm^3/kg). The dried and calcined spheres (Fig. 2.5) are round, and cracking and surface imperfections do not represent a problem.

Because of the nature of the operation of the nonfluidized sphere-forming column, essentially no uranium is lost; however, some waste, 2.7 and 2.2 wt %, was generated during the demonstration runs. This waste resulted from sphere samples that were dried in air for size and shape examinations.

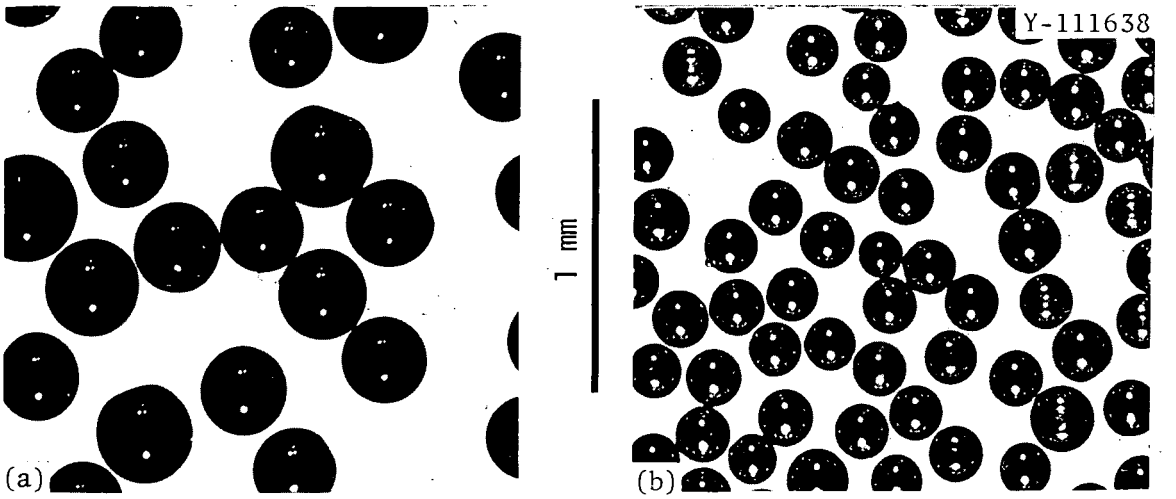

Fig. 2.5. Spheres of UO_2. (a) Gel spheres dried at 170°C in steam-argon. (b) Spheres calcined for 4 h at 1130°C in Ar–4% H_2.

2.3.5.5 Conclusions

The following conclusions are drawn with regard to the preparation of high-density UO_2 spheres from CUSP sols in a nonfluidized forming column when hot 2EH is used as the dehydrating agent.

1. The U(IV) feed can be routinely prepared in a batch slurry uranium reductor. Vigorous agitation is required for uniform reduction, and the completion of the reduction can be determined by monitoring the redox potential.

2. CUSP is an instrumented batch process for preparing 1.0 to 1.4 *M* UO_2 sols that are fully crystalline and have U(IV) concentrations of 85 to 87%. Reproducible sols can be prepared in relatively simple equipment by following the standard operating procedure. Some uranium is lost to the organic solvent; a loss also occurs as the result of equipment cleanout between batches. Uranium in the waste solutions can be recovered easily. The sol yield varies from 92 to 98%.

3. The operation of the nonfluidized sphere-forming column was quite satisfactory at about 3 kg UO_2/d. Although the production capacity of the 100-mm-ID (4-in.) column has not been established, it is greater than 3 kg UO_2/d. Some difficulty was encountered with plugging of the glass two-fluid nozzle capillaries; however, this was greatly minimized by installing a glass frit filter in the sol line. The 2EH was recycled, and good-quality, round spheres were prepared by

small periodic additions (~0.1 vol %) of Span 80. Two additions were needed during the demonstration runs. An on-stream factor of 96% was attained for each run.

4. The feasibility of the CUSP nonfluidized column process for the preparation of high-density medium-size UO_2 spheres has been demonstrated, and the process can be adapted to commercial use.

2.3.6 Application to $(Th,U)O_2$

Three sol preparation processes were used with water extraction for gelation to prepare $(Th,U)O_2$ spheres. These are:

1. Mix ThO_2 sol from hydrothermal denitration (Sect. 2.3.4) with UO_2 sols (Sect. 2.3.5). These sols can be mixed in all proportions. The mixed sols have the behavior and limitations of UO_2 with some improvement toward the properties of ThO_2 for Th/U > 4. For Th/U < 10, it is adequate to assume that the limitations and results already described for UO_2 sols apply, and this approach will not be discussed further.

2. Add UO_3 or uranyl nitrate to ThO_2 sols prepared by hydrothermal denitration. This is suitable for Th/U ratios less than 10. The U(VI) has a significant effect on the behavior of the sol, and these sols have gelation behavior and limitations similar to ThO_2-UO_3 sols that are prepared by an amine extraction process.

3. Extract with a liquid amine.

The gelation procedures and results for the third method are also applicable to the mixture of ThO_2 sol with UO_3 or uranyl nitrate above the limit of Th/U > 10. For the preparation of ThO_2-UO_3 sol by amine extraction, gelation by extraction of water was practical for Th/U > 3. Lower ratios were more difficult, with some useful results for ratios of 2 to 3.

2.3.6.1 Sol Preparation

Extraction with a liquid amine will be described in some detail. The preparation of ThO_2-UO_3 sols by the amine extraction process[36,37,49,50] consists of extracting nitric acid from a dilute solution of thorium-uranium(VI) nitrates with a secondary amine (Amberlite LA-2) to form a dilute ThO_2-UO_3 sol that is about 0.3 *M* in heavy metals (Th + U).

The dilute sol is then concentrated to greater than 1 *M* by evaporation of water to give a product that is suitable for use in forming spheres. In the work presented here, a dilute sol having a Th/U atom ratio of 4.25 was evaporated to 1.6 *M* (Th + U). It was very fluid at this concentration. The preparation of the dilute sol by the amine extraction process and the regeneration of the amine were carried out continuously for 10 days, producing an 81% ThO_2–19% UO_3 sol at the rate of 10.4 kg (Th + U)/d. The dilute $Th(NO_3)_4$-$UO_2(NO_3)_2$ feed solution was prepared and the dilute sol concentrated in batch processes at rates of preparation that kept pace with the continuous operation of the amine extraction equipment. The results demonstrated the feasibility of the continuous operation of the amine extraction process and confirmed that a reproducible sol product could be obtained.

2.3.6.2 Preparation of Spheres

In the sphere-forming process, gel spheres are produced as water is extracted from droplets of a given sol by 2EH. The droplets are fluidized by an upflowing stream of 2EH until they are gelled. The settling velocity of the spheres increases as the water is extracted. Proper selection of the fluidizing velocity of 2EH allows preferential removal of gelled product and permits continuous operation.[41]

The addition of surfactants to the 2EH is required to stabilize the spherical shape of the sol droplets during water extraction. Two surfactants are used in combination to facilitate the formation of ThO_2-UO_3 gel spheres: Span 80 and Ethomeen S/15. The proper concentrations of nitric acid and water are also necessary to obtain a spherical gel product. If these proper concentrations are not maintained during operation of the forming column, gel particles that are cracked, distorted, clustered, or surface-pitted are produced.

Periodic addition of surfactants to the 2EH gives satisfactory results for continuous operation of our sphere-forming columns. The rate at which the additions are made is established empirically from visual observations of particles in the column and from microscopic examination of the product.

The sol is dispersed into droplets that are released into the 2EH at the enlarged top of a tapered fluidization column. A throughput of 10 kg (Th + U)/d was achieved by using a multiple two-fluid nozzle disperser and a flow rate of 18.2 cm^3/min for the 1.64 *M* (Th + U) sol. Eleven nozzles produced sol droplets 900 to 1500 μm in diameter. A diameter shrinkage factor of 3 occurs from sol droplet to the calcined sphere for a high-density $(Th,U)O_2$ product prepared from a 1.64 *M* (Th + U) sol.

The most satisfactory method for feeding sol in a large-scale system is the displacement of sol by a stream of wet 2EH. The 2EH is a clean, noncorrosive, self-lubricating fluid that is easily metered with a variable-speed gear pump. A 50- to 150-μm-porosity filter removes any large particles from the sol and minimizes plugging of the sol capillaries.

The column circuit used in the study presented here had been used over a period of several years and had proved to be effective for producing spheres in the 200- to 600-μ-diam (sintered) size range.[41] We believe that this column and all the equipment in the column circuit can be readily adapted to remote operation.

2.3.6.3 Drying and Sintering

A steam atmosphere is used as the purge gas in the drying operation because it is effective in removing imbibed and sorbed organic materials and suppressing exothermic reactions.[42] Exothermic reactions of a magnitude sufficient to cause excessive breakage of the spheres occur even with steam if a uniform temperature is not maintained throughout static beds of spheres.

Operation of the sintering furnace was entirely satisfactory. Sintering-dependent specifications of particle density, carbon content, content of absorbed gases, and O/U atom ratio were met. No sticking occurred.

To remove carbon and densify, the dried spheres are heated in air to 1150°C. They are then reduced at 1150°C in Ar-4% H_2 for 4 h to attain the desired O/U atom ratio. The reduced product is then cooled to room temperature in argon.

Products of this procedure had densities of 95 to 98% T.D., carbon contents of 20 to 40 ppm, and O/U atom ratios of 2.001 to 2.020. They were solid solutions of UO_2 in ThO_2, as determined by x-ray lattice parameter measurements. These gels have a good shrinkage pattern for ease of removal of the remaining volatiles. The density is only about 40% of theoretical at 850°C, and all the pores are open. Thus the sorbed carbon-bearing materials, nitrates, and water could easily be removed before pore closure occurred. The reducing gas flowed through the particle bed rather than across the top. This gave suitably low values for carbon content and O/U ratio.

2.3.6.4 Conclusions of $(Th,U)O_2$ Sphere Production

1. Good-quality spheres can be prepared by using either the continuous or the batch method of surfactant control.

2. The continuous method for controlling the surfactant concentration in the sphere-forming column is definitely superior to the batch addition method.

3. Operation with the multiple two-fluid nozzle unit, which consists of 11 nozzles, is entirely satisfactory; however, a multiple-orifice, gravity-type disperser has performed satisfactorily in other tests and should also be applicable for this type of operation.

4. Yields of 90 to 95% for 250- to 450-μm-diam product spheres can be expected from the sphere-forming process at the current level of development. Control of the mean diameter size in the 300- to 400-μm-diam size range can be attained to ±3% of the specified diameter.

5. The forming, drying, and firing operations in the preparation of spheres appear adaptable to remote operation at this time. The column circuit, as it now stands, is sufficiently developed to allow immediate adaptation.

2.3.7 Application to $(U,Pu)O_2$

All sols for preparing $(U,Pu)O_2$ spheres resulted from blending UO_2 and PuO_2 sols. The U/Pu ratios are greater than 1 and the gelation and drying requirements are essentially those described for UO_2 sols in

Sect. 2.3.5. Therefore, only the PuO_2 sol preparation is described in detail. While PuO_2 sols are more difficult to prepare than ThO_2 sols, the stability and ease of sphere preparation for PuO_2 sols are similar to those for ThO_2 sols. The most completely demonstrated process for PuO_2 sols is a combination of precipitation and thermal denitration. A more recently developed liquid extraction of HNO_3 has important advantages and should be developed further for future applications. Both sol preparation procedures will be described.

2.3.7.1 Precipitation, Thermal Denitration for PuO_2 Sol Preparation

Figure 2.6 presents the generalized flowsheet for preparing plutonia sol. (The digestion step shown was not used initially.) This is a flexible flowsheet, as shown by the ranges of concentrations over which it has been demonstrated; the batch size given is 150 g Pu. Before precipitation, a feed adjustment is made, if necessary, by passing NO gas through the $Pu(NO_3)_4$ solution to convert both Pu(VI) and Pu(III) to the desired Pu(IV). Most $Pu(NO_3)_4$ solutions do not require a plutonium valence adjustment. A minimum HNO_3 concentration of 1 *M* is maintained in the feed to prevent polymerization; however, sols have been successfully prepared starting with free HNO_3 concentrations as high as 3 *M*. In the precipitation step, as little as 48% excess NH_4OH has proved to be satisfactory as long as the concentration of this base in the final solution is at least 1 *M*. The $Pu(NO_3)_4$ feed solution is added to the NH_4OH solution at rates up to 30 cm^3/min. Moderate agitation is used to ensure rapid neutralization and precipitation of the $Pu(OH)_4$. The solution of NH_4NO_3 and excess NH_4OH is drawn off through a filter having 10-μm-diam openings. The precipitate is washed four times to remove NH_4^+; the filter cake is resuspended in each wash. Filtration time is about 30 min per wash. Plutonium losses to the total filtrate have been less than 0.01%. After the washing step, the precipitate is digested for 2 h in H_2O at 95 to 100°C; this treatment stabilizes the crystalline structure and prevents depolymerization during subsequent steps. A high-nitrate sol is then formed by peptizing in dilute HNO_3 at a NO_3^-/Pu mole ratio of approximately 2. All the steps including peptization are

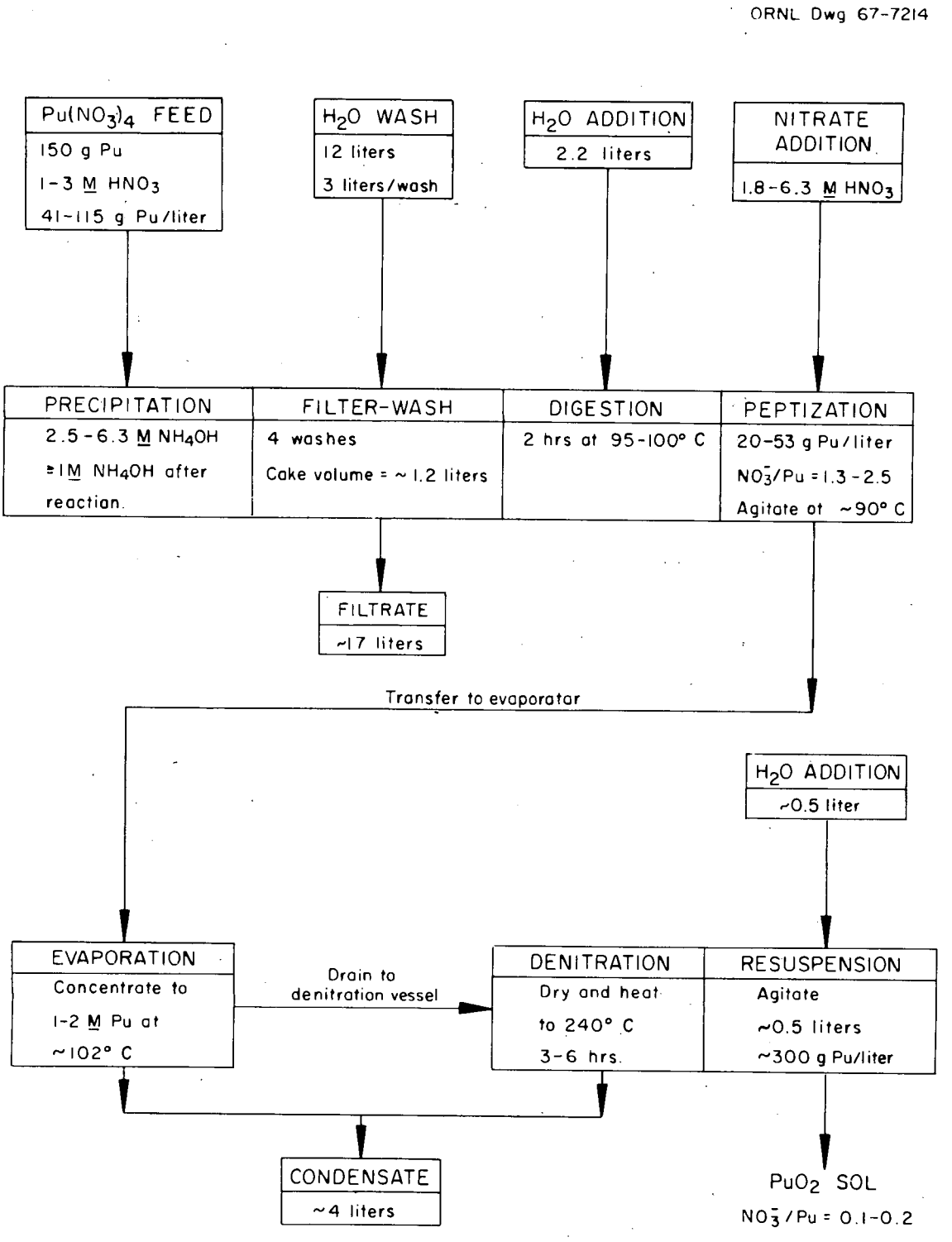

Fig. 2.6. Generalized Flowsheet for Preparing Plutonia Sol.

carried out in a single precipitation-filtration vessel that is 0.20 m (8 in.) in diameter and has a porous stainless steel filter in the bottom. The high nitrate sol passes through the bottom of the vessel, leaving no solids on the filter.

A NO_3^-/Pu mole ratio of 1 or greater is necessary to accomplish peptization. Although ratios as high as 4 have been demonstrated, a ratio of 1.1 is sufficient to produce a sol upon heating to approximately 90°C. At this point, a true sol (crystallite size < 2.0 nm) exists, but spheres formed from this material would have a low density and a low resistance to crushing. To form a desirable product, a sol must have a NO_3^-/Pu mole ratio in the range from 0.1 to 0.2; the appropriate reduction in ratio is accomplished by thermal denitration. Several other methods of precipitation and denitration were attempted; however none produced satisfactory results.

In the thermal denitration step, the sol is evaporated to dryness at 100°C to form a thin, porous cake that remains intact through subsequent heating to 240°C. Excess HNO_3 is evolved during evaporation, giving an initial NO_3^-/Pu mole ratio of 0.8 to 1.0 in the dry solid. In general, after 1 to 2 h at 240°C, this ratio decreases to 0.2 to 0.3; usually an additional 2 to 3 h is required to attain a final NO_3^-/Pu mole ratio of 0.1 to 0.15. Progress of the denitration is followed by periodically resuspending a weighed sample of the dry material and titrating with NaOH to determine the NO_3^- content. It is important that the heating of the solid be uniform in order to produce a homogeneous product. Denitration that is allowed to proceed until the NO_3^-/Pu mole ratio is appreciably less than 0.1 yields a form of PuO_2 that cannot be resuspended. The design of the denitration vessel allows independent control of temperatures of the top and bottom surfaces and limits radial gradients to about 2°C.

The denitration step promotes crystallite growth and agglomeration. After denitration, the average size of the crystallites is approximately 8 nm; these crystallites form agglomerates as large as 100 nm. Crystallite growth is desirable; however, the degree of agglomeration must be limited if a stable sol is to be obtained. Denitrated sols

having a NO_3^-/Pu mole ratio in the range of 0.1 to 0.15 can be resuspended in water, with only mild agitation, to form sols having plutonium concentrations approaching 2 *M*; more concentrated sols may be produced by subsequent evaporation if desired.

2.3.7.2 Solvent Extraction Preparation of PuO_2 Sols

A new solvent extraction process for preparing PuO_2 sols was developed.[51] The process has three major operations:

1. extraction of HNO_3 from $Pu(NO_3)_4$-HNO_3 feed with a long-chain alcohol, such as *n*-hexanol, until a plutonia sol with a NO_3^-/Pu mole ratio of about 1 is obtained;
2. seeding, in which sol is added to the feed solution before or during extraction to create a micelle structure of aggregated crystallites;
3. thermal denitration, which consists of drying and baking the sol.

The aggregated micelle structure promotes rapid denitration and crystallite growth; because these sols denitrate very rapidly and are insensitive to overheating, denitration can be accomplished by a variety of continuous processing methods. As a result, low-nitrate sols (NO_3^-/Pu mole ratio from 0.1 to 0.2) with average crystallite diameters of 6.0 to 7.0 nm are easily prepared. The sols can be mixed with urania or thoria sols in any proportion and used to prepare spheres. These sols, therefore, have all the versatility of application of sols prepared by earlier methods. In addition, considerable advantages are obtained with regard to method of preparation and ease of scale-up.

The process flowsheet, shown in Fig. 2.7, employs continuous extraction with *n*-hexanol, during which the feed solution is added incrementally at the indicated volume ratios. With this procedure, the effect of double seeding is obtained in a single run because extraction is continued after each feed addition until colloidal plutonium polymer is formed. Following the final extraction to a NO_3^-/Pu mole ratio of 0.8 to 1.2, the sol is evaporated to dryness and heated for a minimum of 15 min at 230°C in a dry sweep gas to remove volatile decomposition products. The final sol is prepared by resuspending the denitrated

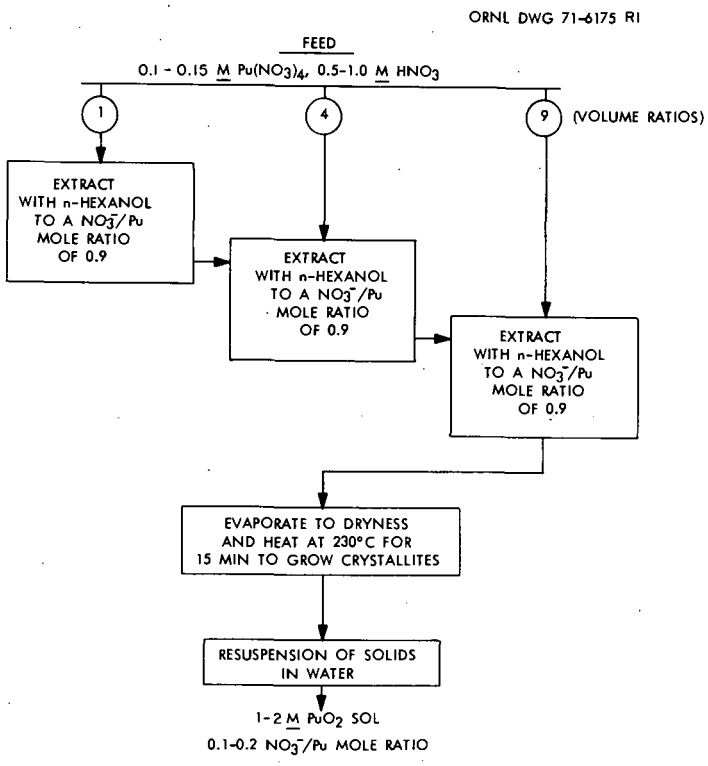

Fig. 2.7. Process for the Preparation of Low-Nitrate Plutonia Sol.

solids in water and evaporating to the desired plutonium concentration. Sols with plutonium concentrations in excess of 2 *M* and having NO_3^-/Pu mole ratios between 0.1 and 0.2 are obtained by the process.

The extraction apparatus used for the small-scale (20 g Pu) laboratory preparation of plutonia sols consists of two identical contactor-separator sections. In the first (or extraction) section, nitric acid is extracted from the aqueous $Pu(NO_3)_4$ solution with *n*-hexanol. After separation of the phases, the alcohol is pumped to the second (or stripping) section, where the acid is stripped from the alcohol into water. The regenerated alcohol is then recycled to the extractor. The plutonium nitrate solution is circulated through the extraction section only, and the water strip is circulated through the stripping section only. The net result of this extraction-stripping cycle is to transport HNO_3 from the plutonium nitrate solution to the water strip, which can either be changed periodically to maintain satisfactory extraction rates or processed continuously to remove extracted plutonium by cation exchange and HNO_3 by anion exchange. The

progress of the extraction is monitored by a conductivity probe located in the circulating plutonium nitrate stream. Further description of this process is available.[51]

Before denitration, the sol must be dried. This was typically accomplished by evaporation at 80 to 100°C; however, it should be possible to perform this step by nearly any desired method, since the sol can be boiled if desired, and the evaporation rate is not critical. The NO_3^-/Pu mole ratio of the sol before concentration to dryness is a critical variable; the optimum value is in the range of 0.8 to 1.0. Lower values of about 0.6 or less result in plutonia solids that will not resuspend in water after thermal denitration, while higher values increase the time required for denitration.

The presence of water vapor had an adverse effect on denitration behavior. Crystallites from high nitrate plutonia sols prepared by any method undergo two growth mechanisms during thermal denitration at elevated temperatures. One is crystallite growth, which is desirable, and the other is irreversible, random aggregation of crystallites, which is undesirable because of the production of large particles that frequently will not resuspend to form a sol. The formation of large particles is readily detected in a sol by accompanying color change. When the crystallites are primarily unassociated, the sol is dark green (nearly black). As large particles form, the color becomes much lighter. In a severe case. the sol is nearly white and solids settle rapidly unpon standing.

A series of tests was made to determine the effects of low nitrate concentration and larger crystallite size on the stability of mixed UO_2-PuO_2 sol. The shelf life of mixed sol prepared from low-nitrate plutonia sol (NO_3^-/Pu mole ratio = 0.2 to 0.4) and CUSP urania sol was 5 to 8 d at 25°C. This compares with a shelf life of only 30 min for mixed sols prepared with high-nitrate plutonia sol (NO_3^-/Pu = 0.7). In both cases, reducing the temperature to about 5°C greatly increased the shelf life. Because of the improved shelf life, a series of mixed-sol (80% UO_2, 20% PuO_2) sphere-forming runs was made in which the sols were not cooled to 5°C, as is required when high-nitrate plutonia sol is used. Yields of 90 to 95% were consistently obtained in these experiments. Pure plutonia spheres were also readily prepared from low-nitrate plutonia sols.

A series of laboratory tests was made to demonstrate the formation of spheres from mixed UO_2-PuO_2 sols prepared from low-nitrate plutonia sols. Several mixed sols containing 80% UO_2 and 20% PuO_2 were prepared from two plutonia sols and two CUSP sols. Good quality sintered spheres were obtained in yields of 90 to 95% in eight consecutive experiments.

The plutonia sols, which had NO_3^-/Pu mole ratios of 0.19 and 0.20, were not cooled but were kept at room temperature. The urania sols were extracted with an equal volume of water-saturated *n*-hexanol to remove formic acid just before mixing the sols.

Two plutonia sols were also used to prepare pure plutonia spheres. The NO_3^-/Pu mole ratios of these sols were also 0.19 and 0.20. High yields of sintered spheres were obtained, and all products were crack free. Surfactant concentrations in the drying alcohol were the same as those used in the mixed-sol experiments, namely 0.15 vol % Span 80 and 0.40 vol % Pluronic L-92.

Although these experiments have been performed only on a laboratory scale, the results indicate that spheres can be prepared by techniques that have been demonstrated on an engineering scale for ThO_2 and ThO_2-UO_2 sols. The sols prepared by this process, therefore, show promise of having all the versatility of application of sols prepared by the earlier methods.

2.4 DROP FORMATION — P. A. Haas

The amounts of metal oxide in the product spheres are those in the broth or sol drop before gelation. Drop formation 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 sintered sphere size can be produced 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/h. For a typical product density of 10 Mg/m^3, the corresponding sphere preparation rates are given in Table 2.3. All the gel processes for sphere preparation require similar liquid drop preparation capabilities independent of the gelation technique. All the drop-formation procedures start with flow of the

Table 2.3. Rates of Drop Formation

Sintered Sphere Diameter (μm)	Sphere Mass (μg)	Drop formation rate, drops/s	
		For 0.1 kg/h product	For 10 kg/h product
900	3820	7.3	730
300	141	196	19.6×10^3
100	5.24	5300	530×10^3
33	0.194	1.4×10^5	14×10^6

broth or sol through small orifices or capillaries. The formation of drops can result from several different mechanisms, and the four most useful mechanisms will be discussed separately below.

2.4.1 Drop Weight Mechanism

The slow formation of a drop from a wetted capilliary tip or a nonwetted orifice is reproducible and is used as a measure of interfacial or surface tension. The theory is that the drop detaches when the gravitational force equals the interfacial tension at the wetted perimeter. In practice, empirical correction factors are required. The rate of drop formation is also a variable because: (1) all practical systems contain surface active materials, which make the interfacial tension of a freshly formed surface time dependent; (2) the kinetic energy or momentum of the liquid adds to the weight of the drop; and (3) flow of liquid into the drop continues until the drop has time to move away from the tip so a new drop can form.

The use of this drop formation mechanism can give good uniformity of drop size from a very simple apparatus. It is useful for small tests where the exact size is not important. It is not very promising for routine operation to prepare sphere-pac fuels. The limitations are:

1. Only the largest size of spheres could be prepared. In theory, the drop diameter is proportional to the one-third power of the orifice diameter, and the orifice sizes for spheres smaller than about 300 μm are not practical.

2. The orifice must operate with a low pressure drop and a low broth or sol flow rate per orifice. A large number of orifices with a

single feed is easily fabricated, but any tendency to plug is not correctable as the flow through the remaining orifices increases and the drop size is affected. This would be particularly troublesome for chemical gelation.

3. The orifice diameter is the only independent variable usable to control the drop diameter, while the dynamic interfacial tension is difficult to measure or predict. Therefore, the average diameter is difficult to control and reproduce; changes require a change (replacement) of the orifices.

4. For the same total flow rate to a single two-fluid nozzle with vibration or multiple orifices, the two-fluid nozzle gives a more uniform, a more predictable, and a more easily controlled drop size.

The theoretical equation for the drop weight mechanism is:

$$D = (6d\gamma/\Delta\rho g)^{1/3}$$

Where D is drop diameter,

d is wetted perimeter of orifice or tip,

γ is interfacial tension (dynamic),

$\Delta\rho$ is the density difference,

g is the gravitional constant.

For practical rates of drop formation, D is generally 80 to 120% of the value predicted by the equation. For good results, the wetted perimeter, d, must be well defined. For a wetted capilliary tip, d will be the outside diameter of the capilliary at low drop formation rates. At higher flow rates, there is a tendency to push the drop formation away from the tip to result in the inside diameter as the value of d. Orifices in a thin plastic surface that is not wetted by the liquid result in d equal to the orifice diameter and are also less likely to plug than capilliaries of the same inside diameter. Maximum practical capacities per orifice are from 0.3 cm^3/min for 1000 μm drop diameter to 10 cm^3/min for 3000 μm drop diameter or about 10 drops per second.

2.4.2 Laminar Breakup of Jets

A liquid jet discharged from a small opening at viscous or laminar flow conditions will tend to break up into short lengths, which then form spherical drops. The cause of this behavior is surface energy, as represented by interfacial tension. The most common drop diameter is about 2 times the jet diameter and is formed from a length of jet about 5 times the diameter. This type of jet breakup persists to high jet velocities if the jet is protected from other disturbances.

Optimum application of this jet breakup to sphere preparation requires procedures to minimize the following problems:

1. The breakup of the jet depends on the size of surface disturbances and normally has a statistical distribution of breakup positions and therefore drop size around the most probable values. The most regular breakup possible is needed to give uniform drop sizes.

2. As the liquid viscosity increases, the growth of a disturbance into a break becomes slower; therefore viscous jets may require excessive times or distances and may be affected by other disturbances.

3. Conditions that allow any drop-to-drop contact are likely to result in coalescence.

4. If the orifice diameter used to form the jet is the only variable for controlling the drop size, small adjustments are inconvenient; that is, a large number of interchangeable nozzles would be necessary.

5. The drops are generally gelled in an organic liquid. A jet operated in a liquid tends to slow to the liquid velocity (thereby increasing the jet diameter). If the drops are formed in a gas, splattering or coalescence at the liquid interface are troublesome.

6. Plugging of small jet openings is troublesome.

One effective technique is to impose a regular vibration on the liquid jet to control the breakup.[52] 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. Frequencies different from the natural frequency by a factor of 2 or more are difficult to impose. The use of vibration is very helpful for dealing with

problems (1), (2), and (4) listed above. Pulsing the liquid can help minimize plugging. In order to estimate the natural frequency of breakup, the liquid flow rate and the jet diameter must be known.

Another effective technique is to use a two-fluid nozzle with a drive fluid in an annulus around the jet. The drive fluid and jet should not have large differences in velocities and the smaller jet will quickly change velocity to the same velocity as the drive fluid. The use of the liquid drive fluid is very helpful for controlling problems (3) and (5). Extension of the drive fluid flow channel minimizes difficulties from problems (1) and (2). The jet size can be varied by accelerating or decelerating it moderately, thus providing some control of the jet diameter and drop diameter without changing the nozzle. The drive fluid flow must be laminar or viscous, as the disturbances from turbulent flow would disrupt the jet. Somewhat larger jet nozzles can be used to minimize plugging with a higher drive fluid velocity than jet velocity to accelerate the jet and give a smaller effective diameter than the orifice diameter.

2.4.3 Laminar Jet Breakup Apparatus

The drop forming techniques described in the previous section have been applied with 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 capilliary or to the liquid feed stream to the jet. The effects of the vibration are observed with a stroboscopic light of the same frequency. The arrangement most commonly used at ORNL is shown as Fig. 2.8. A single vibrator or a single drive-fluid flow can serve multiple jets. But the jets are usually supplied by individually metered flows of sol or broth, as an unequal division of flow and 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. Among these are:

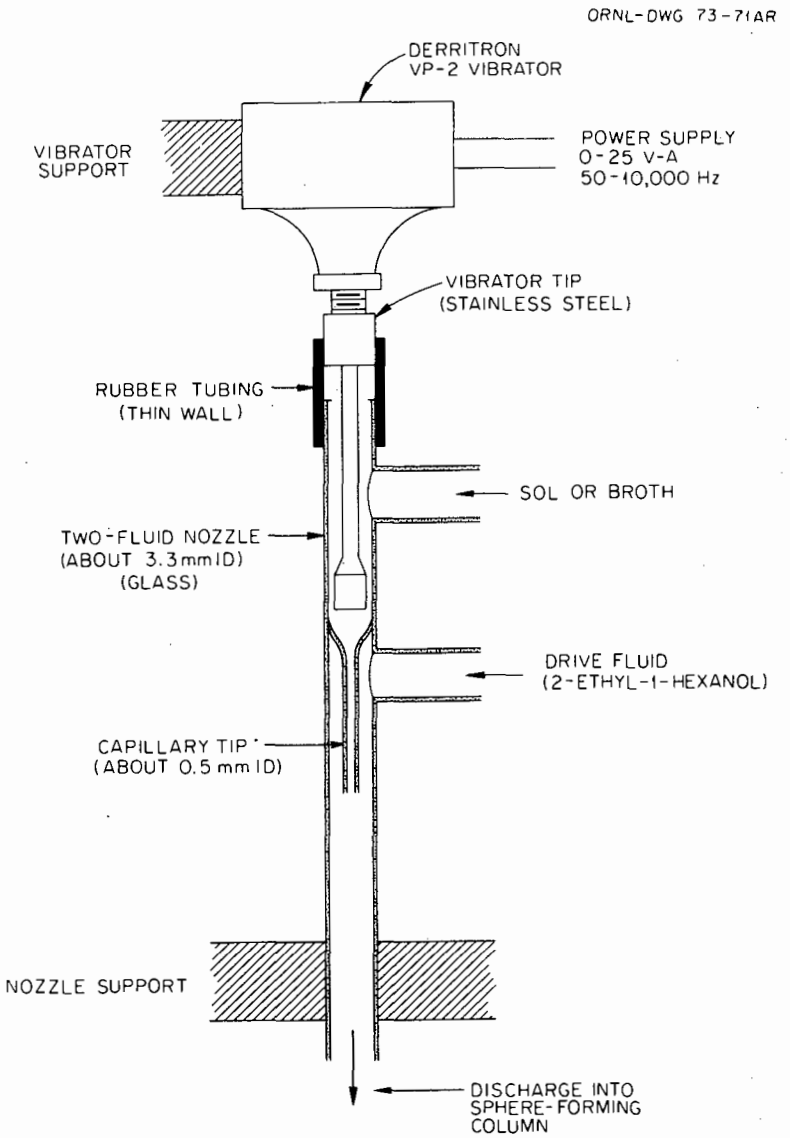

Fig. 2.8. Two-Fluid Nozzle with Vibration.

1. pulse a diaphragm in the feed line near the nozzle;
2. apply the vibration to a rubber or plastic feed line held between a fixed anvil and the vibrator;
3. move the whole nozzle by coupling it rigidly to the vibrator (axial motion);
4. move the capilliary from which the jet discharges transverse to the axis [Fig. 2.9(b)];
5. apply an ac electrostatic potential to the jet [Fig. 2.9(d)].

All these can give a uniform breakup at frequencies near the natural

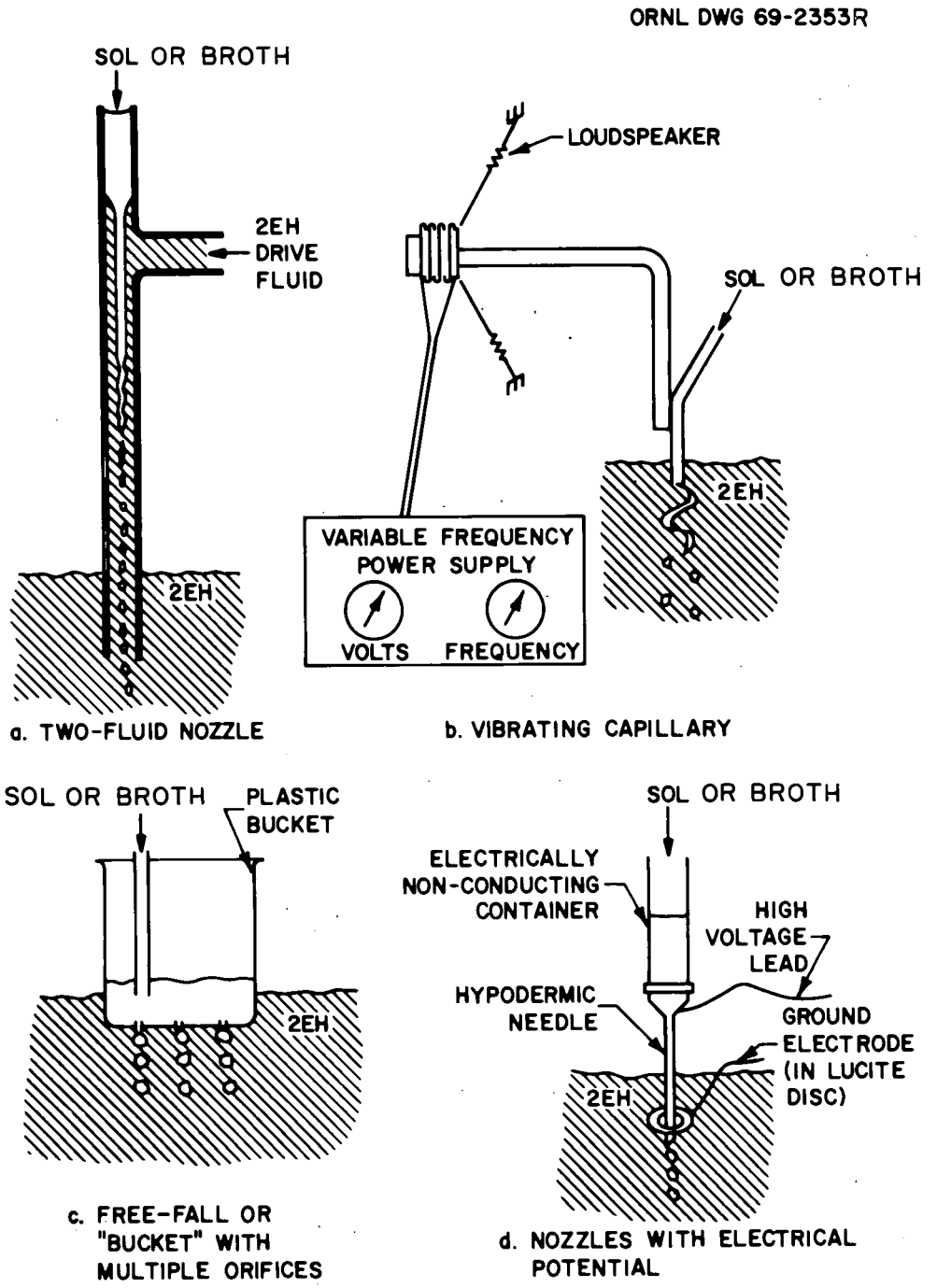

Fig. 2.9. Devices for Dispersing Sol or Broth as Drops in 2-Ethyl-1-Hexanol (2EH).

frequency of jet breakup and are less effective as the difference from the natural frequency increases. The arrangement shown in Fig. 2.8 is believed to be less sensitive to resonances in the apparatus than the other mechanical arrangements and is effective at very low power inputs. The drive-fluid flow carries the drops away from the nozzle into the bulk liquid, where gelation is completed, while the other arrangements [Fig. 2.9(b) and (d)] do not.

The natural frequency of breakup for a laminar jet of sol or broth can be calculated from the volume flow rate and the diameter. For a jet in gas the diameter of the jet is equal to the diameter of the capilliary tip. For a liquid drive fluid (Fig. 2.9), the jet is accelerated to the drive fluid velocity, and the effective diameter is calculated from this velocity and the sol or broth flow rate. The centerline velocity for laminar flow is twice the average velocity. The natural frequency of breakup corresponds to jet lengths about 5 times the jet diameter; then the frequency is the velocity/(5 × diameter). For the two-fluid nozzle, the drop diameter from those relationships is 1.4 $ID(R)^{1/2}$, where ID is the drive fluid channel inside diameter and R is the ratio of sol to drive fluid flow. From a simple volume balance, the rate of drop formation times the drop volume must equal the sol flow rate.

2.4.4 Turbulent Breakup in Two-Fluid Nozzles

Practical capacities for small spheres require very high rates of drop formation (Table 2.3), and the laminar jet breakup or drop weight mechanisms are not practical for production use. A range of sphere sizes for the fines in sphere-pac fabrication is probably acceptable. But the range should be limited, as the two tails of the size distributions are troublesome. If an excessive amount of material is in the tail on the large end, it will have to be separated and recycled. The finest spheres cause difficulties in collection, washing, solids handling, contamination spread, and perhaps clustering during sintering.

A drop-formation mechanism based on turbulent flow of drive fluid in a two-fluid nozzle is useful for production of fines. The sol or broth stream is dispersed into drops whose average diameter depends on

the turbulence and interfacial tension at the nozzle conditions. The average diameter is controlled by controlling the drive fluid flow rate. The turbulent nozzle gives a narrower range of sizes, particularly less 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.

Results and correlations were recently reported by Karabelas[53] for turbulent formation of drops in a 50-mm-ID flow channel. His studies were for dispersion of water into hydrocarbons and were for 10 to 40 times larger flow channels, but the drop formation otherwise corresponds to our use of turbulent two-fluid nozzles. The form of correlation Karabelas recommends appears to apply for a wider range of variables and has a more reasonable theoretical basis than the correlation we have used for our data. Therefore the following relationship is now preferred:

$$\frac{D_S}{D_N} = \frac{3.4}{(We)^{0.6}} = 3.4\left(\frac{\sigma}{D_N V^2 \rho}\right)^{0.6}$$

where

D_S is the average diameter of the sol drops (weight or volume basis),

D_N is the inside diameter of the nozzle,

V is the velocity in the nozzle based on total (organic plus broth) flow,

We is the Weber number (dimensionless),

ρ is the organic density, and

σ is the interfacial tension at the time of drop formation.

The interfacial tensions are very time dependent when surface active agents are present, and we routinely add a surfactant (Span 80) as part

of the flowsheet conditions. However the turbulent nozzle forms drops very quickly before the surface concentration can increase. Therefore organic-broth interfacial tensions are used as follows to predict the drop sizes:

45 mN/m for TCE (trichloroethylene)

15 mN/m for 2EH

4 mN/m for isoamyl alcohol.

The sol drop diameter increases as the broth viscosity increases, and the correlation might be improved by replacing the constant, 3.4, by $3(\mu_s/\mu_o)^{0.2}$ where μ_s and μ_o are the broth and organic viscosities, respectively. The data to justify this viscosity term are limited.

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. This is demonstrated by comparison of the products of the same mean size for a paddle agitator and the two-fluid nozzle (Table 2.4).[46] From visual observations it appears that the differences are even greater at $0.2d_{50}$; however, numerical measurements at the small diameters are not available. Large representative samples of product obtained during operation with two-fluid nozzles under turbulent flow conditions were generally 60 wt % within $0.7d_{50}$ and $d_{50}/0.7$. The size distribution of ThO_2 spheres with a mean diameter of 65 μm is shown in Fig. 2.10.

Table 2.4. Size Distributions for ThO_2 Microspheres Prepared by a Paddle Agitator Compared with Those Prepared by a Two-Fluid Nozzle

Method of Preparation	Mean Diam d_{50} (μm)	Proportion, wt %, Smaller than			
		$0.8d_{50}$	$0.6d_{50}$	$0.4d_{50}$	$0.2d_{50}$
Paddle agitator	92	42	30	24	∿18
Two-fluid nozzle (turbulent flow)	90	30	13	7	∿ 3
Paddle agitator	78	38	26	∿19	∿14
Two-fluid nozzle (turbulent flow)	76	28	11	∿ 4	< 2

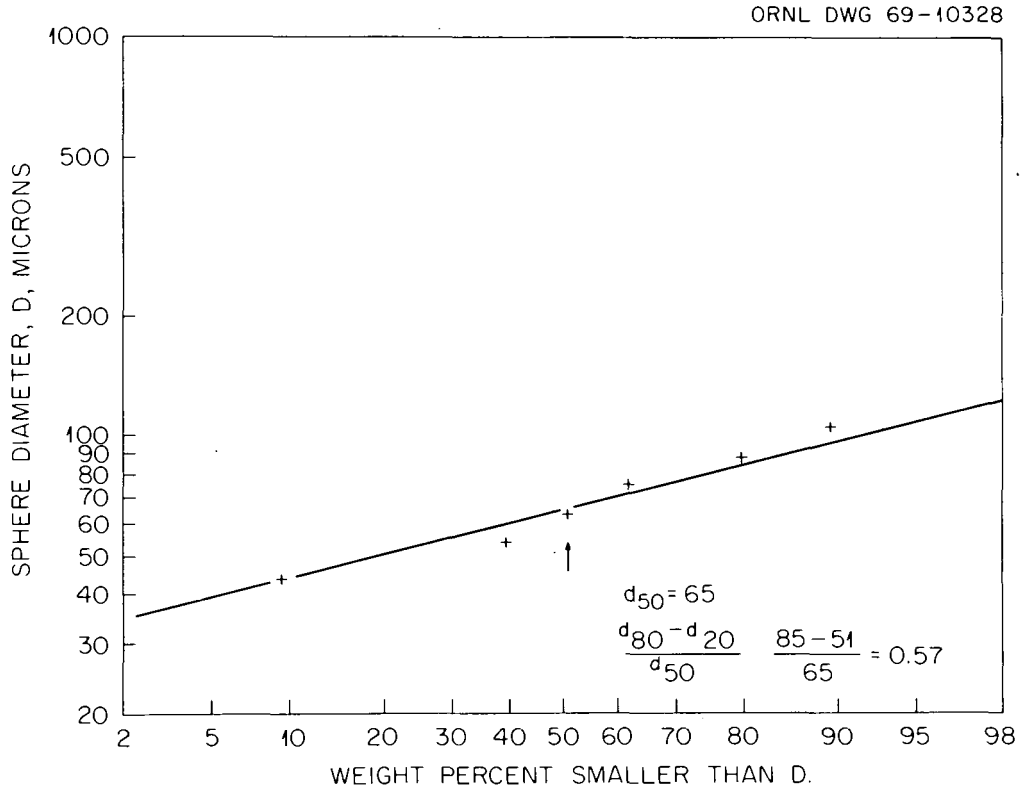

Fig. 2.10. Size Distribution of a Sample of ThO_2 Spheres Prepared by Nonlaminar Flow Dispersion of a Two-Fluid Nozzle.

2.4.5 Capacity Limitations

The capacities of 0.1 to 10 kg/h of product spheres correspond to sol or broth flow rates of 5 to 200 cm^3/min and the corresponding rates of drop formation were given in Table 2.3. The use of the drop weight mechanism will require multiple orifices with difficulties as described in Sect. 2.4.1. Single turbulent nozzles as described in Sect. 2.4.4 can be easily designed for large capacities. The capacity limitations for laminar breakup of jets requires more detailed discussion.

Calculation of maximum capacities per nozzle from the data in Table 2.3 requires information on the sol concentration and the allowable jet velocities. Large drops for external gelation may be formed in air, and the allowable jet velocities may be as large as 2 m/s. For water extraction or for internal gelation, two-fluid nozzles are required, and the drive fluid Reynolds numbers must not exceed 1000 ($\leq$600 preferred) to avoid undesirable turbulent effects at the sol capilliary tip. These requirements give the calculated capacities listed in Table 2.5. The differences in viscosities and densities for

Table 2.5. Calculation of Allowable Nozzle Flow Rates

Diameter, μm		Drive fluid	Dense Sphere Diameter	Calculated Nozzle Capacities					
				For sol jet = 2.0 m/s		For Drive Fluid of 2EH, 30°C, Re = 1000		For Drive Fluid of TCE, 30°C, Re = 600	
Sol Drop	Sol Capilliary	ID (mm)	for 300 kg U/m³ (μm)	sol capacity (liters/h)	Capacity[a] (g U/h)	Velocity (m/s)	Capacity[a] (g U/h)	Velocity (m/s)	Capacity[a] (g U/h)
4000	2000	8	1200	22.6	6870	0.97	3300	0.032	110
2000	1000	4	600	5.65	1695	1.95	1700	0.064	55
1000	500	3	300	1.41	423	2.60	540	0.086	18
500	250	2	150	0.35	106	3.90	150	0.13	7
250	125	1.5	75	0.088	26	5.20	70	0.17	2.2
125	63	1.0	38	0.022	6.7	7.80	26	0.26	0.9

[a]For 300 kg U/m³.

2EH as compared with trichloroethylene (TCE) or tetrachloroethylene result in about 20 times the velocity and 20 times the capacity for the 2EH at the same Reynold's number.

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

1. Large product spheres (above 600 μm diam) at practical rates result from breakup of sol or broth fed through capillaries of 0.5 to 2 mm ID. Maximum capacities per nozzle exceed 1000 g U/h for drops formed in air or 2EH and exceed 100 g U/h in TCE.

2. The uniformity of drops from capillary breakup can be greatly improved and controlled by imposing a vibration.

3. The techniques of (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. The calculated capacities per nozzle are 7 to 150 g U/h for 150-μm spheres.

4. The uniformity of the product using vibration can exceed 95 wt % between $0.9d_{50}$ and $1.1d_{50}$, where d_{50} is the average diameter.

5. For a turbulent nozzle, a typical result is 60 wt % between $d_{50}/1.3$ and $1.3d_{50}$ and less than 3 wt % smaller than $0.2d_{50}$.

6. Turbulent nozzles easily meet the capacity requirements for production operation, while calculated capacities per nozzle for 38-μm spheres and laminar flow jet breakup are 1 to 26 g U/h.

2.5 SPHERES CONTAINING CARBON — P. A. Haas

2.5.1 Sol Preparation

For the preparation of carbide or oxycarbide spheres, commercial carbon blacks are added to the aqueous sols or broths. This carbon is a nonreactive solid through gelation, washing, drying, and low-temperature sintering; then the metal oxides react with this carbon at 1500 to 1900°C. For external gelation with NH_3-NH_4OH or gelation by water extraction, the same sols or broths used to prepare oxide spheres were used to prepare carbide spheres. The carbon black properties and mixing conditions that give usable dispersions were determined empirically. This approach of adding a carbon addition step to developed flowsheets gave useful products, but may fail to determine

the optimum flowsheet conditions. The internal gelation flowsheets for carbide fuels have been more systematically developed.[54,55]

Carbon blacks with a wide range of properties are offered commercially. Dispersion in liquids is commonly required for use in inks or in polymers and emulsions. Dispersing agents are commonly used, and basic pH values are usually most favorable. These preferred dispersion conditions are not commonly applicable to our nuclear fuel processes, as the dispersing agents may have undesirable residues and the U, Pu, and Th sols or broths are acidic.

At ORNL, a channel black* with the following properties was used[56] for gelation by water extraction:

Fixed carbon (portion not volatilized at 1000°C in argon), %	92.4
BET surface area, m^2/g	105
Calculated particle size (from surface area), nm	30
pH of aqueous suspension	4.5

The same properties were recommended elsewhere[54] for both internal gelation and gelation by water extraction. This particular carbon black is no longer manufactured, and channel blacks are obsolete, but similar properties are available in other carbon blacks.

The amount of carbon black added must be empirically adjusted to give the required carbon-to-metal ratio in the calcined spheres before carbothermic reduction. Since the carbon blacks contain some volatile constituents and some oxygen, only 90 to 95 wt % of the carbon black remains as carbon in the calcined spheres. A further contribution to the carbon content is made by the organic dispersing agents, complexing agents for uranium, polymers, and surfactants normally present in the broth or sol.

2.5.1.1 Internal Gelation Broths

The hexamethylenetetramine (HMTA) solutions or slurries used to prepare internal gelation broths provide a favorable pH (>8) for dispersion of carbon blacks. The dispersion can be carried out by

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*Spheron 9, a product of Cabot Corporation.

simple mixing,[57] by ball-milling,[55] or by addition of dispersing agents.[57] The ultrasonic agitation used for other sols[56] would also be applicable. While the dispersions in HMTA solution can be stable, the carbon tends to separate slowly after mixing with the acid-deficient uranyl nitrate, and continued agitation is required until drops are formed. A feed composition used[55] for preparation of 800-μm uranium-plutonium carbide spheres is listed in Table 2.6.

Table 2.6. Feed Composition and Run Conditions for 800-μm Sphere Preparation[a]

Uranyl nitrate solution	U, mol/kg	1.57
	NO_3/U mole ratio	1.50
Pu(IV) nitrate solution	Pu, mol/kg	1.30
	NO_3/Pu mole ratio	3.65
Carbon-HMTA[b] feed	HMTA[a], *M*	3.0
	Urea, *M*	3.0
	Spheron 9, wt %	7.0
Mixed feed mole ratios	C/Me	3.1
	HMTA[a]/NO_3	0.77
	Pu/Pu+U	0.15

[a]From K. Bischoff et al., pp. 95-128 in *Sol-Gel Processes for Fuel Fabrication*, IAEA, Vienna, 1974.

[b]Hexamethylenetetramine.

2.5.1.2 External Gelation Sols

Direct addition of carbon blacks to thoria or urania sols required more intense treatments than simple mixing, as the low sol pH values are unfavorable for dispersion of the carbon. For ThO_2 sol, the procedure and results were described[56] as follows:

> A Branson model S-110 ultrasonic generator, with a power output of about 110 W at 20 kHz, achieved good blending in 7 min. During this time, the dissipated energy heated the sol to about 60°C. After the mixing step, the carbon-thoria sols were screened through a 100-mesh (149-μm openings) sieve to remove any carbon agglomerates that had not been incorporated in the sol. The quantity removed was negligible. Each sol was then poured into a bottle and placed on a rolling mill for 24 h. After agitation on the mill, the sample was allowed to stand for a day before conversion to gel. True sols are formed with carbon black and ThO_2. Similar sols that have been on hand for over a year are still stable. During the blending operation a carbon-thoria interaction disperses and stabilizes the carbon. The thoria

apparently acts as a protective colloid, partially coating the carbon particles and giving the mixed sol a positive zeta potential, even though carbon is normally negative. The effect of added ThO_2 sol on the viscosity of an aqueous suspension of carbon black is that the viscosity decreases drastically when enough ThO_2 has been added to a thick paste of 8 *M* Spheron to "protect" the carbon; this decrease occurs at a C/ThO_2 mole ratio of about 7.5 for Spheron 9 and ThO_2 composed of 7.0-nm crystallites. A reverse viscosity titration starting with 2 *M* ThO_2 shows an end point at a C/ThO_2 ratio of about 7. The maximum carbon concentration used in the present work corresponds to a viscosity of about 70 mPa s.

An ultrasonic dispersion procedure was also described[58] for addition of Spheron 9 carbon black to UO_2 and UO_2-PuO_2 sols.

2.5.2 Sphere Forming and Gelation

Usually the dispersed carbon black particles are coated by the colloidal oxide or gel precipitate so that the carbon has only small effects on the sol or gel behavior and properties. The gelation conditions selected for initial testing are usually those that were successfully used for the same sol or broth without carbon. As a result, most gelation conditions reported for carbide preparation were determined by empirical go no-go tests without any optimization of conditions.

For even the best dispersions of carbon black, a small amount of carbon is not dispersed and some carbon will settle or concentrate slowly. Therefore, most flowsheets provide a screening or coarse filtration to prevent plugging of the drop formation equipment and provide agitation of the sol or broth up to the drop formation operation. Other than these two procedures, the sphere formation conditions and requirements with carbon black present are all within the range of those developed and used without carbon black.

2.5.2.1 Internal Gelation

The characteristics of the gel spheres from internal gelation depend on the broth composition and the gelation conditions, and changes in both are sometimes necessary when carbon black is added. The U-Pu-C broth with the composition listed in Table 2.6 was gelled and processed[55] with conditions listed in Table 2.7. Conditions used for internal

Table 2.7. Internal Gelation, Washing, and Drying of U-Pu-C sol[a]

Solvent	silicon oil "DC 200, 100 cSt" density (25°C), 0.96 Mg/m^3 viscosity (90°C) 34.5 mPa s temperature 80-90°C
Washing	3 times in CCl_4 3 times in 1 *M* NH_4OH
Calcining in argon	4 h to 110°C 2 h at 190-220°C 2 h at 430-450°C
Carbothermic reduction	at 1700-1800°C in argon

[a]From K. Bischoff et al., pp. 95-128 in *Sol-Gel Processes for Fuel Fabrication*, IAEA, Vienna, 1974.

gelation to prepare UO_2 spheres of up to 1200 μm diam were also practical[57] for UO_3-C gel spheres with C/U mole ratios up to 3. In most reports of internal gelation, the conditions developed for UO_2 or $(U,Pu)O_2$ spheres were applied to broths containing carbon without any discussion of optimizing the conditions.

2.5.2.2 Gelation by Water Extraction

The basic gelation flowsheets are unchanged by the presence of dispersed carbon blacks in the sols. The carbon black usually reduces the sticking or clustering of partially gelled drops and therefore often allows use of less or different surfactants in the 2EH or other alcohol. "Shedding" of carbon from the drop surface into the alcohol is sometimes troublesome, and the degree of shedding depends on the alcohol used and on the type and amount of surfactant. For one study,[54] the surfactants used were Ethomeen S/15, a cationic tertiary amine; Ethofat 0/15, a neutral oleic acid ester of polyoxyethylene glycol; and Pluronic L-92, a nonionic polyoxy compound of high molecular weight. A later report from the same group[55] mentioned only the Pluronic L-92. Sols of ThO_2 and carbon were formed into spheres by use of 2EH plus 0.2 vol % each of Span 80 and Ethomeen S/15 or 2EH containing 10 vol % 2-octanol and 0.2 vol % Span 80.[56] For UO_2-PuO_2-C sols,[58] gelation was carried out in 2EH containing 0.6 vol % Pluronic L-92, 0.2 vol % Span 80, and 0.3 vol % Ethomeen S/15.

2.5.2.3 External Gelation with NH_3-NH_4OH

The literature for this external gelation process has little or no separate discussion of gelation conditions with carbon present. Apparently all gelation conditions were unchanged from those used for the same feed solutions or sols without carbon.

2.6 SCALE-UP CONSIDERATIONS — P. A. Haas

A Sphere-Pac refabrication facility for breeder reactors must provide the large coarse (800-1200 μm average diameter), small coarse (200-300 μm average diameter) and fines (20-50 μm average diameter) of dense $(U,Pu)O_2$ or other fuel composition. The internal gelation process using hexamethylenetetramine has been most completely demonstrated for these sizes and $(U,Pu)O_2$ and UO_2, but the fines were difficult to prepare. The British demonstration of the external process for $(U,Pu)O_2$ and $(U,Th)O_2$ is probably equivalent to the Dutch demonstration of internal gelation. Gel-supported precipitation or external gelation processes using water-soluble polymers are simpler than internal gelation from the standpoint of feed stability and the use of aqueous ammonia instead of a liquid organic forming medium. The suitability for both the large coarse size and the fines is less certain. Therefore external gelation processes remain second choices until the preparation of large $(U,Pu)O_2$ spheres is demonstrated. Gelation by water extraction is not practical for large spheres but remains a backup process for the fertile fines.

The schematic flowsheets for internal gelation (Fig. 2.11) and external gelation (Fig. 2.1) show the use of many similar operations with different chemical conditions. For this reason, and also to compare the processes, the scale-up requirements for both types of processes will be discussed together in the order of process steps.

2.6.1 Feed Preparation

The feed preparation is a simple solution makeup operation with no significant scale-up problems for external gelation, but is more complex for internal gelation. The three complications for internal gelation are:

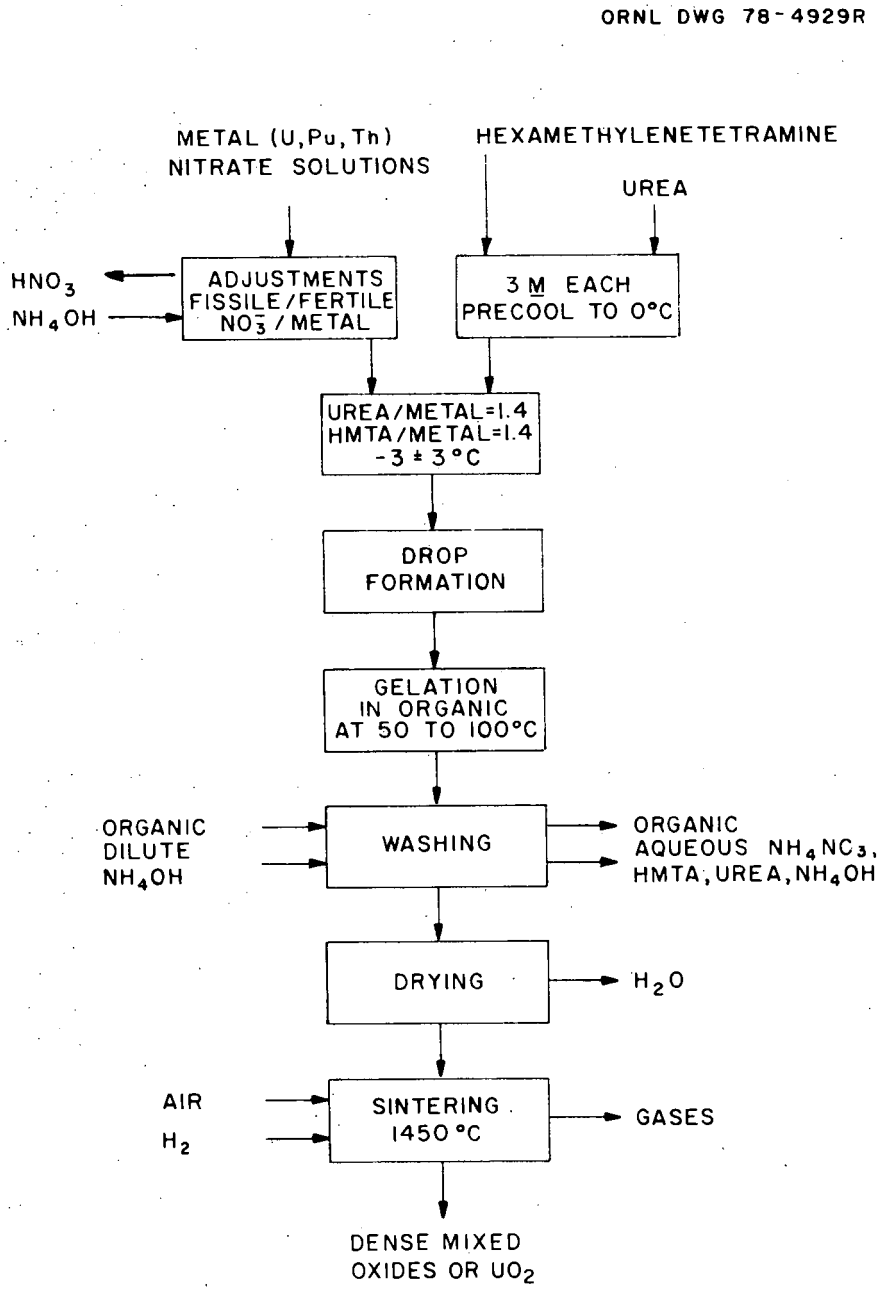

Fig. 2.11. Sphere Preparation by Internal Gelation.

1. the NO_3^-/U mole ratio should be ≤ 1.6, while solvent extraction purification processes usually produce a value exceeding 2;
2. the feed constituents must be precooled to about 0°C before final mixing;
3. the feed has a limited life, which is very temperature dependent; premature gelation gives solids in process vessels, valves, lines, etc.; such solids are troublesome to dissolve and remove.

The NO_3^-/U ratio can be adjusted by several procedures, and all appear practical for large-scale operation. If all or part of the feed uranium is in the form of UO_3, then UO_3 is dissolved in warm HNO_3 or $UO_2(NO_3)_2$ solutions. If all the feed is $UO_2(NO_3)_2 \cdot xHNO_3$ solutions, the extraction of HNO_3 by a liquid organic amine and vacuum evaporation can give the required compositions. The extraction of HNO_3 to give an NO_3^-/U ratio of 1.5 was developed and demonstrated for a resin-based preparation of HTGR fuels.[59] The preparation of acid-deficient uranium-plutonium nitrate solutions by vacuum evaporation has recently been demonstrated. If the NO_3^-/U is not too far above 1.6, NH_4OH solutions or NH_3 gas can be added to partially neutralize. This has undesirable effects on the properties of the gel spheres, so the first two procedures are preferred.

Continuous or in-line cooling and mixing of two feed solutions appears necessary for the scale-up of internal gelation. Careful design should provide adequate precooling and minimize the problems of limited life after mixing. All components from final mixing to drop formation will probably have to be designed for replacement, as an occasional failure with solidification throughout these components is possible.

2.6.2 Sphere Forming and Gelation

Sphere sizes required for sphere-pac are met more easily by internal gelation than by external gelation. This results from the difference in surface gelation times, which are 1 to 10 s for internal gelation and at most 0.1 s for external gelation. The drops for internal gelation can be formed in gas above the hot organic medium or in the organic, as they have adequate time to assume a spherical shape

before surface gelation begins. For external gelation, the surface gelation of the drops is generally accomplished in at most 0.1 s in NH_3 gas, after which the drops fall into an NH_4OH solution. These external gelation operations do not appear practical for fines. For very large drops, it is difficult to form a surface shell of adequate strength to survive the impact at the solution interface. For internal gelation, distortion of the large drop from impact is not harmful as long as the drop does not split into two drops or encapsulate an organic bubble; the drop will return to a spherical shape before gelation occurs.

The capacity limitations for scale-up are most severe for the small coarse size. A 0.1 Mg/d plant would require about 3 kg/h for the large coarse size and 1 kg/h for each of the two smaller sizes. The capacity of a single drop-forming nozzle for either large coarse or fines or of a single broth feed to a gang of capillaries for falling drops can be 1 kg heavy metal per hour or greater. For the small coarse size, the capacity for a single feed system and nozzle is 0.02 to 0.2 kg heavy metal per hour. The internal gelation pilot plant in the Netherlands used a spinerette disperser for larger capacities, but this results in a moderately less uniform size.

Scale-up of gelation and aging process steps is not difficult and has little effect on process selection. The cross section of the columns or vessels will be limited to control nuclear criticality. Therefore the time and volume requirements will probably be met by continuous flow through longer vessels.

2.6.3 Washing

Continuous countercurrent washing has been demonstrated for both internal and external gelation particles. Drop formation and gelation are continuous processes, and continuous washing is desirable for large capacities even when the drying or sintering are batch operations. The minimum holdup times during washing are about 2 h, and the bulk concentration of heavy metal is about 200 kg/m^3. Thus a wash column for 5 kg heavy metal per hour might be 0.12 m ID and 2 m in length. Development of conditions for improved washing of fines is in progress.

2.6.4 Drying

External gelation processes have required careful control of drying conditions, with use of a monolayer of particles as a common requirement. Internal gelation particles have been dried in thick beds with only small effects from atmosphere and temperature. Therefore, scale-up of drying is easier for internal gelation. Final evaluation of the scale-up requirements is not possible until the process steps up to drying are fixed.

2.7 REMOTE APPLICATION — C. C. Haws

An extensive sol-gel program was conducted at the Oak Ridge National Laboratory over an approximate 15-year period, beginning in the late 1950s. In these, kilogram (to ton) quantities of sintered spherical particles were prepared in a number of demonstrations. Particles of UO_2, ThO_2, PuO_2, and mixtures of these oxides were prepared, as well as the same oxides in mixtures with other oxides. The problems encountered and the solutions developed therein will be of particular interest to this program because they are shared. Specifically, the information and/or experience gained in remote equipment design, containment, shielding, remote (and semiremote) operations, and material handling of high-level alpha and gamma active substances are expected to be largely the same. A brief description listing the principal engineering features of each of these demonstrations follows.

2.7.1 Process Chemistry

The chemical flowsheets of more recently developed processes differ from earlier ORNL work, which used sols as feeds and accomplished gelation by extraction of water into an alcohol. The spherical particles produced at ORNL were in the 200 to 500-μm-diam range, being intended mainly for HTGR use. Particles were also produced in the range 20 to 80 μm diam in experimental quantities. The water extraction method cannot produce the large (i.e., 800-1200-μm-diam) particles needed for high-density sphere-pac fuels. The more recently developed processes are more flexible in that they can produce the very large particles as well as the medium size. Because it is undesirable to provide two

operating lines — that is, a water extraction line for the intermediate-size spheres and an internal (or external) gelation line for the large size — effort must be directed toward providing a single broth-fed internal or external gelation line capable of providing both large and medium size fractions. Either a broth-fed or water extraction flowsheet may be used to produce the fines. The change to an external (or internal) gelation flowsheet should only moderately impact engineering design and operational features since, as previously stated, so many of these problems are shared.

2.7.2 Significant Engineering-Scale Demonstrations

The first sol-gel hot demonstration processing a high-level alpha and high-energy gamma emitter was the Kilorod program.[60] The facility was designed as a semiremote operation but depended upon direct maintenance. Principal shielding was 0.1 m (4 in.) of boiler plate. More than 1 Mg of 3% $^{233}UO_2$-97% ThO_2 shards* was prepared at a rate of 10 kg/d, then crushed and loaded into approximately 1000 fuel rods by vibratory packing. Reactor chemical and physical specifications were met by the shards and the rods. Personnel exposure levels were below permissible limits.[61] Whole-body doses for all operations averaged about 19 mrem/week. Hand and forearm doses averaged about 60 and 113 mrem/week for sol-gel and rod fabrication operations, respectively. Doses to maintenance workers were about 10% that to the operators on an individual basis.

An iostopic heat-source program based upon sol-gel technology was conducted in the late 1960s at ORNL.[62] This program culminated in the construction of a remotely operated pilot plant designed to produce 200 g/d (24 h) of $^{238}PuO_2$ spheres. In a preparatory glove box demonstration, $^{239}PuO_2$ spheres were routinely prepared at a 150 g/d rate. Also, start-up operations of a pilot plant at 150 g/d, using ^{239}Pu as a stand-in, were successful. Radiolytic effects from the ^{238}Pu made operation of the unit for its intended purpose difficult. The fact that ^{239}Pu operations were successful is of interest to breeder fuel programs.

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*38 ppm ^{232}U in the uranium.

In a later demonstration performed in the same cell, using the same equipment and behind the same shielding as for the isotopic heat-source effort, 32 kg of spheres containing 25% $^{233}UO_2$-75% ThO_2 were prepared.[63] These particles were subsequently used to prepare HTGR fuel elements and shipped to Pacific Northwest Laboratories. There they were placed in the High-Temperature Lattice Test Reactor for determining the extent of Doppler broadening in the HTGR. In this operation sols were prepared in a glove-box operation using the Solex flowsheet and converted to spherical products in the cell. It is noted that a thorough remote-maintenance design was considered unnecessary in the original design, since the operation of the assembly was expected to cover only the $^{238}PuO_2$ and the ^{233}U programs. Maintenance-sensitive equipment had been located and trimmed for replacement by master-slave manipulators, but general remote maintenance was not provided or needed. After start-up, the equipment operated satisfactorily with overall process yields of 95% from feed to sintered product.

2.7.3 Engineering Design and Operational Concepts

An engineering-scale facility preparing spheres from highly radioactive feed materials can be visualized by using previous and existing installations for models. Perhaps the Transuranium (TRU) operation at ORNL possesses as many conceptually desirable features as any other in the country. Using this facility as a principal model, operations would be carried out in a series of alpha-contained, shielded cells. Equipment would be located on racks for ease of mounting and removal from the cell. Two or possibly three racks would be located in any one cell, depending upon accessibility and process complexity factors. One basic process operation (depending upon its complexity and the size and number of equipment pieces required) could be accomplished on one rack or in one cell. For example, feed solution preparation is a comparatively simple operation and thus might occupy a single rack; sphere preparation might require a complete cell.

Beyond TRU, however, operational manipulations would be as completely automated as possible with actuating devices fixed to the equipment and operated by means external to the cells, such as toggle

switches, servo-devices, and computers (where a number of sequential operations were required). Instrumentation would be required not only to control the process but to indicate failure in the completion of any operation and the stage at which failure occurred. All equipment within the cell would necessarily require a high degree of reliability and be rigidly designed for indefinite service life. Unavoidably, some operations would require viewing windows and master-slave manipulations, but these would necessarily be minimized.

Maintenance to replace equipment that had failed physically as well as for equipment suffering from temporary operational breakdowns (e.g., a plugged needle in a feeding device) would be no more severe than those normally encountered in TRU operations today. Rack mounting permits removal of individual equipment pieces, modules especially designed for removal, or removal of entire racks. Rack mounting also allows the mounting of connectors (electrical, instrument, and process line) in locations of good visibility and accessibility for maintenance. Maintenance is accomplished primarily by use of impact wrenches and master-slave manipulators. Means for removal of equipment from the cells and return to the cells must be provided as well as transport to and from a designated cleanup and repair cell. Access from each cell to such a common transport canyon, preferably above the cells, must be provided. This must be accomplished under the imposed alpha contaminant and shielding requirements. Failed equipment would be thrown away or repaired, as seen fit. Spares would be provided in the immediate operating area for all equipment presenting a high maintenance problem, as determined in the cold engineering and prototype phases of development. Such equipment would also be mounted in a location readily accessible to maintenance operations and designed for ease of removal and repair.

2.7.4 Potential Operating Difficulties

Operating difficulties can be anticipated in preparation of feed materials, dispersing the droplets in the forming columns, and washing and drying the formed spheres. Of these difficulties, those associated with the dispersal of the feed into droplets and operation of the forming

columns will probably be the most frequent and difficult. A plugged (or partially plugged) feeding device (needle) would require switching to a standby device. Design of the feeding system would also necessarily provide for quick removal and replacement of the needle. Removed needles would either be discarded or have to be thoroughly cleaned, dried, and inspected to make certain that they were in operable condition before reusing. This is a tedious task for manipulator operations. Therefore a needle assembly containing several needles might be replaced rather than individual needles. Engineering design and operational controls would have to provide reliable start-up and shutdown measures to minimize scrap recycle. Early detection of maloperation (i.e., off-size or misshapen droplets) would also be required. Means of detecting and correcting other types of problems, such as clustering of spheres in the bottom of the column, would also have to be provided. At present, maloperation can be detected only by visual means, and therefore certain operations would necessarily be mounted at a viewing window or, less desirable, provided with TV viewing. The buildup of impurities in the recycling solvent must be monitored and means necessary to purify the solvent sufficiently for recycle must be provided.

Maintenance and operational difficulties in the feed preparation, washing, and drying stages are expected to be similar to those encountered in other, conventional remote operations. For example, operational upsets would result in rejection of feed batches or batches of cracked spheres, thus requiring a short shutdown and a scrap disposal problem. Inadvertent plugging of equipment typically would offer more serious problems since shutdown, dismantling, and cleaning out of equipment are required. The effects of problems such as these are usually mitigated by good engineering design practices, and as long as dismantling and reassembly can be accomplished with reasonable ease by manipulators, they pose no unusual problems in the present processes. As soon as reliable cold pilot plant equipment is operating, data on equipment and process performance and reliability must be collected to permit assessment of the impact of operational and equipment failures on the operability of the ultimate hot pilot plant.

The complexity of the process and the equipment would demand the construction and operation of a cold prototype if the operation is to be successful. As individual pieces are proved, complete systems should be assembled and tested cold. Testing must be continuously pursued until culminating in the pre-hot operational testing of the completed pilot plant in-place. This latter testing period should be sufficiently long to confirm previously obtained performance and reliability and to assure that all equipment can be repaired and/or replaced as designed.

2.8 REFERENCES

1. J.B.W. Kanij, A. J. Noothout, and O. Votocik, "The KEMA U(VI)-Process for the Production of UO_2 Microspheres," pp. 185-95 in *Sol-Gel Processes for Fuel Fabrication*, IAEA-161, International Atomic Energy Agency, Vienna, 1974.
2. Private communication, K. J. Notz, ORNL, December 16, 1977.
3. K. P. Louwrier and H. Schönherr, "Fabrication of (Pu-U) Oxide Microspheres Using an Internal Gelation Method," *J. Nucl. Mater* 51: 232-36 (1974).
4. K. P. Louwrier and T. Steemers, "Sol-Gel Process Development at the European Institute for Transuranium Elements, Karlsruhe, Germany," pp. 244-63 in *Symposium on Sol-Gel Processes and Reactor Fuel Cycles*, CONF-700502 (May 1970).
5. R. Förthmann and G. Blass, "Fabrication of Uranium-Plutonium Oxide Microspheres by the Hydrolysis Process," *J. Nucl. Mater* 64: 275 (1977).
6. M. H. Lloyd et al., "Crystal Habit and Phase Attribution of U(VI) Oxides in a Gelation Process," *J. Inorg. Nucl. Chem.* 38: 1141-47 (1976).
7. Private communication, R. D. Zimmerman, General Atomic, Jan. 3, 1978.
8. F. W. van der Brugghen et al., "A U(VI)-Process for Microsphere Production," pp. 253-63 in *Symposium on Sol-Gel Processes and Reactor Fuel Cycles*, CONF-700502 (May 1970).
9. R. Förthmann et al., "Investigations on the Preparation of UO_2 Microspheres by Internal Gelation of a UO_2 Sol and from a Uranium (VI) Solution," pp. 551-66 in *Symposium on Sol-Gel Processes and Reactor Fuel Cycles*, CONF-700502 (May 1970).

10. H. Huschka et al., "Kernel Fabrication for Different Fuel Cycles in Germany," pp. 37-47 in *Sol-Gel Processes for Fuel Fabrication,* IAEA-161, International Atomic Energy Agency, Vienna, 1974.
11. H.W.H. Lahr, "Fabrication, Properties, and Irradiation Behavior of U/Pu Particle Fuel for Light Water Reactors," *Nucl. Technol.* 31: 183-90 (1976).
12. G. Brambilla, P. Gerontopulos, and D. Neri, "The SNAM Process for the Preparation of Ceramic Nuclear Fuel Microspheres: Laboratory Studies," *Energ. Nucl. (Milan)* 17: 217-24 (1970).
13. A. G. Facchini, "The SNAM Process for the Preparation of Ceramic Nuclear Fuel Microspheres: Continuous Production Technique," *Energ. Nucl. (Milan)* 17: 225-33 (1970).
14. C. J. Hardy and E. S. Lane, "Gel Process Development in the United Kingdom," pp. 137-49 in *Symposium on Sol-Gel Processes and Reactor Fuel Cycles,* CONF-700502 (May 1970).
15. M.E.A. Hermans, *Sol-Gel Process and Reactor Fuel Cycles,* RCM-KEMA 27/70 (1970).
16. M. Kadner and J. Baier, "Production of Fuel Kernels for High-Temperature Reactor Fuel Elements," *Kerntechnik* 18: 413-20 (1976).
17. F. W. van der Brugghen et al., "Sol-Gel Processes for the Preparation of Spherical Thorium-Containing Fuel Particles," pp. 370-90 in *Thorium Fuel Cycle* (Proc. 2nd Int. Symp. Gatlinburg, Tenn. May 3-6, 1966), CONF-660524 (February 1968).
18. M.E.A. Hermans et al., "Status Report from the Netherlands: Sol-Gel Fuel Studies," pp. 21-32 in *Sol-Gel Processes for Ceramic Nuclear Fuels,* International Atomic Energy Agency, Vienna, 1968.
19. J.B.W. Kanij et al., "Sol-Gel Development at K.E.M.A.," pp. 139-60 in *I Processi Sol-Gel per la Produzione di Combustibili Ceramici* (Proc. Int. Nucl. Symp. Turin, Oct. 2-3, 1967), Comitato Nazionale Energia Nucleare, Rome, 1968.
20. M. P. Simpson and C. L. Stockwell, *Method of Producing Gel Spheres and Gelation Apparatus,* U.S. Pat. 3,886,086, May 27, 1975.
21. H. Bairiot, L. Aerts, and M. Gaube, "Work Performed in Belgium on Particles Obtained by a Liquid Route," pp. 79-95 in *Sol-Gel Processes for Fuel Fabrication,* IAEA-161, International Atomic Energy Agency, Vienna, 1974.

22. V. M. Kakarov, B. A. Semenov, and A. S. Skotnikov, "Study of Sol-Gel Processes in the USSR," pp. 71-78 in *Sol-Gel Processes for Fuel Fabrication*, IAEA-161, International Atomic Energy Agency, Vienna, 1974.

23. E. Zimmer, P. Naefe, and H. Ringel, *Development of a Method and Experimental Installation for Refabricating HTGR Fuels*, GERHTR-59 (1973).

24. E. Zimmer, P. Naefe, and H. Ringel, "Continuous Working Process for the Production of ThO_2 and $(Th,U)O_2$ Fuel Kernels," *Trans. Am. Nucl. Soc.* 20: 591-93 (1975).

25. A. G. Facchini, "Ceramic Nuclear Fuel Microspheres by the Gel-Supported Precipitation Process," *Trans. Am. Nucl. Soc.* 13: 46-47 (1970).

26. A. G. Facchini and P. Gerontopoulos, "Present State of Art of the SNAM Process for Preparation of Ceramic Nuclear Fuel Microspheres," pp. 227-45 in *Sol-Gel Processes for Fuel Fabrication*, IAEA-161, International Atomic Energy Agency, Vienna, 1974.

27. C. J. Hardy, "Status Report from the United Kingdom: Sol-Gel and Gel-Precipitation Processes," pp. 33-42 in *Sol-Gel Processes for Ceramic Nuclear Fuels*, International Atomic Energy Agency, Vienna, 1968.

28. H. D. Ringel and E. Zimmer, "Simplified Preparation of ThO_2 and $(Th,U)O_2$ Fuel Kernels," *Trans. Am. Nucl. Soc.* 27: 292-93 (1977).

29. G. Cogliati and A. Facchini, "A Pilot Plant for Continuous Preparation of U-Pu Oxide Spheres," pp. 210-26 in *Symposium on Sol-Gel Processes and Reactor Fuel Cycles*, CONF-700502 (May 1970).

30. A. G. Facchini, "Wet Route Microsphere Production and Evaluation," pp. 49-70 in *Sol-Gel Processes for Fuel Fabrication*, IAEA-161 International Atomic Energy Agency, Vienna, 1974.

31. S. Gallone, G. Schileo, and M. Zifferero, "Laboratory Studies and Pilot Plant Development of Sol-Gel Processes in Italy," pp. 150-63 in *Symposium on Sol-Gel Processes and Reactor Fuel Cycles*, CONF-700502 (May 1970).

32. H. A. Taylor, "Gel Precipitation Process Development in the UK," pp. 1-7 in *Sol-Gel Processes for Fuel Fabrication*, IAEA-161 International Atomic Energy Agency, Vienna, 1974.

33. E. S. Lane, *Improvements in the Manufacture of Microspheres by Gel-Precipitation Methods*, U. K. Pat. 1,313,750, May 1974.

34. E. Zimmer, unpublished KFA Report (1977).

35. G. Brambilla et al., "The SNAM Process for the Production of Ceramic Nuclear Fuel Microspheres," pp. 191-209 in *Symposium on Sol-Gel Processes and Reactor Fuel Cycles*, CONF-700502 (May 1970).

36. J. P. McBride, comp., *Laboratory Studies of Sol-Gel Processes at the Oak Ridge National Laboratory*, ORNL/TM-1980 (September 1967).

37. P. A. Haas, C. C. Haws, Jr., F. G. Kitts, and A. D. Ryon, *Engineering Development of Sol-Gel Processes at the Oak Ridge National Laboratory*, ORNL/TM-1978 (January 1968).

38. P. A. Haas, *Process Requirements for Preparing ThO_2 Spheres by the ORNL Sol-Gel Process*, ORNL/TM-3978 (December 1972).

39. *Denitration Furnace*, CAPE-1041, available from National Technical Information Service, U.S. Department of Commerce.

40. E. N. Nelson, *Fluid-Bed Denitration of Thorium Nitrate*, MCW-1511 (Jan. 19, 1966).

41. P. A. Haas, *Sol-Gel Preparation of Spheres: Design and Operation of Fluidized Bed Columns*, ORNL-4398 (September 1969).

42. P. A. Haas, F. G. Kitts, and H. Beutler, "Preparation of Reactor Fuels by Sol-Gel Processes," *Chem. Eng. Progr. Symp. Ser.* 63 (80): 16-27 (1967).

43. B. C. Finney and P. A. Haas, *Sol-Gel Process — Engineering-Scale Demonstration of the Preparation of High-Density UO_2 Microspheres*, ORNL-4802 (November 1972).

44. J. P. McBride, comp., *Preparation of UO_2 Microspheres by a Sol-Gel Technique*, ORNL-3874 (February 1966).

45. *Chem. Technol. Div. Annu. Progr. Rep. May 31, 1968*, ORNL-4272, p. 142.

46. P. A. Haas, "Preparation of Sol-Gel Spheres Smaller than 200 Microns Without Fluidization," *Nucl. Technol.* 10: 283-92 (1971).

47. S. D. Clinton, *Mass Transfer of Water from Single Thoria Sol Droplets Fluidized in 2-Ethyl-1-hexanol*, M.S. thesis, University of Tennessee, Knoxville (1968); also issued as ORNL/TM-2163 (June 1968).

48. D. A. Schneider and N. I. Salas, *Gelation of Small Diameter Thoria Sol Microspheres in Non-Flowing Alcohols*, ORNL-MIT-95 (1970).

49. J. G. Moore, *Sol-Gel Process for Preparing ThO_2-UO_3 Sols from Nitrate Solutions by Solvent Extraction with Amines*, ORNL-4095 (October 1967).

50. R. G. Wymer, "Laboratory and Engineering Studies of Sol-Gel Processes at Oak Ridge National Laboratory," pp. 131-72 in *Sol-Gel Processes for Ceramic Nuclear Fuels*, International Atomic Energy Agency, Vienna, 1968; also published as ORNL/TM-2205 (May 1968).

51. M. H. Lloyd and O. K. Tallent, "A New Solvent Extraction Process for Preparing PuO_2 Sols," *Nucl. Technol.* 18: 205-15 (1973).

52. P. A. Haas and W. J. Lackey, *Improved Size Uniformity of Sol-Gel Spheres by Imposing a Vibration on the Sol in Dispersion Nozzles*, ORNL/TM-4094 (May 1973).

53. A. J. Karabelas, "Droplet Size Spectra Generated in Turbulent Pipe Flow of Dilute Liquid/Liquid Dispersions," *AIChE J.* 24(2): 170-80 (March 1978).

54. K. Bischoff, V. Scherer, and H. Schumacher, "Sol-Gel Processes for the Preparation of U-Pu-Carbide Fuels," pp. 164-77 in *Symposium on Sol-Gel Processes and Reactor Fuel Cycles*, CONF-700502 (May 1970).

55. K. Bischoff, M. H. Lloyd, and H. Schumacher, "Sol-Gel Processes for Carbide Preparation," pp. 95-128 in *Sol-Gel Processes for Fuel Fabrication*, IAEA-161, International Atomic Energy Agency, Vienna, 1974.

56. K. J. Notz, *Preparation of Porous Thoria by Incorporation of Carbon in Sols*, ORNL/TM-1780 (December 1968).

57. P. A. Haas, unpublished data, Oak Ridge National Laboratory, 1978.

58. K. J. Notz et al., "Carbothermic Conversion of Sol-Gel U and Pu Oxides to Carbonitrides," pp. 434-47 in *Symposium on Sol-Gel Processes and Reactor Fuel Cycles*, CONF-700502 (May 1970).

59. P. A. Haas, *Resin-Based Preparation of HTGR Fuels: Operation of an Engineering-Scale Uranium Loading System*, ORNL-5300 (October 1977).

60. C. C. Haws, J. L. Matherne, F. W. Miles, and J. E. VanCleve, *Summary of the Kilorod Project — A Semiremote 10 kg/day*

Demonstration of $^{233}UO_2$-ThO_2 Fuel Element Fabrication by the ORNL Sol-Gel Vibratory-Compaction Method, ORNL-3681 (August 1965).

61. R. E. Brooksbank, J. P. Nichols, and A. L. Lotts, "The Impact of Kilorod Facility Operational Experience on the Design of Fabrication Plants for ^{233}U-Th Fuels," pp. 321-40 in *Thorium Fuel Cycle* (Proc. 2nd Int. Symp. Gatlinburg, Tenn., May 3-6, 1966), CONF-660524 (February 1968).
62. *Chem. Technol. Div. Annu. Prog. Rep. May 31, 1968*, ORNL-4272, pp. 169-70.
63. *Chem. Technol. Div. Annu. Prog. Rep. May 31, 1969*, ORNL-4422, pp. 183-87.

3. SINTERING AND CHARACTERIZATION

This section describes the various heat treatment and characterization techniques applied to assure high-density, chemically acceptable oxide or carbide spheres of potential reactor fissile or fertile materials. Heat treatment may be considered in four steps: (1) drying; (2) calcination, to eliminate excess volatiles; (3) sintering, to densify the material; and (4) reduction, to produce the desired oxygen-to-metal ratio, or in the case of carbide fuels, conversion of oxide to carbide. Inasmuch as sintering and reduction ordinarily occur simultaneously, these latter two steps will be considered as one operation herein.

This section deals first with the calcination and sintering of UO_2 and ThO_2, since they have been studied very thoroughly. Information on $(U,Pu)O_2$ is included where available. The last portion of this section considers the preparation of carbide fuels. Characterization of the feed and intermediate products will be discussed in relation to calcination and sintering processes, while characterization of the final product will be presented separately.

3.1 SINTERING — A. E. Pasto

As indicated in preceding sections, the "recipes" for producing a dense sphere of given composition vary widely among the different preparation schemes. Indeed, even within a given process (e.g., the KEMA internal gelation process), the times, temperatures, rates, and atmospheres used for sintering vary from one report to another. In large part, this is due to the lack of basic knowledge of the complex sintering processes occurring within the spheres. Investigators have concentrated on attempting to produce a high-quality product in the shortest feasible development time, which leads to a "shotgun" approach. As many reasonable variables as possible are evaluated and whatever works is settled upon. Assessment of what has happened during calcination and sintering is performed later. That this approach works is attested to by the large number of patents granted for the described processes. However, the lack of basic knowledge means that whenever

another sphere forming, washing, or drying process variation occurs, unpredictable changes may be required in the calcination and sintering steps.

Hence, one attempting to devise densification routines must consider the phenomenology of the process and try to control the attendant phenomena to his advantage. To this end it would be helpful to discuss first the observable internal processes occurring in the spheres during heat treatment. These are as follows:

Elimination of volatiles (H_2O, NH_3, NO_3^-, organic compounds)

Particle rearrangement

Crystal growth

Phase changes (e.g., $UO_3 \rightarrow U_3O_8 \rightarrow UO_2$)

Initial stage sintering

Final stage sintering

These phenomena are unfortunately not separable during the processing, as several may be occurring simultaneously. However, elimination of volatiles and phase changes are easily followed through use of differential thermal analysis, thermogravimetric analysis, off-gas analysis, and x-ray diffraction. The first noticeable change on heating dried spheres is the weight loss due to elimination of H_2O. Commonly this occurs[1-4] between 80-220°C (physically combined) and 350-450°C (chemically combined) for UO_2 and $(U,Pu)O_2$ products. Ammonia is released at intermediate temperatures. The latter, however, along with residual organics, can be removed at quite different rates and temperatures depending on the atmosphere in the calcining furnace.[4,5] The atmosphere must be chosen so as to eliminate these phases without disrupting the sphere's integrity or compromising its sinterability by changing the pore structure or oxidation state of the uranium. A further consideration in volatile elimination is the structure of the porosity within the sphere. Landsperský and Spitzer[6] used porosimetry to show that some types of gel spheres have large pores, which are very permeable to the volatiles, but other types do not. These two types of spheres require different thermal treatments to avoid cracking. The nature of the porosity is subtly influenced by any of the steps preceding sintering. Normally, careful heating in a controlled

atmosphere will eliminate most of the volatile constituents at temperatures below 600°C.

The initial stage of sintering of ThO_2 has been studied by Bannister,[7] and of UO_2 by Suzuki et al.,[8,9] Landsperský et al.,[6,10] and Breschi et al.[11] Bannister found that for ThO_2 gel produced by the ORNL water-extraction technique, the first 4% of linear shrinkage was due solely to elimination of volatiles. After this, the remainder of the shrinkage was controlled by grain boundary diffusion of thorium. Particle shape did not change on sintering to 900°C (in air), but extensive crystal growth occurred; for example, 6.0 nm as received to 30 nm at 900°C. On the other hand, Suzuki et al. found that the initial stage of sintering UO_2 sol-gel material proceeded in two steps: up to 675°C (in H_2), the shrinkage was proportional to time, implying a grain rearrangement through boundary sliding (plastic flow); and from about 750 to 800°C volume diffusion controlled the rate. Above 800°C, grain growth occurred normally up to about 1080°C, where grain size increased abruptly. The shape of the grains changed from spherical to polyhedral at this temperature. Above 1080°C normal grain growth continued and sintering proceeded. Breschi et al. studied changes in "ammonium polyuranate" under Ar-4% H_2. By 500 to 600°C, the material was completely transformed to UO_2, in agreement with other work[12] on SNAM material. They determined that the onset of grain growth was always above 700°C, agreeing with Suzuki, and stated that below 700°C grains agglomerated only. They further determined that calcination at a temperature above the grain-growth onset caused too rapid sintering, preventing residual volatiles from escaping. This leads to a dense outer layer of large grains and an inner region that is poorly densified. Calcination below 700°C resulted in a more homogeneous product.

Landsperský's[10] preliminary investigations covered UO_2 produced by the KEMA process and KFA-Jülich's H-Process. Calcining in air led to removal of the majority of volatiles in the range 200 to 250°C, which was considered to be the critical range for crack formation. If cracks were not formed in this range, there would be no cracking on sintering. Spheres produced by these two processes consisted of UO_3 after heating

to 360-450°C in air. However, if the heating rate was too rapid and the material pore structure prohibited rapid release of the volatiles, self-reduction occurred. In air, UO_3 was stable to 510-570°C.

Calcination under Ar-4% H_2 yielded three distinct weight loss maxima, in agreement with studies by others.[1] Elimination of volatiles was completed by about 600°C. Initial stage sintering (neck growth) proceeded from 600 to 800°C. Only above 800°C did intensive sintering and pore closure occur, again in agreement with others.[9]

In more detail, Landspersky et al[6,13] further investigated KEMA and H-Process UO_2. Drying both at room temperature in air and at 220°C was compared. Room-temperature drying left the two types of spheres in different states, resulting in KEMA spheres being more sinterable than H-Process material. However, drying at 220°C brought both types to stages where they could be easily sintered to high density. Air calcining to much above 500°C resulted in conversion of UO_3 to U_3O_8.

Landspersky's sintering study[13] on the same materials in Ar-4% H_2 elucidated an important point. *With particles that had been air dried to 220°C, then sintered in Ar-4% H, U(VI) was reduced to U(IV) at temperatures as low as 280°C.* If calcination in air or inert atmosphere to U_3O_8 was allowed before reduction, a different microstructure was formed, resulting in different sintering rates for the materials. Apparently above about 600°C, sintering begins in either the UO_2 or U_3O_8, whichever is present. In UO_2, this occurs with pore elimination and shrinkage, the originally formed pore shape and diameter remaining unchanged and only the pore volume decreasing. On the other hand, in U_3O_8 the porosity is redistributed, with pore size distribution shifting to larger diameter as fine porosity is eliminated. Once formed, the larger pores are retained. Several groups[2,12,14] have used this technique to prepare sintered spheres of controlled porosity, mainly by varying the maximum calcination temperature to vary the amount or structure of U_3O_8 formed.

Having now discussed volatile elimination, reduction, particle rearrangement, crystal growth, and initial-stage sintering, only final-stage sintering remains. This process is the elimination of

closed porosity coincident with normal grain growth. All the materials being considered will sinter by the same type of process, which is controlled by mass transfer, usually diffusion of the cation along grain boundaries. The principal determinant of final density will then be the microstructure produced by the preceding steps. That is, given the appropriate temperature and time, materials containing fine porosity and small grain size will sinter to high density. However, if large pores and/or large grains have been left in the structure, the densification will be impeded, as noted in the work on material with controlled porosity.

Considerable experience is available concerning the sintering and stoichiometry control of $(U,Pu)O_{2-x}$ sol-gel-derived spheres.[15] Generally $(U,Pu)O_2$ sintered to densities greater than 95% T.D., with the remaining pores being rather large and presumably introduced during sphere forming rather than resulting from pore agglomeration during sintering. With improved sol or broth and better sphere forming, higher densities are realistic.

Substoichiometry was controlled in $(U,Pu)O_{2-x}$ batches of several hundred grams. The rate of reduction of the mixed oxides by hydrogen in argon was found[16] to be controlled by the removal of water vapor from the furnace by the gas stream; the moisture content of the furnace atmosphere is often controlled by the previous history of the furnace and not by the incoming gas.

3.2 CARBIDE PREPARATION — D. P. Stinton

Carbothermic reduction of oxides produced by the gel processes with the addition of finely dispersed carbon is used to produce carbide spheres. The very intimate mixing of the oxide and carbon is expected to minimize the difficulties encountered during carbothermic reduction of other starting materials. Previous sections of this report have discussed the calcination of sol-gel-produced oxides. Very similar calcination procedures are appropriate for production of the carbides. After calcination, the UO_2, PuO_2, or $(U,Pu)O_2$ spheres that contain carbon must be converted to carbides and sintered to a high density.

Numerous reports have been written[3,12,17-26] concerning the carbothermic reduction of oxide spheres to carbides. Most of this work deals with the reduction of UO_2, but some work has also been performed with PuO_2 and $(U,Pu)O_2$. The applicable work will be discussed briefly.

Uranium carbide spheres can be produced by carbothermic reduction of the oxides at temperatures above about 1400°C. In order to densify the carbide spheres, they must be sintered at temperatures between 1600 and 1900°C in an atmosphere of argon or in vacuum. By controlling the amount of carbon added, the composition of the resulting spheres can be varied from UO_2 through UC_xO_y to UC_2. Because of the relatively poor sinterability of carbide spheres containing an excess of carbon, no more carbon than necessary should be added. Control of the carbon content is complicated by the presence of several sources. The primary source is that added as carbon black, but organic substances already in the sol or broth also contribute, and their content is potentially variable, depending on the thoroughness of sphere washing and calcination.

The reaction taking place during carbothermic reduction is not well understood. Investigators have reported that both monocarbide and dicarbide of uranium were present after carbothermic reduction and sintering. Phase stability is influenced by the amount of carbon initially present, time, temperature, and atmosphere. Densities of the sintered product range from 90 to 96% T.D. The highest densities were obtained by sintering in a high vacuum at temperatures as high as 1900°C.

Research dealing with PuO_2 and $(U,Pu)O_2$ shows that these compounds behave somewhat similar to UO_2. Densities as high as 95% of theoretical were obtained after carbothermic reduction and sintering in vacuum at 1900°C. However, sintering of compounds containing plutonium is complicated because plutonium vaporizes at high temperatures. Sintering methods must be developed that produce high-density spheres of the desired stoichiometry but also minimize plutonium vaporization. Since PuC vaporizes to a much greater extent than does (U,Pu)C, the ability to obtain a solid solution of $(U,Pu)O_2$ in the gel spheres before converting to (U,Pu)C is a potentially important advantage for the gel process.

3.3 SPHERE CHARACTERIZATION — A. E. Pasto

3.3.1 Density

Since any porosity in the sintered spheres lowers the fuel pin smear density, the spheres need to be as dense as practical. The pertinent density value is the bulk or geometric density. This is readily determined on spheres larger than tens of micrometers in diameter by immersion in mercury at about 500 kPa (75 psi). For finer spheres, the void spaces between particles are very small, so that higher pressures are required to penetrate them with the mercury. The key is to completely surround the particle with mercury but not penetrate any sphere porosity.

Other techniques include immersion in water or other liquids. However, care must be exercised in the use of the data since pores of nanometer size will be penetrated and falsely high density values obtained.

Another technique is size measurement (either by optical or electronic means) of a given batch along with weighing. This process is ideally suited for automation to the production line, since particles can be continuously removed, measured, and returned to the line, yielding density and size data simultaneously.[27]

3.3.2 Size and Shape

Particle size may be measured in numerous ways: sedimentation, light blockage, microscopy, radiography, etc. Shape, however, is only measured optically, comparing diameters in different orientations from a photograph. Should there be any nonspherical particles, they may be separated out by use of a tilted vibrating plate. This technique is not useful for fines smaller than about 100 μm, and no shape separation technique is available for these.

3.3.3 Chemistry

Standard techniques for chemical analysis of nuclear fuel materials have been developed, especially for pellet fuel. These can be applied

to sol-gel sphere fuel, since it is also a sintered solid material. However additional specifications will be required for $(U,Pu)O_2$ fuels for breeder applications.

3.3.4 Strength

Loading sphere-pac fuel into full-length rods will impose considerable stress upon the spheres, so that a high strength will be required. Strength is commonly determined by loading a sphere in compression between two flat steel plates. An ORNL modification[28] involves use of a steel holder plate drilled with 64 flat-bottom holes into which the particles are placed. A pin with flat ends is then put into the hole and the load applied. Crushing strength, actually load, is read from a strip-chart recorder. Two advantageous features were designed into the holder for greater flexibility and speed. Plates that mate to the holder were fabricated with holes of appropriate size and depth so that a batch of particles is simply poured onto it, the plate is tilted, and automatically only one particle is loaded per hole. The plate can then be x-radiographed to determine particle size. When mated to the holder and inverted, particles of known size are loaded into indexed holes in the holder. After crushing strength determination, the mating plate can be reattached and crushed particles retrieved in known orientation for further analyses. An automated, remotely operable device for measuring crushing strength of spheres is currently under development for HTGR fuels.

3.3.5 Microstructure

Particle microstructure is of course determined microscopically, by standard mounting and polishing techniques coupled with optical or microprobe examination or by fracturing and electron microscopic examination. Several papers[8,11,29,30] have been published illustrating the use of these techniques with sol-gel spheres.

Parameters of interest in microstructural evaluation include grain shape, size, and distribution; porosity shape, size, location, and distribution; and the presence of defects such as voids, cracks, and

excessive surface roughness. Generally the microstructure of sintered spheres is characterized by high density and fine to medium grain size.[29]

3.4 SCALE-UP CONSIDERATIONS — A. E. Pasto

Most of the work described in the literature was performed on small amounts of material in batch operations. However, scaling of the sintering processes to larger batches and continuous operation has been reported, with only minor problems occurring. Two problems are: (1) difficulty in controlling heat released in exothermic reactions on calcination and (2) difficulty in obtaining uniform temperatures and gas atmosphere circulation through the mass of spheres. These problems have been attacked through use of fluidized-bed techniques and/or use of thin beds.

A large batch dryer and calciner allowing semicontinuous operation was developed and applied at ORNL for remote use.[31] For larger throughput operation, a continuous, vertical tube, moving-bed calciner was developed by ORNL.[32] In this device, the temperature profile along the tube was controlled so that the moving charge underwent the correct temperature-time program. The countercurrent flow of gas up the tube provided excellent utilization of the atmosphere. A further advantage was that interparticle sticking, a potential problem particularly with fines, could be avoided. A similar device was used in a SNAM process pilot plant.[33,34]

The KEMA process has been scaled up to pilot-plant operation.[1] Calcination was performed in shallow beds in a large forced-convection furnace. The particles were then transported in boats through a furnace, which provided atmosphere control and the required time-temperature profile. The same sort of apparatus was employed for $(U,Th)O_2$ by Hobeg and KFA[3] in their production plant, turning out 4 kg heavy metal per hour.

The SNAM[33,34] 8-kg/d pilot plant used a moving-bed calciner (as noted above) followed by a continuous-throughput horizontal furnace (pusher-type). Apparently particle sticking was not a problem during sintering. Thus, it appears that large batches of UO_2, ThO_2, or $(Th,U)O_2$

can be readily produced on a semicontinuous or continuous basis with no real problems, by use of available technology. Preparation of substoichiometric $(U,Pu)O_{2-x}$ requires extremely good sphere-sintering atmosphere contact in order to maintain a suitably low oxygen potential to promote reduction, and thus scale-up for $(U,Pu)O_{2-x}$ might require fluidized beds or other means for providing good gas-solid contact.

3.5 REMOTE APPLICATION — W. J. Lackey

Suitable remotely operable furnaces for calcination and sintering do not exist. Similar furnaces such as the one planned for coating of HTGR fuel particles are at an advanced stage of development. In addition to using minimum floor space, the required furnace must have atmosphere control; either oxidizing or reducing for the calcining furnace and reducing for the sintering furnace. Automated particle handling must be an integral part of such furnace systems.

3.6 REFERENCES

1. Personal communication, F. de Rooy and F. W. Hamburg, ECN Petten, the Netherlands.
2. R. Förthmann et al., "Investigations on the Preparation of UO_2 Microspheres by Internal Gelation of a UO_2 Sol and from a Uranium(VI) Solution," pp. 551-66 in *Symposium on Sol-Gel Processes and Reactor Fuel Cycles*, CONF-700502 (May 1970).
3. H. Huschka, R. Förthmann, and E. Zimmer, "Kernel Fabrication for Different Fuel Cycles in Germany," pp. 37-47 in *Sol-Gel Processes for Fuel Fabrication*, IAEA-161, International Atomic Energy Agency, Vienna, 1974.
4. R. G. Wymer and A. L. Lotts, comps., *Status and Progress Report for Thorium Fuel Cycle Development Dec. 31, 1966*, ORNL-4275 (January 1969).
5. R. G. Wymer, "Laboratory and Engineering Studies of Sol-Gel Processes at Oak Ridge National Laboratory," pp. 131-72 in *Sol-Gel Processes for Ceramic Nuclear Fuels*, International Atomic Energy Agency, Vienna, 1968.

6. H. Landspersk̀ý and Z. Spitzer, "Changes in Pore Structure of Polyuranate Gels in Various Stages of Their Thermal Treatment: Part I — Drying and Calcination," *Jad. Energ.* 22(2): 59-67 (1976).
7. M. J. Bannister, "Sintering Mechanisms in Thoria Gel," *J. Am. Ceram. Soc.* 58(1-2): 10-14 (1975).
8. H. Suzuki, T. Hase, and T. Iseki, "A New Aspect of Grain Growth of Sol-Gel Urania," *J. Nucl. Sci. Technol.* 11(4): 146-52 (1974).
9. H. Suzuki et al., "Initial-Stage Sintering of Sol-Gel Urania," *J. Nucl. Sci. Technol.* 11(5): 208-15 (1974).
10. H. Landspersk̀ý and I. Vaněček, "Thermal Processing of Intermediate Products Prepared by the Sol-Gel Method for the Production of Sintered Uranium Dioxide Spheres," *Jad. Energ.* 21(1): 11-16 (1975).
11. R. Breschi, A. Camanzi, and A. Olivi, "Changes of Microstructure on Uranium Oxides During the Sintering Process," *Energ. Nucl. (Milan)* 23(6): 317-22 (1976).
12. A. Facchini and P. Gerontopulos, "Present State of the Art of the SNAM Process for the Preparation of Ceramic Nuclear Fuel Microspheres," pp. 227-45 in *Sol-Gel Processes for Fuel Fabrication*, IAEA-161, International Atomic Energy Agency, Vienna, 1974.
13. H. Landspersk̀ý and Z. Spitzer, "Changes in Pore Structure of Polyuranate Gels in Various Stages of Their Thermal Treatment: Part II — Reduction and Sintering," *Jad. Energ.* 23(5): 169-75 (1977).
14. C. J. Hardy, K. R. Hyde, and C. E. Lyon, "Investigations on Porous UO_2 Spheres Made by a Sol-Gel Process," pp. 510-20 in *Symposium on Sol-Gel Processes and Reactor Fuel Cycles*, CONF-700502 (May 1970).
15. A. L. Lotts, comp., *Fast Breeder Reactor Oxide Fuels Development — Final Report*, ORNL-4901 (November 1973).
16. R. A. Bradley and T. B. Lindemer, *LMFBR Fuel Cycle Studies Prog. Rep. January 1971*, ORNL/TM-3312, p. 64.
17. C. J. Hardy, "Status Report from the United Kingdom: Sol-Gel and Gel-Precipitation Processes," pp. 33-42 in *Sol-Gel Processes for Ceramic Nuclear Fuels*, IAEA-161, International Atomic Energy Agency, Vienna, 1974.

18. C. J. Hardy and E. S. Lane, "Gel Process Development in the United Kingdom," pp. 137-49 in *Symposium on Sol-Gel Processes and Reactor Fuel Cycles*, CONF-700502 (May 1970).

19. K. P. Louwrier and T. Steemers, "Sol-Gel Process Development at the European Institute for Transuranium Elements, Karlsruhe, Germany," pp. 244-52 in *Symposium on Sol-Gel Processes and Reactor Fuel Cycles*, CONF-700502 (May 1970).

20. M. Kadner and J. Baier, "Production of Fuel Kernels for High-Temperature Reactor Fuel Elements," *Kerntechnik* 18: 413-20 (1976).

21. T. B. Lindemer, "Factors That Control the Carbothermic Synthesis of Advanced Fuels," pp. 423-33 in *Symposium on Sol-Gel Processes and Reactor Fuel Cycles*, CONF-700502 (May 1970).

22. K. J. Notz, R. G. Haire, W. D. Bond, and L. G. Farrar, "Carbothermic Conversion of Sol-Gel U and Pu Oxides to Carbonitrides," pp. 434-47 in *Symposium on Sol-Gel Processes and Reactor Fuel Cycles*, CONF-700502 (May 1970).

23. J. P. McBride et al., "Laboratory Studies of Sol-Gel Processes at the Oak Ridge National Laboratory," pp. 161-225 in *I Processi Sol-Gel per la Produzione di Combustibili Ceramici* (Proc. Int. Nucl. Symp. Turin, Oct. 2-3, 1967), Comitato Nazionale Energia Nucleare, Rome, 1968.

24. K. Bischoff, V. Scherer, and H. Schumacher, "Sol-Gel Processes for the Preparation of U-Pu-Carbide Fuels," pp. 164-77 in *Symposium on Sol-Gel Processes and Reactor Fuel Cycles*, CONF-700502 (May 1970).

25. K. Bischoff, M. H. Lloyd, and H. Schumacher, "Sol-Gel Processes for Carbide Preparation," pp. 95-128 in *Sol-Gel Processes for Fuel Fabrication*, IAEA-161, International Atomic Energy Agency, Vienna, 1974.

26. J. I. Federer and V. J. Tennery, *Synthesis of (U,Pu)C by Carbothermic Reduction of Mixed Oxides and Evaluation of the Sintering Behavior*, ORNL/TM-6089 (January 1978).

27. J. E. Mack and W. H. Pechin, *Automatic Particle-Size Analysis of HTGR Recycle Fuel*, ORNL/TM-5907 (September 1977).

28. W. J. Lackey, D. P. Stinton, L. E. Davis, and R. L. Beatty, "Crushing Strength of High-Temperature Gas-Cooled Reactor Fuel Particles," *Nucl. Technol.* 31(2): 191-201 (November 1976).

29. W. J. Lackey and R. A. Bradley, "Microstructure of Sol-Gel-Derived $(U,Pu)O_2$ Microspheres and Pellets," *Nucl. Technol.* 14: 257-68 (1972).

30. C. J. Hardy et al., "Examination of Sol-Gel UO_2 Surfaces by Scanning Electron Microscopy," pp. 61-69 in *Sol-Gel Processes for Ceramic Nuclear Fuels*, International Atomic Energy Agency, Vienna, 1968.

31. P. A. Haas et al., "Engineering Development of Sol-Gel Processes at the Oak Ridge National Laboratory," pp. 279-318 in *I Processi Sol-Gel Per La Produzione Di Combustibili Ceramici* Turin, (Proc. Int. Nucl. Symp. Oct. 2-3, 1967, Comitato Nazionale Energia Nucleare, Rome, 1968.

32. C. C. Haws and J. W. Snider, *A Vertical-Tube Furnace for Continuously Calcining Sol-Gel Derived ThO_2-UO_2 at a Rate of 35 Kilograms per Day*, ORNL-3894 (January 1969).

33. G. Brambilla et al., "The SNAM Process for the Production of Ceramic Nuclear Fuel Microspheres," pp. 191-209 in *Symposium on Sol-Gel Processes and Reactor Fuel Cycles*, CONF-700502 (May 1970).

34. A. Facchini, "The SNAM Process for the Preparation of Ceramic Nuclear Fuel Microspheres: Continuous Production Technique," *Energ. Nucl. (Milan)* 17(4): 225-33 (1970).

4. SPHERE-PAC LOADING AND ROD INSPECTION

The sphere-pac process is one of several techniques through which an assemblage of small particles can be loaded to high density in a nuclear fuel rod. The techniques are similar in that all of them depend on vibrational agitation of the cladding to compact the particle bed. Feed particles are normally either spheres produced by a sol-gel process or angular shards prepared from sintered, fused, electrodeposited, or pneumatically impacted oxides.[1] A number of alternatives to these processes have been suggested but not widely accepted; for example, a mixture of regularly shaped nodules and irregular shards has been proposed.[2] For the purposes of this report, the term sphere-pac (an abbreviation for spherical-compaction) will be used to describe any process that uses spherical particles as a feed material regardless of the type of compaction force. The term vi-pac (an abbreviation for vibratory compaction) will be used to describe all other forms of the vibratory loading process. Sphere-pac is the most attractive of these packing options since dust problems and packing times are minimized and smear density is maximized.

4.1 PACKING THEORY — R. R. Suchomel

"The principle of the vibratory compaction process is the agitation of a group of particles in the presence of only slight restraint so that they will tend to seek that configuration which offers the closest packing of the associated particles."[3] Studies of the packing patterns of spherical particles have been both theoretical and experimental. Theoretical studies often predict unachievably high densities since they assume long-range packing order of theoretically dense spheres. In practice, neither of these requirements is ever fully met.

The simplest studies involve only one size of sphere. White and Walton[4] described the five theoretically possible ways in which equally sized spherical particles can be arranged. These arrangements are:
(1) simple cubic with a theoretical packing density of 52.36%,
(2) orthorhombic with a theoretical packing density of 60.45%,

(3) double nested (wedge-shaped tetrahedron) with a theoretical packing density of 69.81%, (4) face-centered cubic (fcc), and (5) hexagonal close-packed (hcp) for which the theoretical packing densities are identical at 74.05%.

Experimental work with single size spherical particles indicates that measured packing densities of only about 62.5% of theoretical are usually obtained.[5] This density arises, most probably, from a mixture of orthorhombic and double-nested packing arrangements, since the fcc and hcp forms are not geometrically stable under agitation.[5]

Since a packing arrangement that yields only 62% of theoretical density is inadequate for fuel rod loading, one must consider alternatives. Whenever regular packing is present, then a regular arrangement of void spaces is also present. Smaller spheres could be mixed into the batch to fill these voids and thus increase the density. Conversely, a number of extremely large spheres could be added to the original batch of particles. In this situation, one large particle would replace a number of smaller ones as well as the voids associated with them to again increase density. The optimum "binary packing" arrangement occurs when these two effects combine to minimize void space. For spherical particles, this occurs with a mixture of about 70 vol % coarse and 30% fine material.[5,6]

The two particle size fractions may either be combined and blended before packing or else they may be sequentially packed by infiltrating the smaller particles through the packed bed formed by the larger ones. McGeary,[5] in using the latter approach, found that the coarse component acted as a fixed porous filter bed, which was filled by the fine component. He also found that a seven-fold difference between sphere diameters of the two components was needed to produce effective infiltration. This observation is probably related to the fact that the interstitial void present amid a triangle of three closely packed same size spheres can be best filled by a sphere 0.154 ($\sim$1/7) the diameter of the others. The precise density achieved by binary packing will thus depend on the relative sizes of the two fractions, but will not exceed a limiting density of 86% of theoretical.[5] Experimentally,

fuel rods have been prepared from two sizes of spheres in which 82% of theoretical density was obtained.[7,8] In the preparation of other $(U,Pu)O_2$ pins for irradiation tests, smear densities of 83 to 84% were achieved[8] with microspheres in the range of 450 to 500 μm infiltrated with smaller than 44 μm.

When a diameter ratio less than seven is used, the two particle types must be blended together before loading into the fuel rod. Previous sphere-pac work at ORNL has shown that two sizes of spheres with a diameter ratio of 4 will pack with an observed density almost 73% of theoretical at a mixture of 65% coarse – 35% fines.[8] The ORNL work also reported that, as larger diameter ratios were used, blending became more difficult and some size segregation was evident. Thus while both approaches to binary packing offer density improvements, the improvements are not adequate to allow production of acceptable fuel rods if smear densities in excess of about 84% are desired.

Fortunately, a mixture of three differently sized particle fractions will provide suitable densities. Possible techniques that can be used to pack three sizes of particles into a container include (1) preblending of the three particle types, (2) sequential infiltration of the three sizes, and (3) a mixture of these processes, which involves infiltration of the smallest particles into a bed composed of a blend of the two larger sizes.

The geometrical considerations associated with ternary packing have been identified by Hudson[9] and by White and Walton.[4] These strict theoretical approaches are much too restrictive, however, for use in sphere-pac work. More relevant estimates of the most dense possible ternary packing have been made through observation of the packing density of individual size fractions and with the assumption that the infiltration process will do little to change the packing order. With this approach, Hauth[10] claims that 98.3% of theoretical density should be obtained if the material in each fraction can be compacted separately to a density of 74%. He used calculated diameter ratios between successive fractions of 2000:43.5:1 in determining this density. Ayer and Soppet[11] performed the same calculation but used packing densities of 63.5% for each size

fraction. Using these conditions, they predicted a limiting density of 95.1%. This value is also given in an ORNL report,[8] which presumed the same 63.5% packing density for each size fraction. McGeary[5] determined that the fine component would compact to only 59.5% of its theoretical density, to give a calculated ternary packing density of 93.5%. According to these estimates, a ternary packing arrangement should produce nuclear fuel pins.

4.2 EXPERIMENTAL RESULTS — R. R. Suchomel

Assuming that three sizes of spheres can be used to obtain adequate density in a fuel rod, the problem becomes one of selecting proper loading and vibration conditions. Experimental work should not be expected to duplicate theoretical expectations because of the restraints imposed by such factors as the narrow diameter of the cladding, extreme length-to-diameter ratio of the cladding, and imperfect pre-blending of particles. Also, the theoretical work assumes that all the spheres are of theoretical density. In reality, of course, if a 90% observed packing density is achieved with feed material with 5% porosity (sphere density is 95% of theoretical), then the final smear density of the rod would be (0.90 × 0.95) or 85%.

Much of the available experimental sphere-pac work is contained in an ORNL report.[8] The laboratory investigated the practicality of using three sizes of particles and two sequential infiltrations. The approach was found to be impractical. From observations by ORNL and Ayer,[12] it was judged that the ratio of tube diameter to largest particle diameter as well as the diameter ratios between consecutive particle sizes must be about 10 for optimum packing. Since the minimum practical sphere size was about 20 μm, the largest particles would have to have been 2000 μm in diameter. Not only was this sphere size beyond production capability, but the process would require a minimum cladding diameter of 20 mm or 0.78 in.

To obtain high densities, the ORNL researchers therefore used a single infiltration of a blended bed. This work and a graphical depiction of the loading process (Fig. 4.1) is described in the following excerpt.[8]

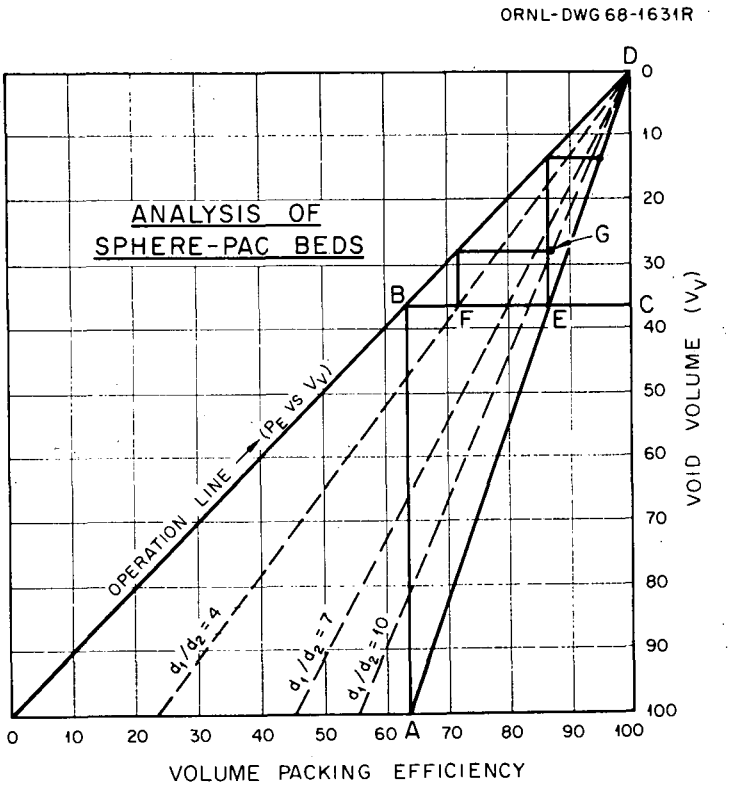

Fig. 4.1. ORNL Analysis of Sphere-Pac Beds.

. . . we developed a graphical construction that may be used to correlate and generalize all our information relating to the Sphere-Pac fabrication procedure. . . ., the horizontal axis represents the volume packing of spheres in a container or bed (packing efficiency), and the vertical axis represents the void volume associated with this volume packing. If a 45° operating line is established between the two zero points of the axes, then the void volume associated with any packed volume may be determined by reading up and then across (line A-B-C). If we now construct a line joining the volume packing efficiency of a given size sphere (% of available void volume filled by spheres) to the void volume zero point, the horizontal distance between this line and the operating line is always proportional to the packing efficiency multiplied by the void volume associated with that packed bed density. Thus the line A-D represents the packing of a single size sphere in a large tube or in a packed bed . . . where the diameter of the sphere is less than approximately 1/25 that of the smallest sphere already in the packed bed.

. . . now see the effects of using a blended bed, or the effect of infiltration at less than the optimum 63.5% packing efficiency. If a d_1/d_2 ratio of 4.0 is used for

> a blended bed, the bed density (volume packing) is increased to 72%, point F. Infiltration with spheres 1/10 the size of the medium fraction produces an 88%-dense bed, point G. This is exactly the density that we have obtained and reproduced by this technique. We have also produced 86.5%-dense beds by infiltration of a blended bed (d_1/d_2 = 3.4) with the 10/1 size ratio of medium to small. This is the density predicted by the graphical correlation for these conditions.
>
> The above discussion shows that to produce a 90%-dense fuel we must use either a double infiltration with very carefully controlled sphere sizes or a blended bed at d_1/d_2 of about 5.8/1, followed by a single infiltration. This requires investigation of the behavior of beds blended at this diameter ratio. They tend to segregate, as was shown, . . .

About 60 plutonium-bearing fuel rods were fabricated for irradiation tests.[8] These rods were loaded by a single infiltration of fines into a pre-packed bed of single size coarse particles. Final smear densities ranged from 73.2% to 86.1% of theoretical in fuel columns up to 0.33 m (13 in.) long. The lower densities resulted from the use of low-density spheres.

Loading results are also available from a number of other laboratories, primarily in the form of irradiation test specimen parameters. Interfuel B.V. of the Netherlands used the sequential infiltration method to load three sizes of spheres to acceptable densities. P. F. Sens[13] of Interfuel B.V. used particles having diameters of 1000 μm, 100 μm, and 10 μm in his studies to produce up to 92% smear density. He observed that spread in both the smeared fuel density and the axial density variations could be decreased to 2% when high-density fuel particles, about 99% of theoretical, were used. Sens[14] has also summarized Interfuel's sphere-pac irradiation test program; nearly 100 fuel rods having smear densities of up to 85% have been loaded and irradiated.

Other sphere-pac loading studies have been reported in the open literature for which two sizes of spheres were used. Lahr[15,16] recently discussed irradiation test rod fabrication at Gelsenberg AG, in which seven plutonium-uranium-bearing rods were loaded. Smear densities of up to 76.6% were obtained, apparently by infiltration of small particles (125-200 μm) into a bed of 800-1100-μm-diam coarse

particles. He also reported that three rods loaded with 1000 to 1250-μm coarse particles and smaller than 90-μm nonspherical fines for a second irradiation test achieved densities of 77.8% (0.12-m fuel length) and 77.3% (0.39-m fuel length). The large diameter of the fine fraction probably accounts for the low smear densities.

Other irradiation test rods have been loaded by the Swiss;[17] they also used two sizes of spheres. Working with monocarbide spheres of 600-800-μm and 40-60-μm-diam fractions, they achieved densities of 65 to 80% of theoretical. Low smear densities are the result of porous spheres.

In Italy[18] oxide spheres of 707-840-μm-diam and 70-100-μm-diam were loaded to 80% smear density for an irradiation test program.

From the literature review just given, fuel rods clearly can be and have been loaded to high density by the sphere-pac technique. Two suitable loading methods have been developed; they are: (1) double or sequential infiltration and (2) a blended binary bed with single infiltration. The third option, a blended ternary bed, was not mentioned in the experimental literature for sphere-pac. However, it is the usual practice for vi-pac fuel fabrication. Particle segregation may be an insurmountable problem with the blended ternary bed approach. The sequential infiltration method using three sizes of spheres and two infiltration steps would appear to be too slow for commercial application. Thus, according to the literature it would seem that the blended binary bed with single infiltration is most attractive for further development.

4.3 LOADING EQUIPMENT AND METHODS — R. R. Suchomel

The techniques and equipment components needed for sphere-pac loading will be reviewed in this section. Other pertinent fuel fabrication technology will be discussed whenever applicable to the sphere-pac process.

The equipment needed for rod loading obviously depends on the sophistication of the technology. Primitive packing studies can easily be performed with only a section of cladding, a supply of spheres, and some device to compact or vibrate the bed. To pack rods to optimum

density and with good reproducibility, other items such as a follower rod, hold-down screen, and coarse-bed particle blender should be included. For the fabrication of a few irradiation test rods, equipment must be provided for outgassing and pressurizing the loaded rods as well as for welding the end plugs. Advancement to an automatic or remotely operable system would surely require the addition of components needed for sphere transfer, sphere lot blending, particle batch weighing and sampling, fuel rod handling, and many other processing steps. Since no such automatic systems have been developed for sphere-pac, this section will assess equipment items required only for performing loading tests and fabricating irradiation specimens. More sophisticated systems are discussed later in sections regarding scale-up and remote considerations.

4.3.1 Vibrational Input

The input of vibration is basic to the sphere-pac process, and it is natural that considerable information exists concerning selection of the correct vibrator and proper mode of vibrational input. Unfortunately, not all the available information is consistent. Traditionally, the sphere-pac process has been thought to require only low-energy vibration. High energy, high acceleration forces were considered necessary only to compact the angular, poorly sized particles used in the vi-pac process. Since this distinction is not maintained throughout the literature, it may be expedient to review all types of vibrational input that have been used either for sphere-pac or vi-pac development.

Most vibrational modes used in fuel compaction are sinusoidal. The most important variables in such motion have been found to be frequency and acceleration; most vibrations are usually described in terms of these variables. Electromechanical vibrators, which operate at a fixed frequency of 60 Hz, were the first units to be adopted for sphere-pac use. They are quite inexpensive, relatively quiet during operation, and well suited for glove box work. After testing a variety of vibrational frequencies and modes of energy input, researchers at ORNL[19] found that frequency had little effect on density and that a frequency of 60 Hz provided the best loading rate. To fabricate irradiation test rods at

ORNL, a 60-Hz electromechanical vibrator was used inside a glove box. The vibrator was tilted 45° to supply both lateral and axial vibration to the vertical fuel rod.[20]

A similar glove box system was set up at Argonne National Laboratory.[21] Accelerations up to 15g were measured during fuel rod vibration from a 60-Hz electromagnetic vibrator. The Swiss sphere-pac program[22] also uses a small fixed-frequency vibrator; in this case, operation is at 50 Hz.

Small pneumatically driven vibrators are noisier but produce approximately the same output as the electromechanical units. McGeary[5] operated such a unit at several frequencies and found that efficiency of the infiltration process increased in the following order: 38 Hz, 2.5g; 49 Hz, 12g; and 56 Hz, 21g. Another type of pneumatic vibrator has been used for compaction studies; this type of vibrator could more aptly be described as an air hammer. A device of this type, having a frequency of about 4 Hz and accelerations of up to 20,000g, was incorporated into a vi-pac loading machine at ORNL.[23]

A third type of vibrator is often used for particle compaction. The electrodynamic vibrator is more versatile and imparts higher energy than either the electromagnetic or the common pneumatic vibrator. Frequency of the vibration can typically be varied and controlled between 0 and 4000 Hz. Electrodynamic devices are routinely used for vi-pac loading and occasionally for sphere-pac work. A recent application to a sphere-pac system in the Netherlands has been reported by Sens.[13] Up to 92% of theoretical density was obtained by continuous sweep through resonance frequencies between 400 and 3000 Hz. The fuel rod was clamped on a horizontal resonance beam, which in turn was attached to the shaker. Use of the beam induced high accelerations in the fuel rod in both the horizontal and vertical directions.

The concept of using an electrodynamic vibrator with an attached resonance beam had been proposed earlier by Hauth.[1] Such a system was employed at Battelle-Northwest in 1964 for a vi-pac fuel program. It was felt that the resonance beam would be useful in a remote fabrication facility by permitting the vibration equipment to be located outside the cell. Two different shakers, one having a rated output of 3.3 kN

(750 lb) force and a second with 22 kN (5000 lb) force, were used. Density increases frequently occurred at discrete resonant frequencies. Use of the resonance beam more than doubled the number of these frequencies at which the applied acceleration was sharply increased by resonance effects. Resonance frequencies were found by a continuous sweep between 250 and 750 Hz. Applied accelerations up to 50*g* were recorded. Even fuel rods having very thin (0.13 mm) end caps were fabricated without damage to cladding or welded closures. Several thousand fuel rods, having lengths of 0.3 to 2.5 m (1-8 ft) were loaded and compacted from vi-pac material to densities of 86 to 88% of theoretical. With this equipment as many as 50 rods were fabricated in an 8-h day.

Hauth[10] has also reported a second vi-pac loading method, which did not use a resonance beam. The same electrodynamic vibrators were used and operated over a range from just below the principal resonant frequency to an upper limit of 3000 Hz. This produced accelerations of 100*g* at resonance peaks.

Sphere-pac work at Gelsenberg AG used a similar electrodynamic vibrator.[15] During the infiltration process, the shaker passed accelerations of 2*g* to 8*g*, at frequencies up to 2000 Hz, to the fuel rod.

Hirose and Takeda[24-27] thoroughly investigated the use of an electrodynamic vibrator for vi-pac applications. They analyzed the relationship between obtainable density and several vibration conditions: namely, frequency, displacement, velocity, and acceleration. Highest density was obtained at highest acceleration, provided that displacements were in the range of 10 to 30 μm. Similar results were obtained with both regular but nonsinusoidal and completely random vibrations. Random wave vibration produced only about half the peak stress on the cladding normally generated by sinusoidal wave forms.

A literature review by Evans and Millman[28] indicates that ultrasonic frequencies were less effective in producing dense fuel rods than were sonic frequencies in the range of 20-5000 Hz.

Naruki[29] proposed an optimum vi-pac loading process that involved several stepwise increases in acceleration. He used a frequency of

300 Hz and 8g while the rod was being loaded. For compaction, a constant sweep between 300 and 3000 Hz was maintained for 15 min with accelerations of 40g and 60g.

From this survey, it appears that at least two types of vibrators should be considered for sphere-pac work. Small devices, either electromagnetic or pneumatic, are desirable from size, noise, and cost standpoints. However, a larger electrodynamic shaker may be required to successfully load long fuel rods or obtain high throughput rates.

4.3.2 Sphere Handling

Spheres must be properly sized and upgraded before being loaded into fuel rods. During loading, they must not be allowed to segregate by size, as this would lead to density reduction. Size distribution of the various particle sizes could be improved, if necessary, by a simple screening operation. Such screens are commercially available over the entire size range of interest. Also, if needed, nonspherical particles could be adequately removed from any batch by passing it over a shape separation table.[30,31]

Vi-pac fuel fabrication requires that all particle types be blended before rod loading since infiltration is impractical for such nonspherical material. A similar blending operation will be required for sphere-pac loading if the two coarse components are to be uniformly mixed before loading. Several blending techniques have been reported in sphere-pac and vi-pac literature. Hauth[10] apparently used conventional powder blending techniques to prepare vi-pac material. He then transferred a weighed amount of fuel to a small conveyor belt, which was driven by a variable-speed motor. This permitted the rod loading rate to be closely controlled. Hauth indicated that with a suitably modified feeder more than 20 rods could be compacted simultaneously. In another report, Hauth[1] stated that both vibratory feeders and small conveyors had been used for rod filling, but that the latter device offered a possible advantage by allowing better control of particle-size distribution of material just before it entered the rod.

Evans and Millman[28] also used a conveyor belt approach to prevent segregation in their vi-pac study. They loaded each of the size

fractions of powder into separate long rectangular boxes of uniform length and width. The boxes were then emptied onto a stationary conveyor belt so that the various sizes were uniformly distributed along the conveyor. Movement of the conveyor caused simultaneous loading of the different size fractions.

ORNL researchers[8] used a batch blending technique in their early sphere-pac work. They placed up to 60 g of spheres in a 35-mm-diam, 120-cm^3 bottle and rolled it at 275 rpm for 5 min to produce a blended mixture.

Ayer[21] used a small V-blender to produce a blended coarse bed in his studies. A suitable blend was obtained in about 3 min.

Once the fuel particles have been loaded into the rod, they must be restrained to prevent segregation during compaction. The binary blended bed with single infiltration loading technique requires that the blended coarse bed be restrained during infiltration of the fines. Both Ayer and Soppet[11] and the ORNL workers[8] used a funnel with a screen in the bottom for this purpose. To aid infiltration of fines in sphere-pac loading and to enhance compaction of a vi-pac bed, some sort of follower rod is almost universally used.[8,10,18] A load of up to 4 kg can be applied to the follower rod to restrain the upper segment of the bed.

4.3.3 Compaction Aids

In 1937, White[4] used a vi-pac loading procedure that included keeping a vacuum of "about 70-cm Hg" (7 kPa) on the tube during loading. This materially assisted the compaction process. McGeary[5] pursued this approach since he felt it was "logical that removal of the air from the binary packing should speed the introduction of fines into it." He obtained a section of tubing with a vacuum nipple at the bottom and a close-fitting leather disk to seal the top. A vacuum of "73-cm Hg" (3 kPa) was maintained on the binary bed during packing. However, contrary to his expectations, the vacuum actually prevented proper infiltration; the fines were observed to merely circulate in the upper regions of the container because of turbulence and updraft currents produced by leakage around the leather disk. He recommended but did not attempt the use of an airtight plunger.

Another method for increasing the rate of bed compaction has been described by Ayer and Soppet.[11] They devised a novel technique for supplying both vertical and horizontal acceleration to the fuel rod during vibration. They designed a series of loose fitting cages, which were placed over the rods during loading. These tubes, called "rattle cages," effectively imparted a vibratory mode perpendicular to the axial vibration. This reduced bridging of particles and improved packing regularity.

Cannon et al.[23] found that compaction density in the ORNL vi-pac program could be increased 4-5% if all looseness was removed between the vibrator and the fuel rod. They designed a chuck that could be securely attached to the base of the fuel rod. A differential pressure switch was included in the design to assure that a proper seat was made before the chuck nut was tightened.

4.3.4 Postloading Procedures

After the fuel is loaded into the cladding tube and compacted, the remainder of the fabrication process should be very similar to pellet fuel fabrication processes. The remaining steps to be completed include: (1) fuel rod outgassing, (2) placement of plenum spring, and (3) end-plug welding.

Fuel rod outgassing removes moisture and other sorbed gas contaminants from the fuel. Hauth[1] chose to outgas fuel particles immediately before loading by holding them in a vacuum at 250°C for 2 h. Olsen et al.[32] outgassed the fuel rod after the fuel had been compacted. This was done by evacuating the rod while heating at 110°C for 30 min. Most sphere-pac irradiation test rods are currently loaded while inside a helium-filled glove box. Pechin[33] has described analytical methods for measuring moisture and sorbed gas content of sphere-pac fuel. Moisture content in the fuel of less than 10 ppm was successfully measured with this technique.

Both pellets and particulate fuels can be held in place through the use of plenum springs. To restrain a sphere-pac bed, a spacer disk possibly made of alumina or thoria would be placed on top of the fuel column to transmit the spring pressure. For the fabrication of

irradiation test rods, ORNL researchers used thoria spacers and small pieces of outgassed ceramic fiber (Fiberfrax) to prevent fuel movement during handling and shipping.[20]

The procedure used for welding the top end plug should be identical for both pellet and sphere-pac fuel. Welding technology is well advanced. Atmosphere control is, of course, important during welding, to prevent contamination and possible corrosion during irradiation.

With the completion of the end-plug welding step, the fabrication process is complete, and the assembled fuel rod is moved to an inspection station.

4.4 ROD INSPECTION — J. E. Mack, P. Angelini, and E. J. Allen

Under a previous program,[8] quality assurance and operating procedure documents controlling the fabrication of sphere-pac and pellet-loaded fuel rods for irradiation testing and performance analysis of fast breeder mixed-oxide fuels were developed. In all, nearly 50 process procedures — 25 operator procedures, 9 material specifications, and 11 test specifications — were prepared in detail. A total of 60 fuel rods was prepared according to these procedures and specifications for irradiation testing.

Many of the rod inspections required are performed in the same manner whether the rod is loaded with pellets or particles.[34] In some instances, instrumentation used to control the loading of spheres may also be utilized to perform the necessary inspections. Should the fuel composition dictate remote fabrication, all postloading rod inspections would have to be performed remotely. While some inspections, such as gamma scan and heavy metal assay, are amenable to remote operation,[35] most are not and would require significant development to enable the inspection to be performed economically with acceptable precision, accuracy, and speed.

4.4.1 Dimensional Inspection

Conventional methods are available for inspecting rod length, diameter, wall thickness, ovality, and camber both before and after loading. Loading methods (particles versus pellets) will have little

influence over these inspections. While most of these inspections are performed on the empty tubing, postloading dimensional inspections such as end-cap concentricity and final visual inspection require development of remote techniques.

4.4.2 Smear Density

Gamma ray attenuation has been used[36] to determine the density profile along sphere-pac-loaded fuel pins at ORNL. In those runs a ^{60}Co radioisotope source and NaI(Tl) detector were used. Fuel rods loaded with a number of different thorium and uranium oxide fuels were scanned. Fuel rods loaded with ^{233}U oxide fuel were inspected in a hot-cell environment for the $(Th,^{233}U)O_2$ (Kilorod) project at ORNL.[37]

A gamma scanning device is under development at ORNL. The device will function as an accurate level-sensing device and can be used to determine the overall length of the packed bed. A weighing fixture will be required to obtain an accurate weight of the packed fuel bed. Alternative methods involving weighing the fuel before dispensing need to be evaluated to determine the smear density measuring method most compatible with the loading technique and with accountability requirements. If fuel weight determination after loading is acceptable, the procedures may be simplified. In any case, the development needed relates more to remote operational requirements than to peculiarities of particle fuels.

4.4.3 Homogeneity

Contact equipment exists for measuring fissile distribution.[38-40] However, these methods would be influenced by high radiation levels. For example, if one is concerned with refabricated fuel of high gamma activity or with spiked fuels, then a delayed fission gamma ray method for detecting the distribution of the fissile material along a fuel pin may not be applicable. In such cases, the detection of prompt fission neutrons from the irradiated sample may be used.[41]

4.4.4 Impurity Analysis

Applicability of conventional methods for determining moisture content and total hydrogen to sphere-pac fuel rods requires further

evaluation. Analysis of samples of spheres and control of the rod loading environment may be the most practical method. Destructive analysis of small sample rods to verify proper gas content and contamination may be required. Development and verification of the technique are then required.

4.4.5 Weld Integrity

Conventional weld inspection techniques can be utilized in a cold facility. Remote inspection of end-cap welds requires the design and development of equipment to remotely radiograph and leak test fuel rods, as well as equipment associated with the remote handling and positioning of the rods.

4.5 SCALE-UP CONSIDERATIONS — R. R. Suchomel and J. E. Mack

Sphere-pac loading is presently performed primarily in conjunction with basic process development or the fabrication of irradiation test specimens. Scale-up of the loading process to the throughput required for a commercial facility will require extensive engineering development. Application of sphere-pac in a facility employing remote operation and remote maintenance would require still further engineering effort since the technology needed for such work is not presently available, even for pellet fuel fabrication. This section will present an engineering evaluation of the areas that will require further development if commercial or remote operations are planned. A flowsheet describing a typical fuel rod fabrication process employing the sphere-pac process is shown in Fig. 4.2. This flowsheet identifies the processing steps required during fuel fabrication, and it is applicable to either a contact or remote production operation.

4.5.1 Sphere-Pac Loading

A review of sphere-pac technology indicates that the most serious problem in the scale-up of the loading process would be in obtaining acceptably short loading times. With use of the present ORNL low-energy, fines infiltration loading method, perhaps more than an hour would be required to completely load a commercial length fuel column. Nearly

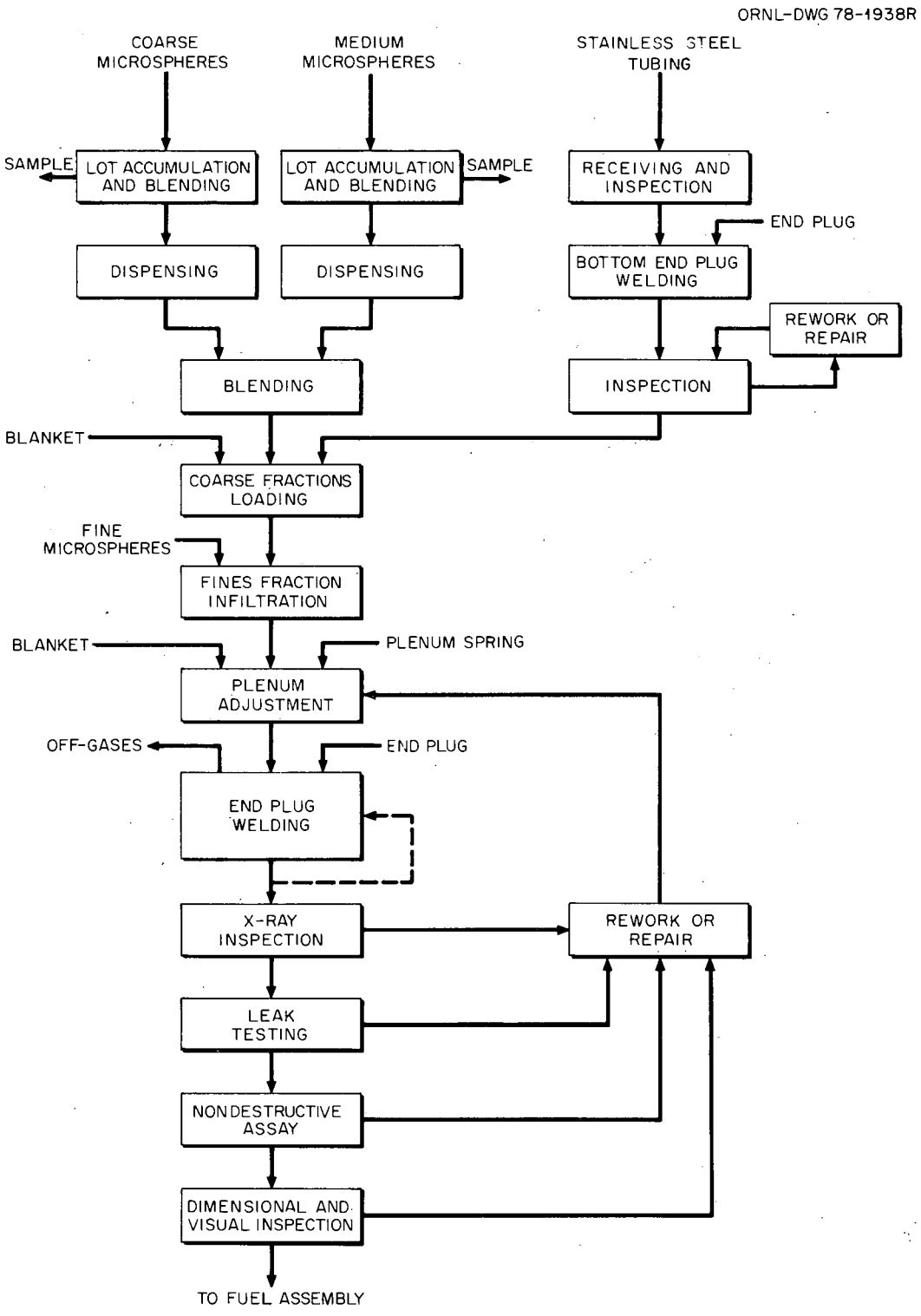

Fig. 4.2. One of Several Possible Flowsheets for Fuel-Rod Fabrication Using the Sphere-Pac Process.

all this time would be taken up by the fines infiltration operation. Such a processing time makes sphere-pac uncompetitive with pellet fuel loading, in which a fuel rod can be filled in a matter of minutes.

A reasonable goal or acceptable criterion for a commercial sphere-pac operation might be a 5-min loading time to fill and compact the full length of a prototype fuel rod. Fortunately, it appears possible to meet this time limit by greatly reducing the time required for fines infiltration.

Infiltration times could be dramatically decreased through the use of a technique that would load alternating layers of blended coarse and fine spheres. A small amount of a blended coarse bed would be put into the cladding and then an appropriate amount of fines, an amount calculated to exactly infiltrate this segment of coarse bed, would be added. Additional layers would be added until the desired fuel column height was obtained. With the use of this approach, the fines fraction would have to infiltrate only a short section of the bed rather than the entire fuel column. The use of smaller and smaller layers finally reaches an end point in which all three size fractions are essentially preblended before loading or simultaneously blended as they are loaded into the rod. Literature reports indicate that through the use of preblending, long fuel columns of vi-pac fuel have been successfully loaded in only 2 to 3 min. These short times were achieved by preblending and then compacting the loaded fuel column at very high accelerations. Recent loading studies at ORNL indicate densities of about 87% T.D. can be achieved in 6 to 8 min by simultaneous loading of three sizes of spheres.

However, if the minimum loading time was found to be about 1 h, the effective processing time could further be reduced by multiple rod loadings. The assumed criterion of 5 min per fuel rod translates to an output of 12 fuel rods per hour. This same output could be achieved in a 1-h batch processing step in which 12 rods were simultaneously loaded and compacted. Large electrodynamic vibrators are commercially available to handle payloads of such size. As discussed earlier, up to 20 fuel rods have been simultaneously compacted with a large electrodynamic vibrator.

4.5.2 Fuel Handling

A pneumatic conveying system for transporting fuel spheres between and within the processing systems was found practical.[42] This type of conveying provides the greatest flexibility in the routing of transfer lines and the resulting easing of restrictions on the placement of process equipment. The system itself is amenable to scale-up; kilograms per minute can be pneumatically transferred. Flow indicators, pressure monitors, and hopper level indicators provide adequate feedback for reliable and efficient operation. Operating parameters can be readily determined. Conveying in the "dilute" phase — where all material is entrained in the gas stream, with no "saltation" or settling out — can be accomplished with low pressure [<0.1 MPa (15 psi)] and moderate flow [<5 liters/s (10 scfm)]. Also, the transfer hoppers and lines constitute a closed system. Thus, use of argon as the motive gas virtually eliminates oxidation and moisture pickup.

Extensive development and operating experience have been acquired under the HTGR Fuel Recycle Development Program at ORNL on pneumatic conveying of nuclear fuel microspheres.[42] This program has also involved the development of auxiliary sphere handling equipment, such as samplers,[43] weighers, and level sensors. The equipment has been developed with the ultimate goal of total remote operation.

4.6 REMOTE APPLICATION — R. R. Suchomel

Two of the major difficulties of any remote operation involve material handling and equipment maintenance. Since the sphere-pac loading process involves relatively few mechanical operations, equipment maintenance should be simplified. Also, much of the engineering work that will be required for construction of a remote sphere-pac process will be focused on equipment items not necessarily specifically required for sphere-pac processing. For example, sophisticated welding equipment may be needed to secure the top end plug, and precise weighing devices could be required to accurately determine the amount of fuel in a loaded fuel rod; however, these equipment items are equally applicable to both pellet and particulate fuel rods.

The flowsheet in Fig. 4.2 shows that many fuel fabrication steps are common to all fuel forms. Once the fuel is loaded and the end plugs are in place, sphere-pac fuel rods are handled no differently from other fuel rods. Equipment items specifically required for the fabrication of sphere-pac fuel rods will be those needed for fuel handling before and while the fuel is loaded into the cladding. In other words, specific design problems will be focused on the handling and processing of the fuel spheres.

The first processing step shown in Fig. 4.2 is the lot accumulation and blending of each of the two larger sizes of spheres. The purpose of this step is to prepare large lots of feed stocks for subsequent loading so that feed controls will not require frequent adjustment. Development of a suitable blender is required.

A sample would be extracted from each blended lot to determine particle size distribution, mean particle diameter, and average particle density. A passive sampler, ideal for remote use, has been developed[43] for the HTGR fuel refabrication program. The sampler was demonstrated to extract a constant representative sample from batches of spheres used in HTGR fuel fabrication. These spheres are very similar in size to the larger sizes required for sphere-pac. The sampler consists of an assembly of several identical stages. At each stage, particles are poured over the apex of a cone and divided by splitters into eight feed streams. These streams are recombined into two flows of equal volume. One of the flows is directed out of the device while the second provides feed material for the following stage of the sampler. At each stage, one-half of the feed particles are selected as a sample and passed to the next stage. After two stages, the sample consists of one-fourth of the total particle batch; after five stages, it is 1/32 of the feed particles; and after ten stages, it is 1/1024 of the initial supply. The number of stages can easily be changed to provide the desired sample size.

From the lot accumulation and blending equipment, particles would pass to a dispensing device. The dispensers meter out precisely the quantity of each sphere size needed to produce the desired blended bed. Dispensers of this type have been employed in the HTGR Fuel Refabrication

Program to measure out the quantities of fissile, fertile, and shim particles needed in the production of HTGR fuel rods.[44] Such devices have been shown to dispense very accurate and reproducible portions. They are mechanically simple, each consisting of only two pinch valves or a pinch valve and a plug valve. The entire unit could easily be removed for service or replacement.

The dispensers feed a blender; the blender must homogeneously mix the two kinds of particles and load them into the cladding. The literature indicates that commercially available blending devices are not suitable for sphere-pac work. It was noted that such devices produce segregation because of the size difference between the two particle types. A number of blenders have been devised and successfully used in laboratory sphere-pac experiments. These techniques employ concepts such as conveyor mixing and vibratory feeding, which should be easily adapted to remote operation.

Vibration of the fuel rods during loading and compacting can be accomplished with equipment identical to that used in nonremote operation. Special fixtures would have to be provided to mount the fuel rod onto the vibrator and to precisely position the cladding under the microsphere feed tube, but no changes would be required in the type or model of vibrator used in a remote operation.

If future development shows that sintered fuel must be handled under inert atmosphere during loading, then considerable development is required to devise atmosphere containment methods suitable for remote operation and maintenance. Several options are available. These are: inert-atmosphere glove boxes within the cell, inert-atmosphere cell, a closed pipe system.

4.7 REFERENCES

1. J. J. Hauth, "Vibrational Compaction of Nuclear Fuels," pp. 253-76 in *Perspectives in Powder Metallurgy; Volume 2, Vibratory Compacting*, ed. by H. H. Hausner, Plenum Press, New York, 1967.
2. A. J. Flipot and P. Papeleux, "Single Cycle Fabrication of Sintered UO_2 Grains for Vibro-Compacted Fuel Elements," *Energ. Nucl. (Milan)* 17(1): 46-52 (1970).

3. W. C. Bell, "An Introduction to the Vibratory Compaction of Powders," pp. 74-77 in *Ceramic Fabrication Processes*, ed. by W. D. Kingery, Technology Press of MIT and John Wiley and Sons, Inc. (New York), Chapman and Hall, Ltd. (London), 1958.
4. H. E. White and S. F. Walton, "Particle Packing and Particle Shape," *J. Am. Ceram. Soc.* 20(5): 155-66 (1937).
5. R. K. McGeary, "Mechanical Packing of Spherical Particles," *J. Am. Ceram. Soc.* 44(10): 513-22 (1961).
6. A.E.R. Westman and H. R. Hugill, "The Packing of Particles," *J. Am. Ceram. Soc.* 13: 767-79 (1930).
7. J. M. Kerr et al., "Fabrication Development of Sol-Gel Particulate Fuels," pp. 342-57 in *Symposium on Sol-Gel Processes and Reactor Fuel Cycles*, CONF-700502 (May 1970).
8. A. L. Lotts, comp., *Fast Breeder Reactor Oxide Fuels Development — Final Report*, ORNL-4901 (November 1973).
9. D. R. Hudson, "Density and Packing in an Aggregate of Mixed Spheres," *J. Appl. Phys.* 20: 154-62 (1949).
10. J. J. Hauth, *Vibrationally Compacted Ceramic Fuels*, HW-67777 (January 1961).
11. J. E. Ayer and F. E. Soppet, "Vibratory Compaction: I, Compaction of Spherical Shapes," *J. Am. Ceram. Soc.* 48(4): 180-83 (1965).
12. J. E. Ayer, "The Packing of Fueled Spheres," pp. 310-22 in *Symposium on Sol-Gel Processes and Reactor Fuel Cycles*, CONF-700502 (May 1970).
13. P. F. Sens et al., "Fabrication of Vibrasol Fuel Rods," pp. 13-19 in *Nuclear Energy Maturity, Vol. 7, Nuclear Fuel Fabrication* (Proc. European Nucl. Conf. Paris, April 21-25, 1975), Pergamon, Oxford, 1976.
14. P. F. Sens and E.B.M. Majoor, "Irradiation Behavior of Vibrasol Fuel," pp. 152-60 in *Nuclear Energy Maturity, Vol. 3, Nuclear Fuel Performance and Management Part 1* (Proc. European Nucl. Conf. Paris, April 21-25, 1975), Pergamon, Oxford, 1976.
15. H.W.H. Lahr, "Fabrication, Properties, and Irradiation Behavior of U/Pu Particle Fuel for Light Water Reactors," *Nucl. Technol.* 31: 183-90 (November 1976).

16. H.W.H. Lahr, "Properties and Irradiation Behavior of Advanced Oxide Particle Fuel," pp. 153-64 in *Advanced LMFBR Fuels* (Proc. Topical Meeting, Oct. 10-13, 1977, Tucson, Ariz.), American Nuclear Society, La Grange Park, Ill., 1977.

17. R. W. Stratton and L. Smith, "The Irradiation Behaviour of Sphere-Pac Carbide Fuel," pp. 349-60 in *Advanced LMFBR Fuels* (Proc. Topical Meeting, Oct. 10-13, 1977, Tucson, Ariz.), American Nuclear Society, La Grange Park, Ill., 1977.

18. A. Calza-Bini et al., "Thermal Behaviour of Vibracompacted Sol-Gel Fuel Pin," pp. 247-89 in *Sol-Gel Processes for Fuel Fabrication*, IAEA-161, International Atomic Energy Agency, Vienna, 1974.

19. A. R. Olsen, J. D. Sease, R. B. Fitts, and A. L. Lotts, *Fabrication and Irradiation Testing of Sol-Gel Fuels at Oak Ridge National Laboratory*, ORNL/TM-1971 (September 1968).

20. F. G. Kitts, R. B. Fitts, and A. R. Olsen, "Sol-Gel Urania-Plutonia Microsphere Preparation and Fabrication Into Fuel Rods," pp. 195-210 in *Int. Symp. Plutonium Fuels Technol., Scottsdale, Ariz., 1967, Nucl. Met.* 13, ed. by K. E. Horton, R. E. Macherey, and R. J. Allio, American Institute of Mining, Metallurgical, and Petroleum Engineers, New York, 1968.

21. J. E. Ayer et al., *Nuclear-Fuel-Element Loading by Vibratory Compaction — Uranium-Plutonium Carbide Specimens for EBR-II Irradiation*, ANL-7075 (February 1966).

22. K. Bischoff, M. H. Lloyd, and H. Schumacher, "Sol-Gel Processes for Carbide Preparation," pp. 95-128 in *Sol-Gel Processes for Fuel Fabrication*, IAEA-161, International Atomic Energy Agency, Vienna, 1974.

23. D. D. Cannon, F. C. Davis, and J. D. Sease, "A Machine that will Remotely Fill and Compact Nuclear Fuel Tubes by Vibration," pp. 60-65 in *Proc. 14th Conf. Remote Systems Technology*, American Nuclear Society, Hinsdale, Ill., 1966.

24. Y. Hirose and S. Takeda, "Vibration Compacted UO_2 Fuel, I. Effects of Sinusoidal Vibration on Compacted Density," *J. Nucl. Sci. Technol.* 5(10): 529-37 (October 1968).

25. Y. Hirose and S. Takeda, "Vibration Compacted UO_2 Fuel, II. Effects of Wave Form on Compacted Density," *J. Nucl. Sci. Technol.* 6(5): 229-36 (May 1969).

26. Y. Hirose and S. Takeda, "Vibration Compacted UO_2 Fuel, III. Effects of Random Wave Vibration on Compacted Density," *J. Nucl. Sci. Technol.* 6(7): 351-58 (July 1969).

27. Y. Hirose and S. Takeda, "Vibration Compacted UO_2 Fuel, IV. Mechanical Response of Vibrating Fuel Rod," *J. Nucl. Sci. Technol.* 6(10): 557-66 (October 1969).

28. P. E. Evans and R. S. Millman, "The Vibratory Packing of Powders," pp. 237-51 in *Perspectives in Powder Metallurgy; Vol. 2, Vibratory Compacting*, ed. by H. H. Hausner, Plenum Press, New York, 1967.

29. K. Naruki, "Vibratory Compaction of Uranium Dioxide, I. Effect of Vibration Character," *J. Nucl. Sci. Technol.* 1(2): 58-67 (1964).

30. F. J. Furman, J. D. Sease, and J. T. Meador, *Microsphere Handling Techniques* ORNL/TM-2782 (March 1970).

31. P. A. Haas et al., *Development, Design, and Preliminary Operation of a Resin-Feed Processing Facility for Resin-Based HTGR Fuels*, ORNL/TM-6061 (January 1978).

32. A. R. Olsen, S. A. Rabin, J. W. Snider, W. S. Ernst, and J. W. Tackett, *Fabrication and Preirradiation Information on Vibratorily Compacted ThO_2-UO_2 Fuel Rods for Experiments ETR-I and MTR-III*, ORNL/TM-1322 (January 1966).

33. W. H. Pechin, R. A. Bradley, W. J. Lackey, and J. D. Sease, "Analysis of $(U,Pu)O_2$ Fuels at Oak Ridge National Laboratory," pp. 279-94 in *Analytical Methods in the Nuclear Fuel Cycle*, International Atomic Energy Agency, Vienna, 1972.

34. A. R. Olsen, *Preirradiation Data for ORNL Series II and B&W Oxide Fuel Tests in EBR-II*, ORNL-TM-3446 (November 1971), p. 52.

35. A. R. Olsen, "ETR Tests — Noninstrumented Series," *Fast Breeder Reactor Oxide Fuels Development — Final Report*, ORNL-4901 (November 1973), pp. 58-72.

36. B. E. Foster and S. D. Snyder, "Evaluation of Variables in the Measurement of Fuel Concentration Variations in Nuclear Fuel Rods," *Mater. Eval.* 26(2): 27-32 (1968).

37. J. D. Sease, A. L. Lotts, and F. C. Davis, *Thorium-Uranium-233 Oxide (Kilorod) Facility — Rod Fabrication Process and Equipment*, ORNL-3539 (1964).

38. R. N. Kubik and W. G. Pettus, "Experience with a Fuel Rod Enrichment Scanner," *Nucl. Mater. Manage.* 4(3): 194-201 (Fall 1975).

39. C. P. Ruiz, A. C. Duckart, and J. E. Menick, "Nuclear Fuel Rod Active Gamma Scan System, *Trans. Am. Nucl. Soc.* 16: 89-90 (June 1973).

40. P. Goris and A. W. DeMerschman, *FFTF Fuel Pin Nondestructive Assay Measurements*, HEDL-SA-950 (October 1975).

41. J. D. Jenkins, S. R. McNeany, and J. E. Rushton, *Conceptual Design of the Special Nuclear Material Nondestructive Assay and Accountability System for the HTGR Fuel Refabrication Pilot Plant*, ORNL/TM-4917 (July 1975).

42. J. E. Mack and D. R. Johnson, *Development of a Pneumatic Transfer System for HTGR Recycle Fuel Particles*, ORNL/TM-6169 (February 1978).

43. R. R. Suchomel and W. J. Lackey, *Device for Sampling HTGR Recycle Fuel Particles*, ORNL/TM-5739 (March 1977).

44. R. A. Bradley, W. H. Miller, Jr., and J. D. Sease, *Volumetric Dispenser for Small Particles from Plural Sources* US Pat. 3,926,344, December 16, 1975.

5. IRRADIATION PERFORMANCE

J. A. Horak

For sphere-pac fuels to be considered as a viable alternative to the current pellet fuels for fast breeder reactors, they must exhibit irradiation performance at least comparable to that of pellet fuels under breeder reactor operating conditions. This section presents the information obtained to date on breeder sphere-pac oxide fuels irradiated in fast and thermal neutron reactors. In addition, irradiation of sphere-pac thermal reactor fuels in thermal neutron reactors is included where the information obtained is meaningful to the breeder fuels program.

5.1 FAST REACTOR IRRADIATIONS OF $(U,Pu)O_2$

The most valuable information on the performance of sphere-pac oxide fuels is obtained by irradiation testing in a reactor where nearly all the fissions are produced in plutonium by fast neutrons. This produces the correct power density in the fuel and the correct temperature, burnup, and fission product profile across the fuel rod. It also produces the correct plutonium distribution; the correct oxygen activity coefficient for oxygen interaction with uranium, plutonium, fission products, and cladding; and the appropriate fast neutron irradiation effects in the cladding. A total of 23 sphere-pac rods have been irradiated in two EBR-II subassemblies. Unfortunately, only four of these rods have received postirradiation examination to date.

5.1.1 Steady-State Tests

In the first irradiation of sphere-pac oxide fuels in EBR-II, five fuel rods of $U_{0.8}Pu_{0.2}O_{1.98}$ were irradiated at peak linear heat ratings of 46 kW/m (14 kW/ft) to between 5 and 6% burnup.[1] Calculated peak inside cladding surface temperatures were from 570 to 590°C. After this irradiation two rods were removed for postirradiation examination and the remaining three rods were reinserted in EBR-II and irradiated to 11.8 at. % burnup at the same linear power and cladding temperature. To date these three rods have not been examined.[2]

The two rods examined at 5% b.u. (burnup measured by ^{148}Nd determination) exhibited irradiation behavior as shown in Fig. 5.1. The figure shows the transverse cross sections near the bottom, center, and top of fuel rod S-1-E after the aforementioned irradiation. For sphere-pac oxide fuel rods the region of the fuel that is operated at temperatures sufficiently high for restructuring to occur develops the same structure as pellet fuel rods. That is, there is an axial central void, which increases in diameter with increased linear power and with decreased fuel smear density. Radial cracks emanate from the central void; these cracks terminate at the outer edge of the restructured region in the sphere-pac fuel.

The nonrestructured annulus that is present in sphere-pac fuel rods should provide two benefits to the irradiation performance. The first is a lower stress that the fuel exerts on the cladding than in pellet fuel rods. The second is that the annulus of microspheres reduces the fission product transport to the cladding since cracks in the fuel do not extend to the cladding.

The lower stress results from the ability of the nonrestructured spheres in the annulus to move a small distance vertically under relatively low stresses. Hence, when the fuel tends to expand as the reactor power level increases, the annular fuel spheres move vertically to relieve the stress before it reaches levels that would strain the cladding.

The nonrestructured annulus also blocks the direct path for fission products and/or oxygen transport to the cladding at radial cracks, and of course direct paths at pellet-pellet interfaces are absent from the sphere-pac fuel. Since the radial cracks end at the end of the restructured region in sphere-pac fuels, the fission products have to traverse the annulus of spheres by some type of random-walk process. Therefore, the mean free path to the inner surface of the cladding from the end of the radial crack is considerably longer than the direct straight line distance to the cladding. This will reduce fission product transport to the cladding. This combined with the decrease in high local stresses in the cladding due to hourglassing and radial cracks in pellet fuel rods should improve fuel element performance and decrease cladding failures.

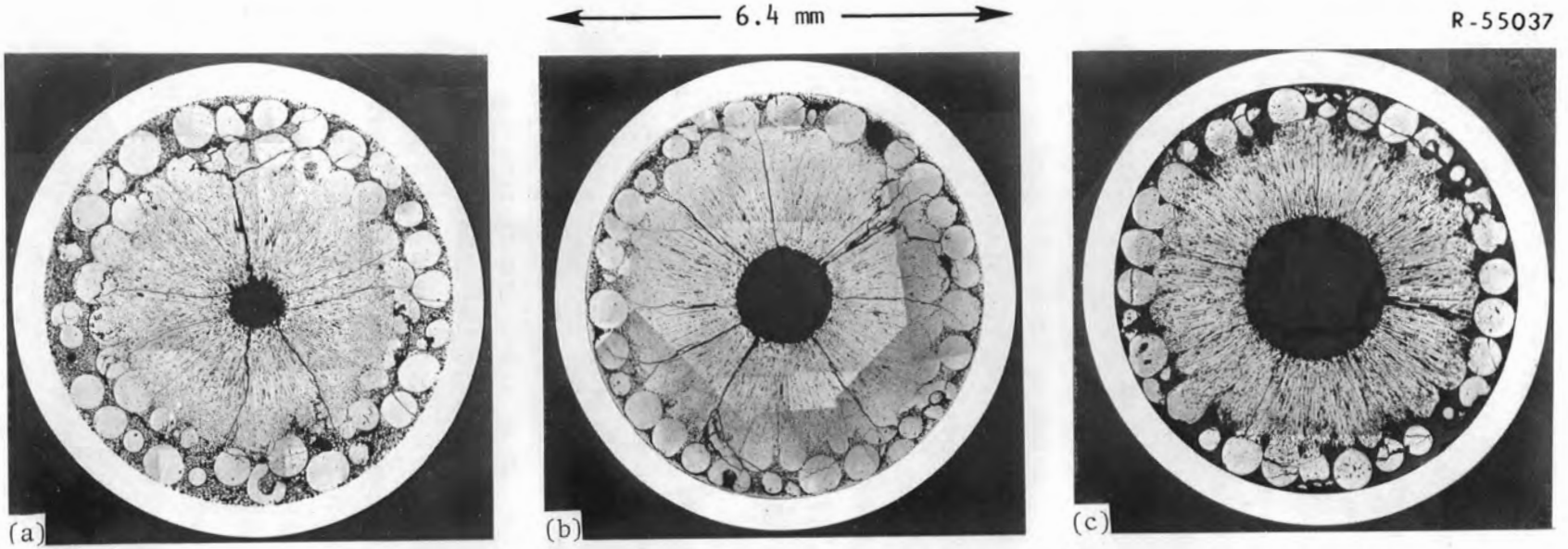

Fig. 5.1. Transverse Cross Section of Sphere-Pac Fuel Rod S-1-E After Irradiation in EBR-II to a Peak Burnup of 5.74 at. % at 46 kW/m and an Average Cladding Temperature of 570°C. Note the annulus of nonrestructured spheres at the periphery of the fuel and absence of fuel and/or fission product interaction with the type 316 stainless steel cladding. The rod had a smear density of 82%, which was obtained with two sphere sizes of 460 ± 30 μm diam infiltrated with spheres <25 μm diam. (a) Bottom, (b) center, and (c) top of fuel rod.

Figure 5.2 provides evidence in support of this hypothesis. Both views show the radial cracks terminating at the boundary between the restructured and nonrestructured fuel, and the circumferential crack also is in this same region. The as-polished micrograph shows some material on the inner wall of the cladding. This material was not retained during etching, as shown in the lower photograph. Note the total absence of interaction of fission products, fuel, and/or oxygen with the type 316 stainless steel cladding.

The oxide fuels irradiated in the second EBR-II experiment are contained in Table 5.1. This experiment is extremely important since pellet, sphere-pac, and vi-pac fuel were all irradiated together in the same experimental subassembly under the same power and burnup conditions, and half the fuel rods contained sphere-pac fuel. For this experiment 19 of the fuel rods were fabricated by ORNL and 18 by Babcock and Wilcox (B&W).[3,4] In addition, ORNL fabricated one additional rod and B&W fabricated 16 additional rods. The additional rods were provided to replace those removed for interim examination at selected burnup levels before the end-of-life target burnup of 12% was achieved.

Subassembly X112 was removed from the reactor for interim nondestructive examination of the 37 fuel rods after they had attained about 4% burnup of the heavy metal atoms. In addition, four fuel rods were removed for destructive examination, which was conducted[5] at ANL. To attempt to determine the relative irradiation performance of pellet, sphere-pac, and vi-pac oxide fuel, two sphere-pac rods, one pellet fuel rod, and one vi-pac fuel rod were removed.

The nondestructive examination[5] of the 37 fuel rods, using neutron radiography for fuel column length changes and visual inspection for discoloration and element bowing, did not reveal any major or unexpected differences among the 37 rods.

Diametral profilometry measurements on the four fuel rods removed for examination did not reveal any significant difference in diameter changes due to the three different fuel forms. The gamma ray scans for immobile fission products such as ^{106}Rh indicated uniformity over the fuel columns for all four rods. Also there was a large ^{106}Rh gamma ray

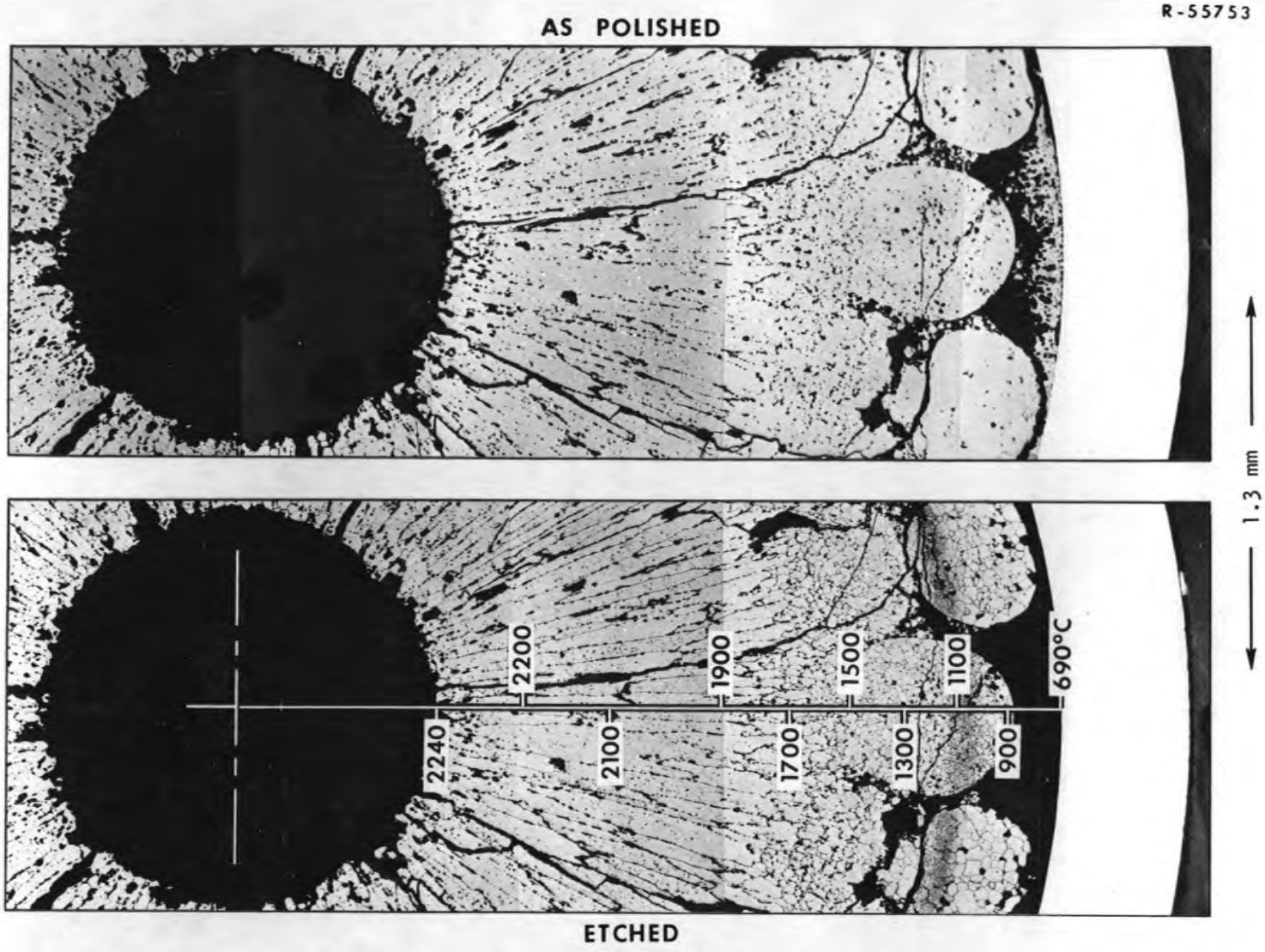

Fig. 5.2. Enlarged View of Transverse Microstructure of Fuel Pin S-1-E at the Region of Maximum Linear Power, 46 kW/m (14 kW/ft). The top figure is as polished, and the bottom figure is after etching. In addition a temperature scale has been superimposed in the bottom figure.

Table 5.1. Fuels in the Second EBR-II Test of Sphere-Pac Fuel, Experimental Subassembly X112

Fabrication Form	Fuel Production Process	Oxygen-to-Metal Ratio	Number of test pins at each design smear density (% of theoretical)				
			80	83	85	90	Total
Sphere-Pac	Sol-gel	1.98	4	4	6		14
Sphere-Pac	Sol-gel	1.94	2	1	1		4
Pellet	Sol-gel	1.98			2	2	4
Pellet	Coprecipitation	1.98		5			5
Pellet	Sol-gel	1.94	2		1		3
Vi-Pac	Coprecipitation	1.98	6	1			7
Totals			14	11	10	2	37

peak in the Fiberfrax (a fibrous pad of Al_2O_3 and SiO_2) above the fuel columns.[5] An insulator pellet of UO_2 or ThO_2 was at the end of each of the fuel columns. Therefore, the ^{106}Rh traveled through and/or around the insulator pellets to get into the Fiberfrax. Although the ^{106}Rh profile along each fuel rod was uniform, the magnitude of the measured ^{106}Rh activity for the sphere-pac and vi-pac fuel rods was at least about 50% greater than the activity for the pellet fuel rod. No explanation has been suggested for this observation and no significance has been associated with it.[5] Also, only one rod provides very poor statistics.

However, for the sphere-pac and vi-pac fuels a large concentration of ^{137}Cs was found in the Fiberfrax. This indicates that aluminum silicate is an effective getter for the volatile cesium and that volatile fission products such as cesium can travel up the fuel column in rods containing particulate fuels. The pellet rod had a small concentration of cesium beyond the insulator pellets at both the top and bottom of the fuel rod.

Eddy-current inspection of the four fuel rods was performed to detect the possible presence of fission product attack of the cladding.[6] Only the fuel rod containing the pellet fuel exhibited a signal that

would indicate any effects on the cladding.[6] Metallographic examination of the midplane sections of each fuel rod revealed that the eddy-current signals in the pellet fuel rod were due to numerous small indentations on the inside surface of the cladding.[7] Initially, these indentationss were attributed to mechanical interaction between the fuel and the cladding. That misconception has been disproven, and the indentations have been correctly associated with the fabrication of the tubing that was used as the cladding for these fuel rods.[8] Similar dimples were found in sphere-pac pins and were also attributed to fabrication of the tubing.

5.1.2 Transient Testing

To determine the performance of sphere-pac fuel rods under transient operating conditions and under overpower conditions two capsules containing unirradiated sphere-pac fuel and unirradiated pellet fuel were subject to transient and overpower testing in TREAT.[9] Figures 5.3 and 5.4 show the appearance of the fuel after testing.[4,10] As expected, considerable fuel melting occurred. Both the pellet and sphere-pac fuels performed admirably.

The steady-state and transient fast reactor irradiations conducted to date indicate that sphere-pac oxide fuel should behave similarly to pellet oxide under fast breeder reactor operating conditions.

5.2 THERMAL REACTOR IRRADIATIONS OF $(U,Pu)O_2$

There have been several irradiations of fast reactor $(U,Pu)O_2$ fuel rods in thermal reactors. The particular advantage of the thermal reactor irradiations is the capability of performing irradiations that are instrumented for measurement and control of temperature and gas pressure. The temperature measurements are extremely valuable in determining restructuring temperatures and kinetics and effective gap conductances for pellet and sphere-pac oxide fuels. The gas pressure measurements are used to determine fission gas release rates and total fission gas release during irradiation of the two fuel forms and to measure gap conductance as a function of fission gas release. Combining thermocouples and pressure transducers provides desired measurements

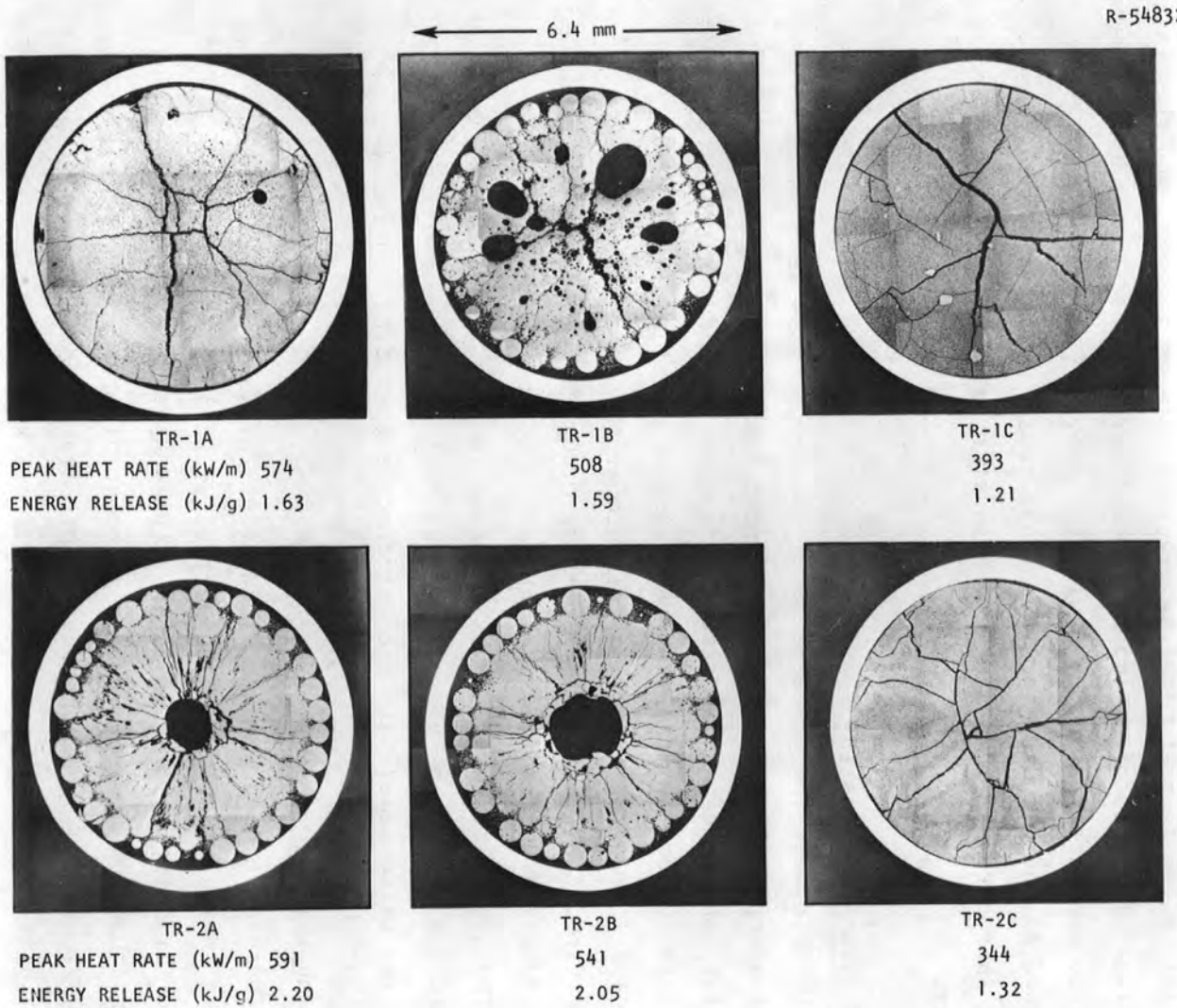

Fig. 5.3. Traverse Cross Sections at the Axial Midplane of $U_{0.8}Pu_{0.2}O_{1.98}$ Pellet and Sphere-Pac Fuel Rods After Transient Irradiations in TREAT. Fuel rods TR-1A, TR-1C and TR-2C are pellet fuel rods with smear densities of 89%, 80% and 80%, respectively, and, TR-1B, TR-2A and TR-2B are sphere-pac fuel with smear densities of 81%, 82% and 81%, respectively.

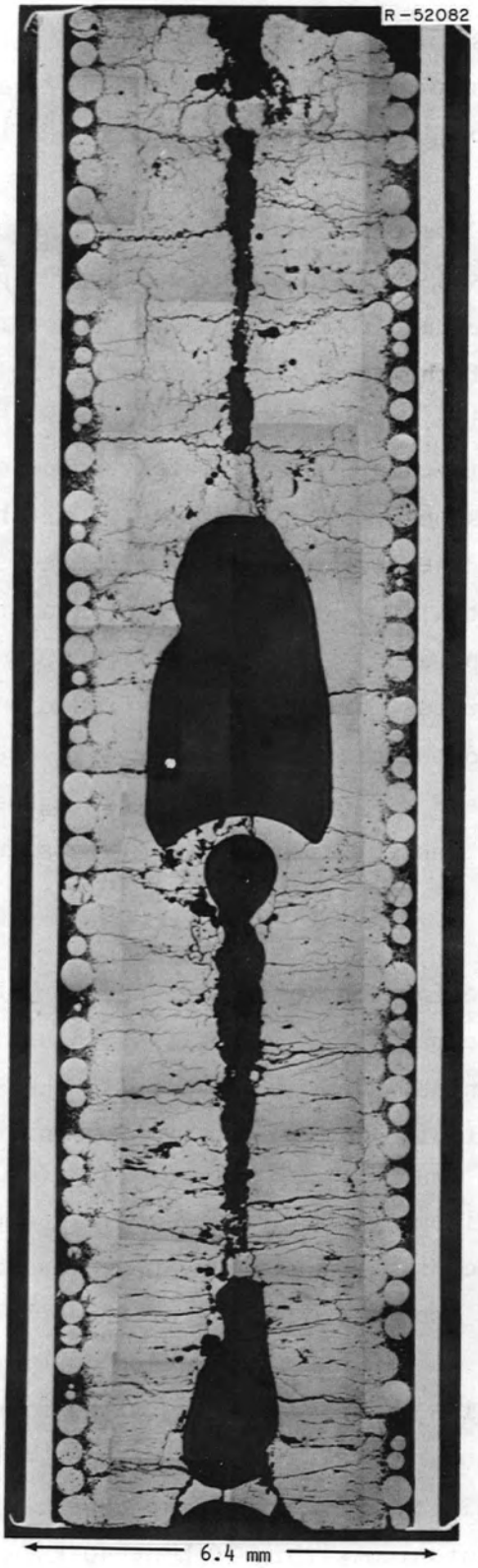

Fig. 5.4. Fuel Rod TR-2B After Transient Irradiation in TREAT that Produced About 50% Melting of the Fuel.

on fission gas release rates and total gas release as functions of linear heat rating and fuel thermal conductivity as a function of fission product and oxygen buildup in the fuel, which are functions of burnup.

The information presented in this section should be used only as a "*relative*" comparison between pellet and sphere-pac fuel. Absolute comparisons cannot be made for fast breeder reactor applications with these data because of the large differences in the radial fission rate profiles. For irradiations in a thermal reactor the surface and near-surface fission densities are approximately an order of magnitude greater than the fission density at midradius of the fuel rod; in a fast breeder reactor the fission density from the surface to the center of the fuel is essentially uniform, not including the effect of plutonium migrating up the temperature gradient in $(U,Pu)O_2$. The high surface fission density liberates more oxygen and produces more fission products in close proximity to the cladding. This would overemphasize interaction of fission products and oxygen with the claddings compared with that produced during fast reactor irradiation of this fuel.

5.2.1 Restructuring

To assess the performance of sphere-pac fast breeder reactor oxide fuel, 19 sphere-pac and 1 pellet fuel rods of UO_2 and $(U,Pu)O_2$ were irradiated in uninstrumented capsules in the ETR. The compositions of sphere-pac fuel studied[11] were $UO_{2.02}$ (20% enriched), $^{235}U_{0.80}Pu_{0.20}O_{2.00}$, and $^{238}U_{0.80}Pu_{0.20}O_{1.97}$. Table 5.2 and Fig. 5.5 show the effect of linear power density at very low burnups on these fuels. Since restructuring of the fuel proceeds exponentially with temperature, most of the restructuring of the spheres occurs early in the life of the fuel.[12] This has also been observed by Lahr,[13,14] who observed the initiation of restructuring within 2 min for $(U,Pu)O_2$ operated at linear power levels from 63.0 to 69.4 kW/m (19.2 to 21.2 kW/ft). In addition, Cervellati and co-workers[15] observed complete homogenization of plutonium within 10 h at 40 kW/m (12 kW/ft) in fuel rods of $U_{0.98}Pu_{0.02}O_2$. The results shown in Fig. 5.5 and those of Cervellati et al. illustrate that restructuring occurs very early in

Table 5.2. Low-Burnup Irradiation Conditions of Sphere-Pac Fuel Rods

Rod[a]	Composition	Maximum Power (kW/m)	Burnup (at. %)	Fission Gas Release (%)	Smear Density (%)	Maximum Cladding Temperature (°C)
A	$U_{0.85}Pu_{0.15}O_{1.97}$	34.5	0.6	4	80	260
B	$U_{0.85}Pu_{0.15}O_{1.97}$	44.5	0.7	27	81	320
C	$U_{0.80}Pu_{0.20}O_{2.00}$	114	1.4	24	76	730

[a]Transverse cross sections shown in Fig. 5.5.

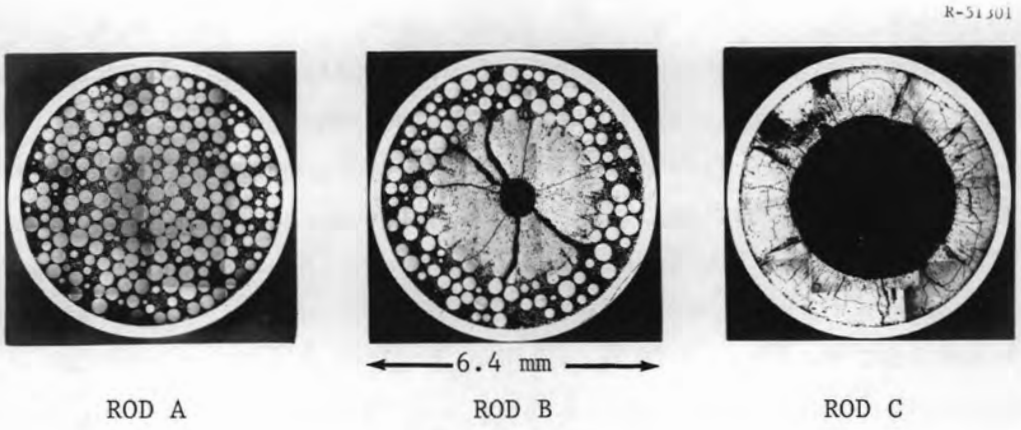

Fig. 5.5. Transverse Cross Sections of Sphere-Pac Fuel Rods After Irradiation at Low Burnup. Note that even at the extremely high linear power of 114 kW/m (Table 5.2) there is a small annulus of nonrestructured spheres between the restructured fuel and the cladding.

the life of the fuel element. This early restructuring in sphere-pac and pellet $(U,Pu)O_2$ FBR fuels has also been confirmed[16] by thermocoupled irradiations in the ORR.

Table 5.3 and Fig. 5.6 show the transverse microstructures for two sphere-pac fuel rods and one pellet fuel rod irradiated in the ETR.[17,18] For the urania-plutonia sphere-pac fuel operated at 65.5 kW/m (20 kW/ft), an annulus of nonrestructured spheres is adjacent to the cladding. For the hyperstoichiometric urania sphere-pac fuel operated at 72.0 kW/m (22 kW/ft), the annulus is much smaller, and most of the radial cracks are terminated at the inner side of the annulus. For the stoichiometric

Table 5.3. Conditions of Irradiation of Sphere-Pac and Pellet Fuels to Higher Burnups

Rod[a]	Composition	Maximum Power (kW/m)	Burnup (at. %)	Fission Gas Release (%)	Smear Density (%)	Maximum Cladding Temperature (°C)
A	$U_{0.85}Pu_{0.15}O_{1.97}$	65.5	6.4	44	82	460
B	$UO_{2.02}$	72.0	5.5	44	73	470
C[b]	$UO_{2.00}$	85.0	4.9	47	84	540

[a]Transverse cross sections shown in Fig. 5.6.

[b]Pellet fuel.

urania pellet fuel operated at 85.0 kW/m (26 kW/ft), the radial cracks propagate to the cladding. Figure 5.6 illustrates that the central void diameter is larger for high linear power and low smear density. Because of the differences in fissile atom density and composition of the fuel shown in Fig. 5.6, only qualitative comparisons can be made.

Only one of the ETR irradiations of urania-plutonia sphere-pac fuel was taken to high burnup. Burnups of 8.6 and 11.3% were attained at linear heat ratings of 29.0 and 33.0 kW/m (8.8 and 10.1 kW/ft), respectively.[19] For these fuels there was an annulus of particles at least 0.6 mm thick between the restructured fuel and the cladding. For the high-burnup $U_{0.85}Pu_{0.15}O_{1.97}$ the fission gas released ranged from 61 to 89%; for $UO_{2.02}$ irradiated with the urania-plutonia at 36.5 kW/m (11.2 kW/ft) to 13.8% burnup the fission gas release was 96%.

To determine restructuring kinetics and to determine effective gap conductances for sphere-pac fuel, three irradiation capsules containing the six fuel rods described in Table 5.4 were irradiated in highly instrumented capsules in the ORR.[4] At the longitudinal center of each fuel rod, 12 thermocouples were used to measure fuel central temperature, cladding temperature at three locations, and the radial heat flow from the center of the fuel rod to the outer capsule wall. The heat flow measurement used four thermocouples in the capsule wall. Cross sections of two sphere-pac fuel rods and one pellet fuel rod are shown in Fig. 5.7.

The sphere-pac fuel rod in SG-2 (rod 3) that operated at a central temperature of 1500°C has not restructured significantly. Some

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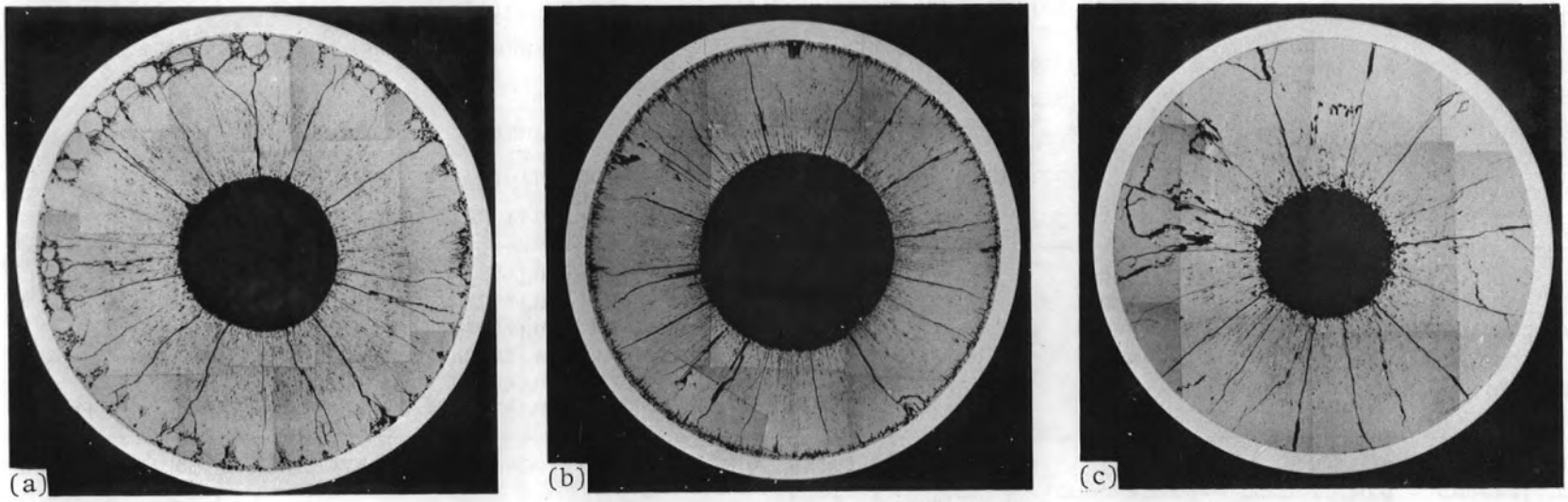

sphere-pac
Rod A

sphere-pac
Rod B

pellet
Rod C

Fig. 5.6. Transverse Cross Sections of Sphere-Pac and Pellet Fuel Rods Operated at High Linear Powers to Burnups of 4.9 To 6.4%. (See Table 5.3.)

Table 5.4. Fuel Parameters and Operating Conditions for Instrumented ORR Irradiations of $(U,Pu)O_2$

Capsule	Fuel Rod[a]	Fuel Parameters: Form	Fuel Parameters: Composition	Fuel Parameters: Smear[b] density (% of theoretical)	Operating Conditions: Total Time (h)	Operating Conditions: Maximum[c] Temperature (°C)	Operating Conditions: Time at maximum temperature (h)	Operating Conditions: Maximum heat generation (kW/m)
SG-1	1	Sphere-Pac	$U_{0.85}Pu_{0.15}O_{1.99}$	81	1200	>1800	*d*	49
	2	Sphere-Pac	$U_{0.85}Pu_{0.15}O_{1.99}$	81	1200	*e*	*d*	49
SG-2	3	Sphere-Pac	$U_{0.80}Pu_{0.20}O_{1.99}$	81	1763	1500	72	39.5
	4	Sphere-Pac	$U_{0.80}Pu_{0.20}O_{1.99}$	82	1763	*e*	72	39.5
SG-3	5	Sphere-Pac	$U_{0.80}Pu_{0.20}O_{1.98}$	82	2180	2000	35	52.5
	6	Pellet[f]	$U_{0.80}Pu_{0.20}O_{1.98}$	82	2180	2000	120	47.5

[a] Clad with titanium-modified type 304 stainless steel 9.52 mm OD by 0.38 mm wall (3.75 by 0.015 in.).

[b] Fuel density between central thermocouple and cladding inner surface.

[c] Maximum fuel central temperature.

[d] Not determined.

[e] Not recorded, no central thermocouple.

[f] Pellet was 83.5% dense, pellet-cladding radial gap was 36 mm, pellet OD = 8.694 mm.

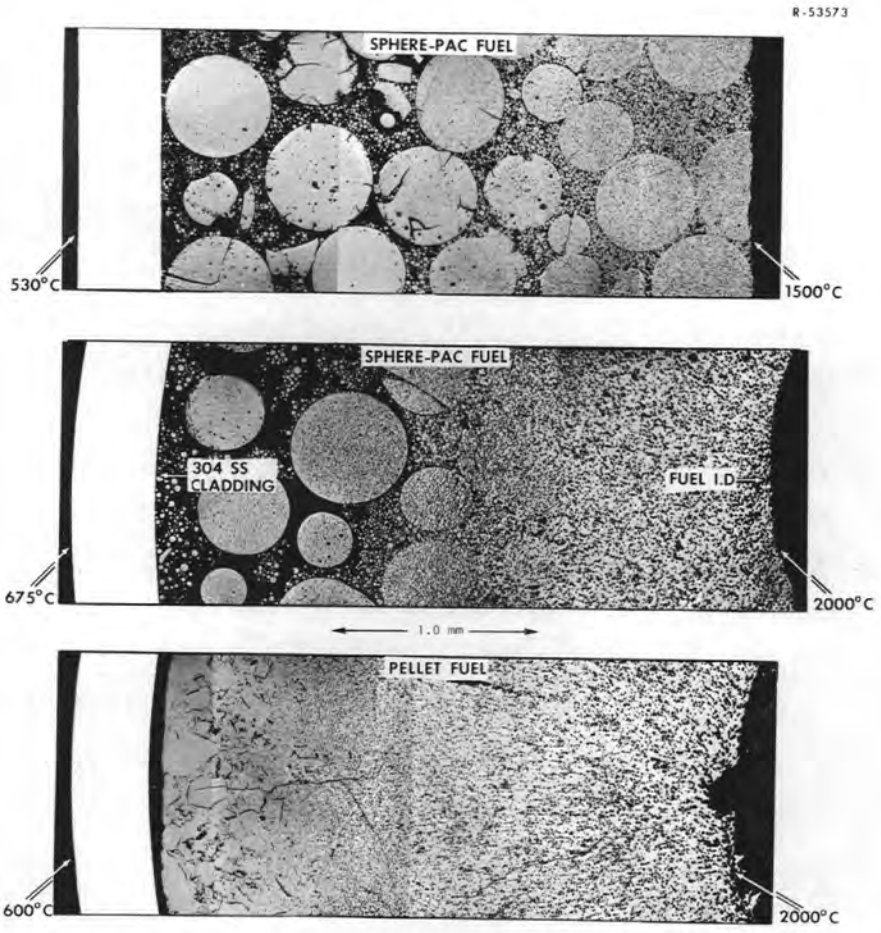

Fig. 5.7. Cross Sections of Sphere-Pac and Pellet Fuels Irradiated to Determine Restructuring Kinetics. Irradiation conditions and other information are given in Table 5.4. Top, rod 3; middle, rod 5; bottom, rod 6.

restructuring has begun in the central part of the fuel. In the cooler outer half of the fuel some of the particles were lost during ceramographic preparation; this also occurred in the outer region of the sphere-pac fuel rod in SG-3. The higher maximum temperature of 2000°C experienced in SG-3 resulted in restructuring in the hotter portion of the fuel. Considerable restructuring occurred in the pellet fuel that also operated at a maximum central temperature of 2000°C. Note that a linear power of only 47.5 kW/m produced the 2000°C central temperature in the pellet fuel, while a power of 52.5 kW/m was required to produce the 2000°C central temperature in the sphere-pac fuel. This resulted in the 75°C higher outer cladding temperature in the sphere-pac fuel rod than in the pellet fuel rod.

5.2.2 Gap Conductance

The use of the 12 thermocouples at the longitudinal center of each fuel rod provided the measurements required to determine the gap conductance between the outer fuel surface and inner cladding surface for the sphere-pac fuel and the pellet fuel of identical chemical composition. These measurements[4] revealed that the gap conductance for $U_{0.80}Pu_{0.20}O_{1.99}$ in pellet fuel rods is 7.3 kW/m^2 °C and in sphere-pac fuel rods it is 19.3 kW/m^2 °C. Figure 5.8 shows the transverse fuel temperature profile for the sphere-pac and pellet fuel rods irradiated in ORR capsule SG-3 for central temperatures of 2000°C. Because of the lower gap conductance for the pellet fuel the surface temperature of the pellet fuel is higher than that of the sphere-pac fuel.

5.2.3 Fuel-Cladding Interaction

Figure 5.9 shows the longitudinal fuel-cladding interfaces for the portions of the sphere-pac and pellet fuel rods that operated[4,20] at the same cladding inner surface temperature during irradiation in ORR capsule SG-3. No detectable interaction occurred between the fuel, oxygen, fission products, and cladding in the sphere-pac fuel rod. However, interaction to a significant depth of the cladding occurred in the pellet fuel rod, and there is a significant deposit on the cladding in this rod. The fuel-cladding interaction is at the interface between two pellets and/or where radial cracks meet the cladding. The sphere-pac rod has no such interfaces.

In addition to uninstrumented ETR irradiations of sphere-pac and pellet urania-plutonia fast breeder reactor fuels, two instrumented capsules, each containing four fuel rods of urania-plutonia fast breeder reactor fuels were irradiated in the ETR. Each fuel rod contained nine thermocouples for temperature measurements and pressure transducers for fission gas release measurements. The pertinent information on the fuel operating conditions and on performance is contained in Table 5.5.

The most important information obtained in this irradiation is contained in Figs. 5.10 and 5.11. For the pellet rod shown in Fig. 5.10 melting has apparently occurred in the central region of the fuel. The

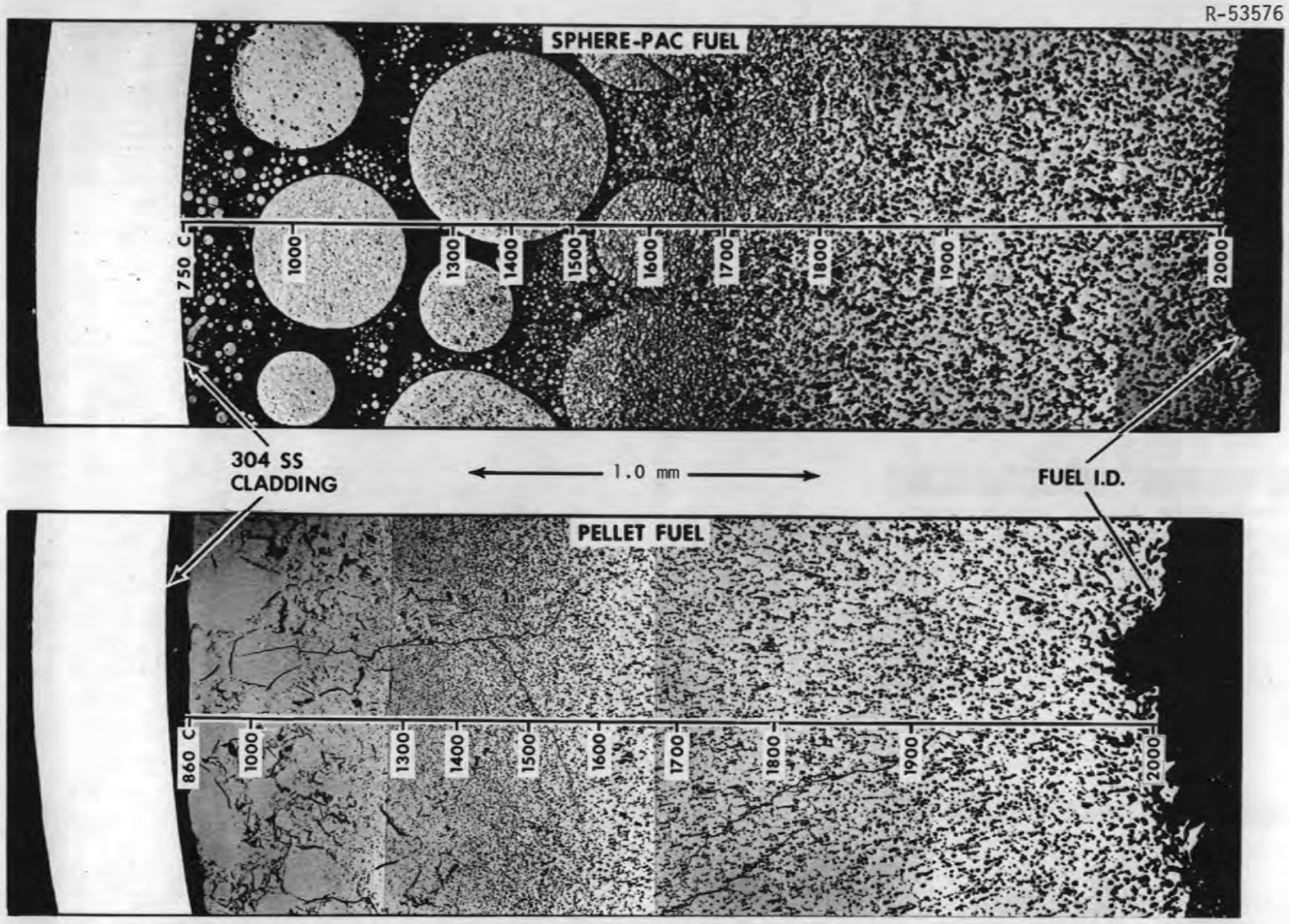

Fig. 5.8. Transverse Temperature Profile for $U_{0.80}Pu_{0.20}O_{1.98}$ Sphere-Pac and Pellet Fuel Irradiated in Instrumented ORR Capsule SG-3. The temperatures on the extreme left are the fuel surface temperatures.

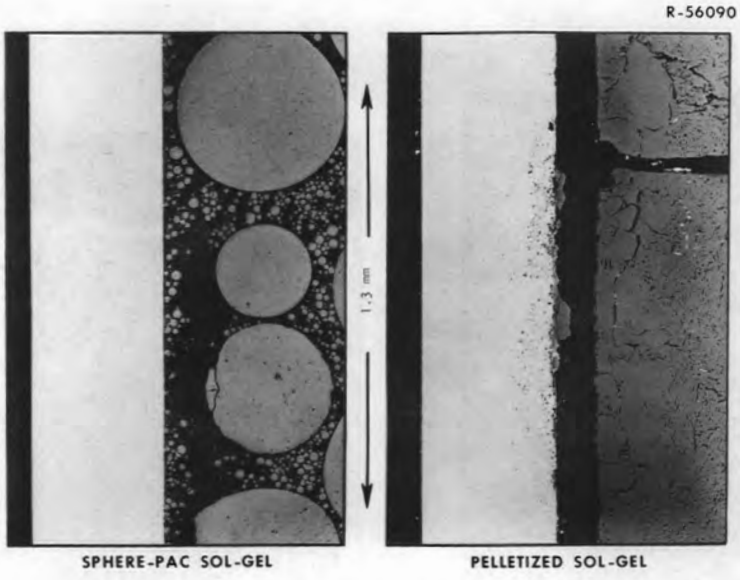

Fig. 5.9. Absence of Fuel-Cladding Chemical Interaction for Sphere-Pac $U_{0.80}Pu_{0.20}O_{1.98}$ Fuel Irradiated in ORR Capsule SG-3. Cladding inner surface was above 650°C for 430 h in sphere-pac rod (1eft) and for 265 h in pellet rod (right).

Table 5.5. Fuel Rod Parameters for Instrumented ETR Capsule 121 Containing $U_{0.80}Pu_{0.20}O_{1.98}$

Fuel Rod	Fuel Form	Smear Density (%)	Peak Power (kW/m)	Peak Inner Cladding Temperature (°C)	Peak Burnup (%)	Fission Gas Release (%)
121-1	pellet	81.0	51.5	575	9.3	81.2
121-2	pellet	81.2	57	625	9.8	99.3
121-3	sphere-pac	83.9	54	605	9.5	86.3
121-4	sphere-pac	85.5	39.5	460	6.7	74.9

small white spots in the columnar grain region and in the equiaxed grain region are unoxidized metallic fission products. The fuel and cladding have interacted chemically. Figure 5.11 shows no apparent melting at the center of the sphere-pac fuel and no detectable chemical interaction between the fuel and cladding. Rod 121-3 has a very large central void, and restructuring appears to have occurred over the full fuel radius. The circumferential cool-down crack in Rod 121-4 follows the outline of

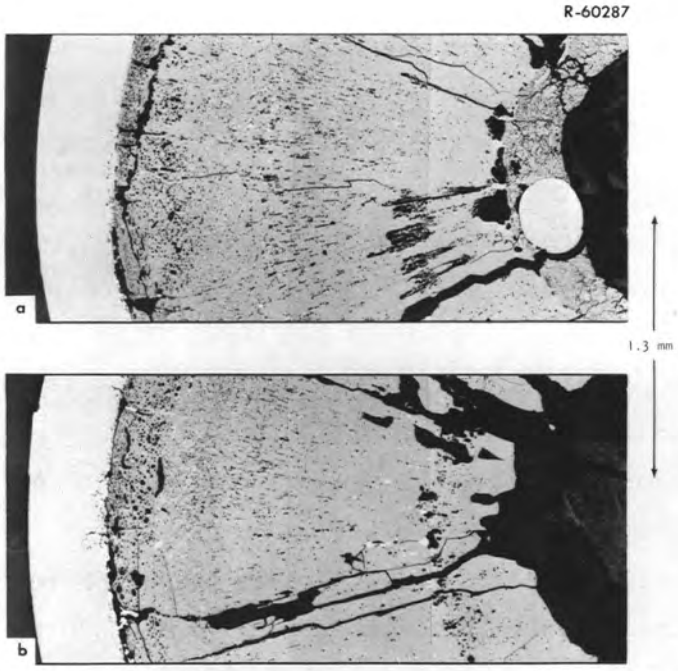

Fig. 5.10. Transverse Cross Section Through Two Pellet Rods Irradiated in ETR Instrumented Capsule 121. Melting or near melting has occurred near the center, and the fuel and cladding have interacted chemically. (a) 121-1 (b) 121-2.

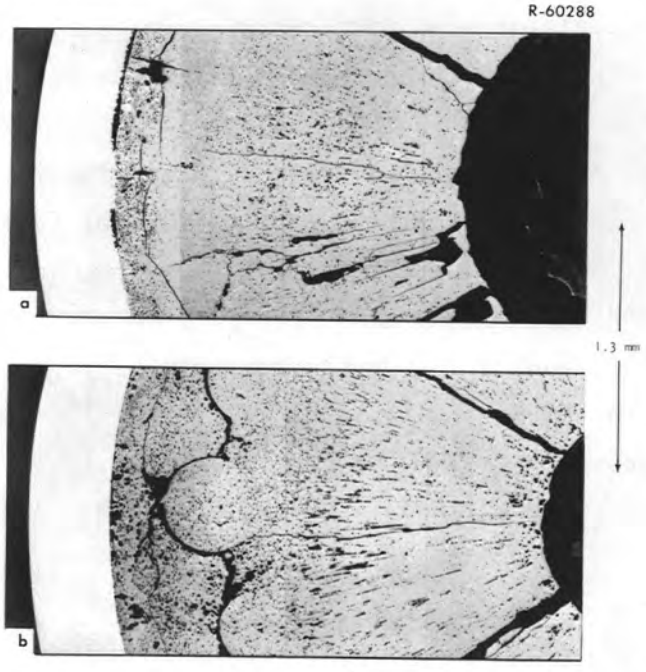

Fig. 5.11. Transverse Cross Section Through Two Sphere-Pac Fuel Rods Irradiated in ETR Instrumented Capsule 121. Large radial cracks terminate at the outer edge of the restructured region. No detectable chemical interaction has occurred between the fuel and the cladding. (a) 121-3 (b) 121-4.

the partially restructured spheres. The large radial cracks do not propagate to the cladding but are terminated at the outer edge of the restructured region.

In addition, in the work for the German fast breeder reactor fuel development program at Karlsruhe, eight fuel rods of $(U,Pu)O_2$ clad with alloy 1.4988* have been irradiated in the helium-cooled loop of the FR-2 reactor at Karlsruhe in capsules containing thermocouples.[13,14] The plutonium contents ranged from 9.29 to 21.5%. They used two size fractions: 1000 to 1000-μm particles of PuO_2 and 125 to 200-μm particles of UO_2 to obtain smear densities from 40 to 81%. Irradiation times ranged from 2 min to 10 h at average linear powers ranging from 63.0 to 69.4 kW/m (19.2 to 21.2 kW/ft). The principal information obtained from these irradiations was that restructuring begins in both pellet and sphere-pac within 2 min at the linear power levels used. Average cladding temperatures at the center of the fuel rod ranged from 280 to 392°C. Although the fissile content of the fuel is in the range of interest for fast breeder reactors, these cladding temperatures are too low.

A second group of three UO_2 (6.08% ^{235}U) fuel rods with Zircaloy-2 cladding was irradiated in the helium-cooled loop in the HFR at Petten.[13] These contained two particle sizes of 6% enriched UO_2 with a smear density of 77 ± 1%. The rods were irradiated at average linear powers ranging from 51.5 to 59.0 kW/m (15.7 to 18.0 kW/ft) to burnups of 1.8 to 3.1 MWd/kg heavy metal. Average cladding temperatures were 130, 140, and 230°C. These temperatures are too low for fast breeder applications. No deleterious effects of sphere-pac fuels were found in these irradiations.

In the Italian fuel development program 16 sphere-pac fuel rods were irradiated in the RS-1 swimming pool reactor.[15] Two fuel rods of solid solution $U_{0.982}Pu_{0.018}O_2$† with a smear density of 80% and clad with Zircaloy-2 were irradiated in the Halden HBWR. After irradiation

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*Alloy 1.4988 is similar to AISI type 316 stainless steel with a nominal composition of 67 Fe, 16 Cr, 14 Ni, 1-3 Mo, 1.1 Mn, 7 V (wt %) and low limits on impurities C, Si, P, S, Co, Cu, N, Ta, and Nb.

†In the original conference proceedings there is a mistake in Table 1 on p. 377, indicating the fuel to be $U_{0.982}Pu_{0.18}O_2$ instead of the above composition.

at a maximum linear power of 52.0 kW/m (15.8 kW/ft) to 0.5 MWd/kg heavy metal, the rods were removed from the reactor because of an apparent fission product leak from the experimental assembly. No cladding breach of the assembly could be detected during postirradiation examination. At this low burnup the maximum diametral strain was 1.8%, maximum ovality was 0.7%, and no detectable increase in the fuel column or fuel rod length was observed. The average temperature of the Zircaloy-2 during the 50-d irradiation was 250°C. The restructuring profile and central void profile for the two fuel rods are shown in Fig. 5.12. Figure 5.12 was prepared from radial cross section ceramographs of the fuel rods at many locations along the rod. The central void profile offers direct evidence that particles do not fall down the central void from the top of the fuel column during irradiation. The central void is closed at the top and bottom of the fuel column; the particles that are observed in the central void during postirradiation examination are transported there during ceramographic preparation of the fuel rod.

Restructuring was observed within approximately the outer 1 mm of the fuel. This is consistent with the ORNL results reported earlier and results from Petten[21] (Sect. 5.5.1.).
For the conditions used restructuring occurred in fuel that operated above 38.0 kW/m (11.6 kW/ft).

In the regions of highest linear power the Zircaloy cladding was severely corroded and hydrided.[15] This phenomenon has been observed in other fuel rods where poor hydrogen and moisture control existed during fabrication of the fuel and during loading of the helium into the fuel rod.[8,21,22]

A second experiment in the Italian sphere-pac program contained a fully instrumented assembly containing eight fuel rods of overall composition $U_{0.98}Pu_{0.02}O_2$. The rods contained 500 ± 20-μm-diam UO_2 spheres mixed with 53 ± 8-μm PuO_2 spheres to produce a smear density of 82%. The original fuel was not uniform in PuO_2 content along the fuel columns; however, the thermocouples included in the experiment indicated complete homogenization of the PuO_2 content in less than 10 h of operation at fuel central temperatures above 1400°C.[15]

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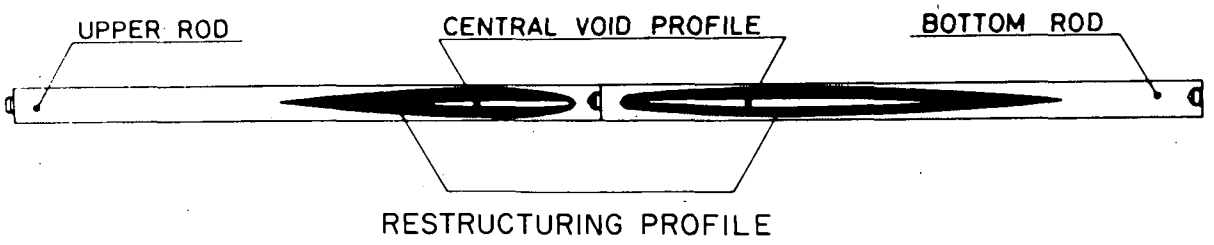

Fig. 5.12. Central Void and Restructuring Profiles in Two Fuel Rods of $U_{0.982}Pu_{0.018}O_2$ Irradiated in the Halden Reactor at a Maximum Power of 52.0 kW/m to 0.5 MWd/kg heavy metal. The reactor control rods were inserted from the left in the figure, producing a shorter restructured zone in the upper fuel rods. From A. Cervellati et al., pp. 324-413, CONF-700502.

5.3 FAST-REACTOR IRRADIATION OF (U,Pu)C

The Swiss have irradiated one sphere-pac $U_{0.85}Pu_{0.15}C$ fuel rod in the Dounreay Fast Reactor (DFR).[23,24] Two size fractions 600 to 800 μm and 40 to 60 μm were used to obtain a smear density of 76 to 77%. The fuel was helium bonded to 20%-cold-worked type 316L stainless steel cladding. The rod was scheduled to be operated at a linear power of 60 kW/m and a peak cladding temperature of 650°C. The fuel rod exhibited good irradiation performance after irradiation to an average burnup of 6.4 at. % (7.7% peak burnup). However, the heat ratings and associated temperatures were considerably lower than those scheduled.[25] The mean cladding diametral strain was 0.84% and the cladding did not rupture even though the fine fraction of the fuel had a $(U,Pu)_2C_3$ content of 30 to 40%. Sesquicarbide contents in this range resulted in cladding failures by carbon embrittlement of the stainless steel cladding for this fuel irradiated in thermal reactors when operated[25] at linear power levels between 60 and 100 kW/m.

5.4 THERMAL REACTOR IRRADIATION OF (U,Pu)C

The Swiss have irradiated 19 $U_{0.85}Pu_{0.15}C$ fuel rods in thermal reactors and two rods in a reactor facility that had a large epithermal component of neutron flux.[25] Unfortunately, the fuel compositions and

the irradiation conditions used so far have not provided the information required for an objective assessment. Fuel rods that were irradiated at linear powers of interest for FBRs (35 to 90 kW/m) achieved burnups of 8 to 39 MWd/kg heavy metal. Some fuel rods were irradiated to burnups from 45 to 57 MWd/kg heavy metal; however, the linear power ratings were from 70 to 107 kW/m. In addition, these rods were highly hyperstoichiometric with respect to carbon content and had high oxygen levels. They had sesquicarbide contents from 5 to 40%. The oxygen, excess carbon, and high linear powers resulted in longitudinal splits in the type 316 stainless steel cladding during irradiation. Postirradiation examination revealed that the cladding was heavily carburized.[26]

It is noteworthy that even under the high linear power ratings to which the fuel was exposed there was always an annulus of nonrestructured particles between the cladding and the restructured fuel.[27]

5.5 IRRADIATION PERFORMANCE OF SPHERE-PAC FUELS FOR THERMAL REACTORS

A considerable number of sphere-pac fuel rods have been irradiated as part of Light Water Reactor (LWR) programs. This section discusses work pertinent to understanding breeder sphere-pac fuel.

5.5.1 Studies at ECN, Petten, Netherlands

The major LWR sphere-pac irradiation test program has been conducted by the Petten Laboratory of the Energy Center of Netherlands (ECN). Petten workers have irradiated over 100 fuel rods in three water-cooled reactors: the high-pressure loop in the High Flux Reactor (HFR) at Petten, the Halden Boiling Water Reactor (HBWR), and the Boiling Water Reactor at Dodewaard. Individual fuel rod tests were conducted in the HFR in an instrumented pressurized loop and in the HBWR. Two complete assemblies containing 36 fuel rods per assembly are being irradiated in the Dodewaard Reactor.

Table 5.6 summarizes the ECN irradiation program[28] on sphere-pac fuels for LWRs. The status of the ECN experiments is as follows:[29]

Table 5.6. Survey of Sphere-Pac Irradiations at ECN

Experiment	Number of Fuel Rods	Max. Linear Heat Rating (kW/m)	Maximum Burnup (MWd/kg U)	Smear Density (% T.D.)	Fuel Type
B-72	2	70	4	86	U-sphere pac
B-73	2	70	10	88	U-sphere pac
B-71	2	75	21	87	U-sphere pac
R-109	4	57	11	84	U-sphere pac
IFA-204	4	65	20	86	U-sphere pac
IFA-205	7	65	23	85	U-sphere pac
IFA-416	4,3	50	5	89	U-sphere pac, pellets
B-202	35	40	25	87	U-sphere pac
B-203	35	40	25	87	U-sphere pac

B-71, -72, and -73	Report being prepared
R-109	Destructive examination in progress
IFA-204	Destructive examination completed
IFA-205	Irradiation Continuing
IFA-416	Irradiation Continuing
B-202 and -203	Nondestructive examination initiated

Table 5.7 contains more details[30] for the R-109 experiment irradiations conducted in the HFR. Emphasis is placed on the R-109 irradiations at this time because R-109-2 and R-109-3 each contained a pellet and a

Table 5.7. Fuels and Irradiation Parameters for the ECN R-109 Experiments[a]

Experiment	Fuel Rod	Smear Density (% T.D.)	Helium Pressure (MPa)	Helium Pressure (atm)	Max. Linear Heat-Rating (kW/m)[b]	Max. Burnup (MWd/kg)[b]	Fuel Type
R-109-1	306	84	0.1	1	60	10.8	$(U,Pu)O_2$-sphere pac
	307	84	0.1	1	62	1.9	$(U,Pu)O_2$-sphere pac
	308	84	2.5	25	66	9.3	$(U,Pu)O_2$-sphere pac
	309	84	2.5	25	64	11.4	$(U,Pu)O_2$-sphere pac
R-109-2	302	87.5	0.1	1	48	3.9	UO_2-sphere pac
	314	87.5	0.1	1	44	3.6	UO_2-pellets
	317	87.5	0.1	1	46	3.8	$(U,Pu)O_2$-sphere pac
R-109-3	303	87.5	2.5	25	67	5.4	UO_2-sphere pac
	315	87.5	2.5	25	64	5.3	UO_2-pellets
	318	87.5	2.5	25	66	5.4	$(U,Pu)O_2$-sphere pac

[a] From ref. 30.

[b] Calculated from loop calorimetric data.

sphere-pac fuel rod, some postirradiation examination has been conducted, and the heat ratings are calculated from calorimeters in the HFR loop, which should provide reliable values. The only other irradiation that contains both sphere-pac and pellet fuels (IFA-416) is still under irradiation. No metallography is available at this time on the pellet fuel rods (314 and 135) from experiment R-109. Because of the extremely limited data available on sphere-pac and pellet fuels irradiated in the same experiment, emphasis is given to the data that are available. The information from the complete subassembly experiments B-202 and B-203 will be very important. In summary, rather extensive postirradiation measurements of fuel pin diameter and length change show no unusual behavior, but testing has been limited to burnup values that are very low for breeder fuels. Pellet and sphere-pac fuels generally behaved similarly.

Important work has been performed by Sens and Majoor.[28] They took two fuel rods, one with pellet fuel and one with sphere-pac fuel, and measured fuel rod elongation upon increasing the power level from zero to almost 40 kW/m. Both fuel rods had the same helium pressure, smear density, and cladding. Figure 5.13 shows the length increases for both fuel rods upon increasing the power level. The strain produced in the pellet rod was more than twice that for the sphere-pac rod. In addition, the strain in the pellet rod increased linearly with power until the average linear power was 30 kW/m and the strain relaxation occurring at any constant power level was extremely slow. For example, at 35 kW/m the relaxation was not complete in 15 h. For the sphere-pac rod at 35 kW/m the relaxation was complete in less than 1 h and the increase in strain during increase in linear power was significantly less than linear. This was most probably due to relaxation of strains via motion of the spheres at the periphery of the fuel column. This should reduce the strains in the cladding in the radial direction as well as in the axial direction.

Knudsen and co-workers[31] at Risö have conducted overpower ramping studies on irradiated sphere-pac and pellet fuel rods of UO_2 clad with Zircaloy-2. As for the Petten studies, all experimental parameters were the same except that one fuel rod was made with pellet fuel and

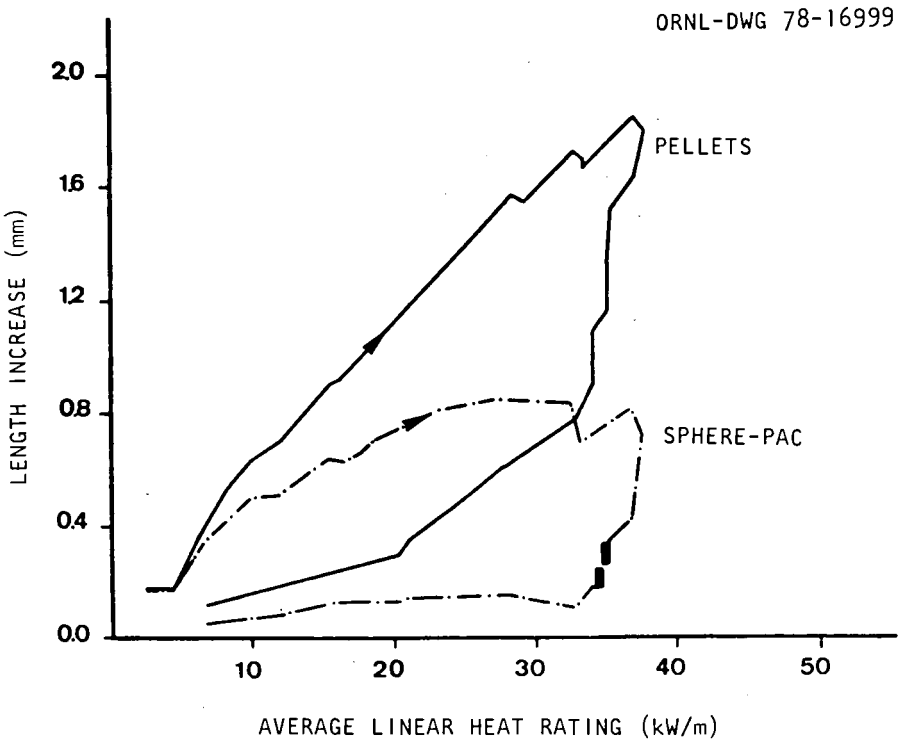

Fig. 5.13. Length Increases in UO_2 Pellet and Sphere-Pac Rods on Increasing the Linear Power from Zero to Almost 40 kW/m. The resultant strain in the pellet rod is more than twice that in the sphere-pac rod. Fuel length is about 0.5 m. Based on ref. 28.

one was made with sphere-pac fuel. The rods were first irradiated in the HBWR to 20.6 MWd/kg at linear powers over the range 28 to 44 kW/m. The overpower studies were conducted in the DR3 reactor at Risö. The rods were ramped at rates of 80 to 100 W/m s from about 35 kW/m to failure. Knudsen et al. used modeling codes to analyze the strains produced during the ramping studies. They concluded "that the performance of sphere-pac fuel rods at high-burnups was not essentially different from that of the pellet fuel rods."

5.5.2 Studies at KFA

From 1965 to 1968 Kernforschungsanlage (KFA) at Jülich, FRG, had an irradiation test program on sphere-pac fuels for use in a Heavy Water Breeder Reactor (HWBR).[29] The program was discontinued when interest in the HWBR diminished in the late 1960s. Reports have been written on the 14 irradiations that were conducted in seven separate experimental assemblies. Their fuel and fertile species are somewhat relevant to

present interests. The fuel was $(Th,U)O_2$ containing 4.45% U, 90% enriched. The fuel rods contained two size fractions of particles; 75 wt % were 630 to 1000 μm in diameter, with the remainder 33 to 100 μm in diameter. The rods had smear densities of 81 to 82% and were 276 mm long for irradiation in the FRJZ Reactor at Jülich. The cladding was Zircaloy-4; no rods containing pellet fuel were irradiated in this program.

A portion of the KFA program included two irradiations containing 14 fuel rods, including four taken to high burnup. The following information is restricted to these four rods. Fuel rod RBE-35 was irradiated to 44.7 MWd/kg(Th+U) at a maximum linear power of about 56 kW/m. Its companion sample RBE-36 was irradiated to 45.2 MWd/kg(Th+U) at a maximum linear power of about 57 kW/m. Both these rods had cladding that was 11.77 mm OD, 0.62 mm thick, and autoclaved before insertion of the fuel. The cladding on fuel rods RBE-37 and RBE-38 was 10.75 mm OD and 0.72 mm thick, and only the cladding of RBE-37 was autoclaved before insertion of the fuel. Rod RBE-37 was irradiated to 49.8 MWd/kg(Th+U) at a maximum power of about 58 kW/m, and rod RBE-38 was irradiated to 50.3 MWd/kg(Th+U) at a maximum power of about 60 kW/m. The external pressure on the cladding during irradiation was 12.3 MPa (121 atm). The other ten fuel rods were irradiated to burnups from 0.4 to 10 MWd/kg(Th+U) at maximum powers of 60 to 69 kW/m.

After the aforementioned irradiations of the 14 fuel rods there was no evidence of interaction of the fuel and/or fission products with the cladding. The maximum cladding diametral increases were 20 to 50 μm. Neither axial gaps in the fuel column nor axial shrinkage of the fuel column was detected. Some rods exhibited a very small fuel column elongation. Fission gas releases were 46 to 47% for RBE-35 and -36 and 41 to 51% for RBE-37 and -38. For the rods irradiated to lower burnups the fission gas releases were 22 to 31%.

Autoradiography revealed a higher concentration of ^{233}U in the outer regions of the fuel than near the center.[29] The magnitude of the difference and the absolute concentrations were not provided.

5.6 REACTOR PHYSICS CONSIDERATIONS — D. L. Selby

With the present interest in remote fabrication and sphere-pac fuel, several reactor physics questions have arisen regarding this fuel. Two such questions deal with the Doppler coefficient:

1. What effect does the sphere-pac arrangement have on the Doppler coefficient for a fast reactor system?
2. What is the change, if any, in the time constant associated with the Doppler effect?

5.6.1 Doppler Coefficient

The currently preferred sphere-pac rod design calls for fissile material in only the coarse and medium-size spheres. Thus, the fine spheres contain only fertile material. This results in a very heterogeneous composition, which might affect the magnitude of the Doppler coefficient.

To determine the effect on the Doppler coefficient, first-flight collision probabilities were calculated[32,33] for neutrons at various resonant energies. The hypothesis is there will not be any significant difference in the Doppler coefficient for the sphere-pac and pellet fueled systems if there is no significant difference in the first-flight collision probabilities.

The calculated first-flight collision probabilities for five different neutron energy levels are presented in Table 5.8. All differences between the heterogeneous (sphere-pac) and homogeneous (pellet) fuel mixtures are less than 5%. These differences are considered to be small. Therefore, it is concluded that the Doppler coefficient for the sphere-pac fuel will be esentially the same as for the pellet material with the same fissile-fertile smear mixture.

5.6.2 Fuel Time Constant

The time constant associated with the Doppler coefficient may also be affected by the heterogeneous arrangement if the fertile fines sphere-pac process is used. Thus, an analysis was made[32,33] to determine the effect of this distribution on the time response of the fuel rod to changes in power.

Table 5.8. Calculated First Flight Collision Probabilities for Five Different Neutron Energies

Energy (eV)	Homogeneous			Heterogeneous			Difference, %		
	Oxygen	U^{238}	Pu	Oxygen	U^{238}	Pu	Oxygen	U^{238}	Pu
6.6	0.00253	0.9963	0.001216	0.00252	0.9964	0.00116	-0.6	0.02	-4.6
7.8	0.05093	0.06871	0.8804	0.05155	0.0697	0.8787	1.2	1.4	-0.19
41	0.1120	0.1889	0.6991	0.1137	0.1924	0.6939	1.5	1.8	-0.75
100	0.02088	0.939	0.04011	0.02083	0.9400	0.03913	-0.2	0.11	-2.5
4.5×10^5	0.7727	0.1941	0.03316	0.7727	0.1938	0.03341	0.0	-0.15	0.75

The time-dependent heat conduction equation for a slab fuel rod with uniform thermal conductivity and heat generation rate changes from $\dot{\alpha}_1$ to $\dot{\alpha}_2$ at time zero were used. The results for a bare UO_2 fuel element undergoing a step change in heat generation from $\dot{\alpha}$ to $0.9\dot{\alpha}$ are as follows:

T (pellet)	T (sphere-pac)	% Difference
0.525 ± 0.007	0.555 ± 0.007	5.7 ± 2.8

The results of these calculations demonstrate that the nonuniformity in fuel distribution in the sphere-pac will have little, if any, effect on the time response of the fuel rod. Certainly such an effect will not be measurable since uncertainties in geometry, thermal properties, heat transfer coefficients, etc. will more than mask the change due to nonhomogeneity.

5.7 REFERENCES

1. A. R. Olsen, "Sol-Gel Sphere-Pac $(U,Pu)O_2$ Fuel Performance in EBR-II Irradiation Tests" (Summary) *Trans. Am. Nucl. Soc.* 14(2): 596-98 (1971).
2. A. R. Olsen, L. A. Neimark, J. Case, and W. N. Beck, private communication, July 12, 1978.
3. A. R. Olsen et al., *Preirradiation Data for ORNL Series II and B & W Oxide Fuel Tests in EBR-II*, ORNL/TM-3446 (November 1971).
4. A. L. Lotts, comp., *Fast Breeder Reactor Oxide Fuels Development — Final Report*, ORNL-4901 (November 1973).
5. Argonne National Laboratory, *Reactor Development Progress Report No. 35*, p. 5.12 (December 1974).

6. Argonne National Laboratory, *Reactor Development Progress Report No. 41*, p. 5.6 (June 1975).
7. Argonne National Laboratory, *Reactor Development Progress Report No. 38*, p. 5.17 (March 1975).
8. L. A. Neimark, Argonne National Laboratory, private communication, March 17, 1978.
9. C. M. Cox and R. E. Adams, *Safety Analysis and Test Specifications for Transient Tests of Sol-Gel (U,Pu)O_2 Fuel Pins (ORNL Series 1)*, ORNL/TM-3574 (December 1971).
10. C. M. Cox, D. R. Cuneo, and E. J. Manthos, "Performance of Sphere-Pac and Pelletized (U,Pu)O_2 During Severe Overpower Transients," pp. 701-24 in *Proc. Conf. Fast Reactor Fuel Element Technology*, ed. by Ruth Farmakes, American Nuclear Society, Hinsdale, Ill., 1971.
11. F. G. Kitts, R. B. Fitts, and A. R. Olsen, "Sol-Gel Urania-Plutonia Microsphere Preparation and Fabrication into Fuel Rods," pp. 195-210 in *Int. Symp. Plutonium Fuels Technol., Scottsdale, Ariz., 1967, Nucl. Met. 13*, ed. by K. E. Horton, R. E. Macherey, and R. J. Allio, American Institute of Mining, Metallurgical, and Petroleum Engineers, New York, 1968.
12. A. R. Olsen, C. M. Cox, and R. B. Fitts, "Low Burnup Irradiation Tests of Sphere-Pac Sol-Gel (U,Pu)O_2 Fuels" (Summary), *Trans. Am. Nucl. Soc.* 12(2): 605-06 (1969).
13. H.W.H. Lahr, "Fabrication, Properties, and Irradiation Behavior of U/Pu Particle Fuel for Light Water Reactors," *Nucl. Technol.* 31: 183-90 (November 1976).
14. H.W.H. Lahr, "Properties and Irradiation Behavior of Advanced Oxide Particle Fuel," pp. 153-64 in *Advanced LMFBR Fuels* (Proc. Topical Meeting, Oct. 10-13, 1977, Tucson, Ariz.), American Nuclear Society, La Grange Park, Ill., 1977.
15. A. Cervellati et al., "Irradiation Tests of Sol-Gel Products, pp. 374-413 in *Symposium on Sol-Gel Processes and Reactor Fuel Cycles*, CONF-700502 (May 1970).

16. A. R. Olsen, R. B. Fitts, and W. J. Lackey, *In-Reactor Restructuring Temperatures and Kinetics for $(U,Pu)O_2$*, ORNL/TM-3387 (July 1971); pp. 579-602 in *Proc. Conf. Fast Reactor Fuel Element Technology*, American Nuclear Society, Hinsdale, Ill., 1971.
17. A. R. Olsen, "Intermediate-Burnup Irradiation Tests of Sphere-Pac Sol-Gel Fuels," *Trans. Am. Nucl. Soc.* 13(1): 32-33 (1970).
18. C. M. Cox, R. B. Fitts, A. R. Olsen, and A. L. Lotts, "Irradiation Performance of Sol-Gel $(U,Pu)O_2$ Fuels for Breeder Reactors," pp. 359-73 in *Symposium on Sol-Gel Processes and Reactor Fuel Cycles*, CONF-700502 (May 1970).
19. A. R. Olsen, "High-Burnup Irradiation Tests of Sphere-Pac Sol-Gel Fuels" (summary), *Trans. Am. Nucl. Soc.* 15(1): 181-82 (June 1972).
20. R. B. Fitts, E. L. Long, Jr., and J. M. Leithaker, "Observations of Fuel-Cladding Chemical Interactions as Applied to GCBR Fuel Rods" pp. 431-58 in *Proc. Conf. Fast Reactor Fuel Element Technology*, ed. by Ruth Farmakes, American Nuclear Society, Hinsdale, Ill., 1971.
21. J.H.N. Verheugen, comp., *Post Irradiation Examination of Mixed-Oxide Vibrasol Fuel Rods Third Semi-Annual Report (July-December 1976)*, ECN-77-030 (February 1977).
22. B. Frost et al., *Water Reactor Fuel Performance*, (Proc. ANS Topical Meetings, St. Charles, Ill. May 9-11, 1977), American Nuclear Society, LaGrange Park, Ill., 1977; see especially pp. 274-361.
23. R. W. Stratton, Swiss Federal Institute for Reactor Research, private communication May 15, 16, 1978.
24. A. Boltax, private communication May 24, 1978.
25. R. W. Stratton and L. Smith, "The Irradiation Behaviour of Sphere-Pac Carbide Fuel," pp. 348-60 in *Advanced LMFBR Fuels* (Proc. Topical Meeting, Oct. 10-13, 1977, Tucson, Ariz.), American Nuclear Society, LaGrange Park, Ill., 1977.
26. L. Smith et al., *The Post Irradiation Examination of Four (U,Pu)C Sphere-Pac Fuel Pins Irradiated in the DIDO Reactor at Harwell*, EIR-265 (November 1974).
27. L. Smith et al., *DIDO-II The Post Irradiation Examination of Four (U,Pu)C Sphere-Pac Fuel Pins*, EIR-317 (April 1977).

28. P. F. Sens and E.B.M. Majoor, "Irradiation Behaviour of Vibrasol Fuel," pp. 152-60 in *Nuclear Energy Maturity, vol. 3, Nuclear Fuel Performance and Management Part 1* (Proc. European Nucl. Conf., Paris, April 21-25, 1975), Pergamon, Oxford, 1976.

29. F. J. Homan, private communication after trip to KFA, Jülich and ECN, Petten, January 23-February 2, 1978.

30. J.H.N. Verheugen, compiler, *Postirradiation Examination of Mixed-Oxide Vibrasol Fuel Pins Fourth Semi-Annual Report (January-June 1977)* ECN-77-122 (August 1977).

31. P. Knudsen, C. Bagger, and N. Kjaer-Pedersen, "Analysis of Overpower Performance of High-Burnup Pellet and Vipac UO_2-Zr Fuel Pins," *Trans. Am. Nucl. Soc.* 24: 172 (1976).

32. Unpublished work by J. E. Mott, J. C. Robinson, J. E. Jones, and H. H. Chen of Technology for Energy Corporation, Knoxville, Tenn.

33. D. L. Selby, H. E. Knee, J. E. Mott, J. C. Robinson, J. E. Jones, and H. H. Chen, *LMFBR Designs Using Uranium, Plutonium Oxide Sphere-Pac Fuel,* ORNL-5446 (to be published).

6. STATUS AND RECOMMENDED FUTURE WORK

W. J. Lackey

Although gel-sphere-pac technology has been under development for a number of years in several countries, extensive additional development and demonstration remain to be accomplished before licensing and large-scale industrial application are realized. Areas requiring additional work are discussed below. Much of the technology required for design, construction, and operation of a commercial gel-sphere-pac refabrication plant is common to that required for a similar plant using the pellet route, and only those tasks that are specific to gel-sphere-pac technology are addressed here. A more detailed discussion is available.[1]

Many of these tasks are currently being investigated as a part of programs initiated in October 1977. This work is funded at ORNL by the Department of Energy Division of Reactor Research and Technology and by the Division of Nuclear Power Development as a part of the Fuel Refabrication and Development Program, which is administered by Battelle Pacific Northwest Laboratories.

6.1 SOL AND BROTH PREPARATION

6.1.1 Status

Generally the equipment used for sol or broth preparation has been laboratory and engineering scale, but not prototype. Because of inherent criticality limitations, many of the engineering-scale unit operations are actually equivalent to prototype scale, but integrated operation of prototype systems has not been done. Extensive experience exists for ThO_2, and considerable experience has been accumulated with UO_2, certain $(Th,U)O_2$ compositions, and certain $(U,Pu)O_2$ compositions. Laboratory-scale experience with both sols and broth encompasses virtually all possible compositions of uranium, thorium, and plutonium oxides of interest; however, specific processes need to be selected and optimized.

To achieve fuel smear densities as high as 88% of theoretical requires fissile spheres larger in diameter (800 or perhaps 1200 μm diam) than those that could be routinely prepared with the processes previously

used in the U.S. Thus, the European technology is an important base of information since the U(VI) broth method is the preferred route for preparing larger spheres.

Sphere technology may be ahead of pellet technology in one significant aspect, namely, remote operation. From the very outset, sol-gel methods were aimed at ^{233}U,Th cycles and continuing recycle of plutonium; the former is known to require fully remote fabrication. Therefore, having this objective, sol-gel processes from the outset were selected with the fully remote criteria in mind, and certain compositions have, in fact, been made in hot cells. Much laboratory-scale experience exists in the U.S. for glove-box fabrication of plutonia-bearing spheres but with the older sol-gel flowsheet. Some experience exists in Europe for preparation of plutonia spheres by a broth-type process.

6.1.2 Future Work

It is important to evaluate European broth-type processes for preparing large spheres and to select a process for adaptation and further development as necessary to meet U.S. fuel cycle requirements. All uranium-plutonium processes now in use depend on a pure plutonium nitrate solution. Techniques for utilizing co-processed uranium-plutonium remain to be developed. Similarly, none of the European processes have been used for preparing $(Pu,Th)O_2$ spheres; therefore, a suitable process needs to be developed if on-going reactor design and fuel cycle studies indicate this to be a desirable fuel. The influence of potential spikants must be evaluated if their use is pursued.

Development is required to guide selection of types and amounts of organic additives for preparing broth. This selection is a key technical issue in that it controls the ability to form true spheres with a sufficiently open structure that they can be washed and dried without cracking and can be sintered to high density. Suitable environmental conditions for handling and storing broths must be determined.

Another major need is in the area of fine (20-50-μm-diam) sphere preparation. European programs have had difficulty in preparing this

size material. The initial work with water extraction shows promise here, as does the internal gelation process.

As is true for most steps in the gel-sphere-pac process, there is the need to progress through the normally accepted stages of development necessary to gain the required technology to successfully demonstrate a commercially feasible operation. Currently the technology is best characterized as being in the cold laboratory stage of development. The need exists for hot laboratory tests to verify, among other things, that radiolysis will not be a problem, or define the allowable limits. Additionally, cold development at engineering and full scale is required. Considerable attention must be placed on remote operation and maintenance and on analytical procedures for maintaining and verifying product quality. Design evaluation and prototype testing are required for nitrate feed solution receiving, storage, metering, and blending.

6.2 FORMING AND WASHING OF SPHERES

6.2.1 Status

The status of sphere forming and washing is basically the same as that just discussed for sol preparation. Several designs of pulsed droplet generators capable of producing essentially single-size medium or coarse spheres have been operated. Multi-needle units have also been operated with throughputs of 10 kg/h. Spheres have been washed in a continuous mode with contact engineering-scale equipment. Concerning fine spheres, a turbulent two-fluid nozzle method exists for droplet formation, but the range in sizes is greater than desired, and an improved method is needed.

6.2.2 Future Work

The most important technical issue in sphere forming is the selection of gelation conditions: gelation medium (organic, ammonia gas, ammonium hydroxide solution), gelation temperature and rate, and deceleration and transfer techniques to produce spherical particles of

uniform structure suitable for washing, drying, and sintering. Methods must be devised for the internal recycle of gel support organics and ammonia.

Increasing the feed rate while maintaining a narrow microsphere size distribution is needed for intermediate-size, 200-300-μm-diam, spheres. An improved method for forming fines having higher product yield in the 20-50-μm-diam range is desired. Processes amenable for use with spiked fuel remain to be developed. Remotely operable and maintainable equipment is needed for fissile spheres and contact equipment for fertile fines.

6.3 DRYING OF SPHERES

6.3.1 Status

The status of sphere drying is essentially the same as described previously for sol and broth preparation. With contact equipment used, spheres have been dried continuously on wire mesh belts.

6.3.2 Future Work

The influence of drying conditions, such as temperature and relative humidity, on sphere integrity and subsequent sinterability must be investigated further. Existing hydraulic and pneumatic techniques for handling wet and dry products must be demonstrated. Remote equipment development is required.

6.4 SINTERING

6.4.1 Status

Spheres of ThO_2 are easily sintered to densities in excess of 99% of theoretical at temperatures below 1450°C. Urania and urania-plutonia spheres of various compositions have been routinely sintered to densities greater than 95% at 1550°C or below. Recently broth-derived urania spheres were repeatedly sintered to over 99% of theoretical density. Sphere sintering, however, has not been demonstrated for all breeder

fuel compositions being considered. Most experience is with batch operations. Plutonia experience is limited to batch sizes of several hundred grams except for the recent British work with somewhat larger batches. Extensive development is required regarding preparation of carbide spheres. Only the Swiss have appreciable experience in this area.

6.4.2 Future Work

The sintering of spheres of the required composition(s) must be developed for the specific gel process(s) selected. Variables that must be considered are heating rate, sintering temperature and time, and calcining and sintering atmosphere. Development of a sintering process requiring temperatures no greater than about 1450°C would be of considerable benefit in that simpler more reliable heating elements could be used. While sintering furnace development can draw from previous pellet work, there may be special requirements for providing improved gas-sphere contact; for example, a fluidized bed might be advantageous. A suitable continuous or batch remote furnace with high material throughput remains to be developed.

It has been shown with $(U,Pu)O_{2-x}$ sol-gel spheres that stoichiometry, moisture, and gas content can be controlled to currently specified limits for pellet fuels. However, in this earlier work following sintering, the product was always handled in inert-atmosphere glove boxes. Since numerous equipment items could be simpler and more reliable if some exposure to air and moisture is not deleterious, it is important to determine the exact degree of precaution necessary in the subsequent handling of sintered coarse and fine spheres.

Sintering of fine spheres presents two special problems that must be overcome. First, the fines tend to be blown out of the furnace by the flowing gas atmosphere. Also fine spheres tend to adhere slightly to one another during sintering; in some instances subsequent agitation is required to break up the agglomerates. Elimination of fines sticking would be advantageous. Improved control of the carbon content of carbide spheres, particularly the fines, is required.

6.5 CHARACTERIZATION OF SPHERES

6.5.1 Status

Contact or glove-box laboratory-scale techniques have been used in the past to thoroughly characterize spheres of numerous compositions including $(U,Pu)O_{2\pm x}$. With only a few exceptions, this equipment was not remotely operable and not suitable for on-line inspection. Except for the fines, sphere size distribution can currently be measured automatically by an analyzer developed for remote operation.

6.5.2 Future Work

Remotely operable equipment is needed for most of the required analyses. A faster technique is needed for size and shape analysis of fines. Faster techniques are needed for residual gas and moisture determinations. Improved techniques are needed for determination of density and oxygen-to-metal ratio. Improved specifications for sphere shape and microstructure are required.

6.6 SPHERE-PAC LOADING AND ROD INSPECTION

6.6.1 Status

Satisfactory smear density is presently being achieved with the sphere-pac process for rods up to 2 m long by using three distinct sizes of spheres. Two possible loading procedures are currently being investigated. In one, all three particle sizes are either preblended or simultaneously fed into the fuel rod. In the second process, the two larger particle types are simultaneously loaded into the rod and the smallest spheres are subsequently infiltrated through this initial bed. The process is understood at the laboratory scale but not developed at the engineering scale. Hundreds of rods about 0.5 m or less in length have been loaded manually, but automatic loading of 2- or 4-m-long rods is just beginning. Much of the particle dispensing and blending technology developed for HTGR fuels is applicable.

6.6.2 Future Work

Extensive development is required to optimize the blend of spheres of various sizes, to specify allowable size range limits, and to develop the optimum loading scheme (preblending vs infiltration). The loading process must be optimized to yield not only high smear density but reasonable loading times. The nature of the imposed vibration and the method of attaching the vibrator to the cladding or cladding support remain to be optimized. Multiple-rod loading devices may need to be devised.

Existing pneumatic transfer techniques must be modified to accommodate the largest coarse spheres, which are denser and larger than HTGR fuel particles for which the technology was initially developed. Similarly, modifications are required for the pneumatic transfer of fines, which are much smaller than HTGR fuel particles. Volumetric or gravimetric sphere dispensers are required for the three size fractions. Equipment for blending two or three sizes of spheres is required.

Dust control and atmosphere containment must be demonstrated. Procedures must be developed to minimize cladding contamination. Techniques for accountability and inventory control must be developed. A gamma interrogation device is needed to monitor fuel level within a pin during loading and to subsequently verify axial and perhaps radial fuel homogeneity. Techniques for restraining the fuel column during and after loading must be proven. Fuel relocation, after loading but before irradiation, must be investigated. The possible need for thermally assisted outgassing of loaded pins must be considered.

6.7 IRRADIATION PERFORMANCE

6.7.1 Status

Nearly 200 oxide or carbide sphere-pac fuel rods have been irradiated in fast or thermal reactors. There have been 23 $(U,Pu)O_2$ fast reactor pins irradiated in EBR-II, but only two have been examined thoroughly. A very abbreviated examination was given two others, and

the rest have not been examined. About 20 sphere-pac carbide rods have been tested, nearly all in thermal reactors.

The overall irradiation performance of sphere-pac fuels has been encouraging. Initial results indicate that sphere-pac fuels exhibit less fuel-cladding mechanical and chemical interaction. Also, sphere-pac fuels operate cooler than pellet fuels for a given heat rating because of improved conductance between the fuel and cladding.

6.7.2 Future Work

Extensive additional irradiation testing is required before the potential performance advantages of sphere-pac fuels can be proven and such fuels licensed. Steady-state tests are required for oxide spheres made and loaded by new processes. The fertile fines concept must be evaluated. Testing is required for spiked fuel, new compositions containing thorium, and carbides. Transient testing of both fresh fuel and previously irradiated rods is required. Attention must be given to the possibility of in-reactor axial fuel relocation and sphere washout from failed rods. Existing rods that were irradiated in EBR-II should be examined more extensively. Performance codes should be modified to model the behavior of sphere-pac fuel.

6.8 SCRAP RECYCLE AND WASTE TREATMENT

6.8.1 Status

Work in these areas is in its infancy for all fuel forms except for HTGR-related engineering analyses. A large quantity of thorium-uranium scrap has been processed at ORNL to recover the ^{233}U. The recovery used a batch dissolver designed specifically for scrap, fluoride in nitric acid dissolution, and cleanup by solvent extraction and/or ion exchange. This operation was performed remotely but directly maintained after facility cleanout.

6.8.2 Future Work

An engineering analysis of the type and quantity of scrap and waste is required, including an analysis of utilization of the reprocessing

line for scrap recovery rather than an independent scrap line. Obviously scrap recovery processes and equipment are undeveloped.

6.9 COMMERCIAL FACILITY

6.9.1 Status

Very little attention has been directed toward planning and analysis of an integrated commercial refabrication plant based on gel-sphere-pac technology. However, those portions of such a plant that are common with HTGR particulate fuel technology have been thoroughly considered. Concepts for gel-sphere-pac processes and equipment are rapidly progressing to the point where meaningful evaluation can be performed.

6.9.2 Future Work

An engineering study of a commercial-size refabrication plant using gel-sphere-pac technology is needed. Equipment and facility concepts should be generated for a complete integrated refabrication facility. Material throughput, surge capacity, and space requirements would be estimated. Schemes for sampling, inspection, accountability, safeguards, maintenance, scrap recycle, and waste handling would be generated. An economic analysis for such a commercial plant should be performed.

6.10 REFERENCE

1. Battelle Pacific Northwest Laboratory, *The Technical Program Plan for the Department of Energy's Fuel Refabrication and Development Program* (in preparation).

7. SUMMARY

J. E. Selle

The concept of gel-sphere-pac fuel has received considerable attention in the U.S. and in European laboratories. The gel-sphere-pac process is one of several techniques by which small particles can be loaded to high density in a nuclear fuel rod. For the gel-sphere-pac process, the particles are properly sized spheres with controlled size ratios and proportions. When spheres are used instead of powder, dust problems are eliminated, good particle size control is possible, and packing times are minimized.

Spheres are produced by gelation processes capable of producing uniformly sized spheres with good sphericity at high production rates. Several techniques have been developed: (1) internal gelation, (2) external gelation, and (3) gelation by water extraction. Each of these techniques has its own advantages and disadvantages, and these are discussed in detail. Following gelation, the spheres are washed, dried, and sintered in a series of steps developed by empirical methods. Spheres of ThO_2 and UO_2 are consistently produced with densities greater than 99% of theoretical; additional development is required to routinely produce $(U,Pu)O_2$ and $(Th,Pu)O_2$ spheres this dense.

No significant scale-up problems were identified for the external gelation process, although this process does not appear practical for fine particle production. Several complications arise in the internal gelation process. The most severe complication is the "shelf life" of the feed, which is limited and temperature dependent. The lines and valves can become prematurely clogged, producing cleanup and maintenance problems. None of these problems appear insurmountable, although development effort is clearly required.

Considerable technology has been developed for sphere characterization. Contact or glove-box techniques have been developed for the determination of particle density, size, shape, composition, crushing strength, and microstructure.

The sphere-pac process for loading spheres into a fuel rod involves vibratory packing of carefully sized spheres of the proper

size ratio. Considerable technology has been developed regarding the identification of proper sizes, size ratios, blending ratios, and loading sequences to produce maximum smear densities and minimum loading times. By proper control of the process variables, smear densities up to 88% can be obtained.

Some scale-up problems are anticipated in sphere-pac loading of long fuel rods. Some effort has been expended in resolving this problem, and it does not appear to be insurmountable. Simultaneous loading of three size fractions and a layering technique show promise of overcoming the problem of excessive vibration times for long rods. In general, microsphere handling and pneumatic transport are very adaptable to remote operation.

Significant development is required to enable economic inspection of fuel rods with acceptable precision, accuracy, and speed, although most of the development is required for remote inspection, regardless of whether the fuel rod is fabricated from pellet or gel-sphere-pac fuel.

Preparation of carbide fuels by gelation is also feasible. Carbon powder is dispersed in the broths before gelation. Some agitation is required to prevent separation of the dispersion. More intense treatments are required for external gelation than for internal gelation because the lower pH values inherent in the external gelation process are unfavorable for carbon dispersion. Sphere formation conditions are essentially the same with or without carbon. Extensive development is necessary in sintering and carbothermic reduction of carbide spheres in order to produce higher density spheres of controlled stoichiometry with minimum plutonium loss.

An analysis of the reactor physics indicates no significant change in the Doppler coefficient associated with the use of the fertile fines concept. Similarly there should be no effect on the time response of the fuel pin.

Data available to date indicate that sphere-pac fuels will perform as well as or better than pellet fuels under fast breeder reactor operating conditions.

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