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Gel-Sphere-Pac Fuel for Thermal Reactors—Assessment of Fabrication Technology and Irradiation Performance

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METALS and CERAMICS
ENERGY
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OAK RIDGE NATIONAL LABORATORY

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METALS AND CERAMICS DIVISION
CHEMICAL TECHNOLOGY DIVISION

GEL-SPHERE-PAC FUEL FOR THERMAL REACTORS — ASSESSMENT OF FABRICATION TECHNOLOGY AND IRRADIATION PERFORMANCE

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GEL-SPHERE-PAC FUEL FOR THERMAL REACTIONS — ASSESSMENT OF FABRICATION TECHNOLOGY AND IRRADIATION PERFORMANCE

Compiled by R. L. Beatty, R. E. Norman,* and K. J. Notz*

ABSTRACT

Recent interest in proliferation-resistant fuel cycles for light-water reactors has focused attention on spiked plutonium and ^{233}U-Th fuels, which will require remote refabrication. The gel-sphere-pac process for fabricating metal-clad fuel elements has drawn special attention because it involves fewer process steps and fewer mechanically intensive steps than pellet technology; all operations deal with either liquids or microspheres, which are free-flowing and relatively dust-free. These fabrication process characteristics should also enable lower personnel exposures during both fabrication and maintenance operations.

Gel-sphere-pac fabrication technology involves two major areas: the preparation of fuel spheres of high density and loading these spheres into rods in an efficiently packed geometry. Gel sphere preparation involves three major steps: preparation of a sol or of a special solution ("broth"), gelation of droplets of sol or broth to give semirigid spheres of controlled size, and drying and sintering these spheres to a high density. Gelation may be accomplished by water extraction (suitable only for sols) or ammonia gelation (suitable for both sols and broths but used almost exclusively with broths). Ammonia gelation can be accomplished either externally, via ammonia gas and ammonium hydroxide, or internally via an added ammonia generator such as hexamethylenetetramine. Sphere-pac fuel rod fabrication involves controlled blending and metering of three sizes of spheres into the rod and packing by low- to medium-energy vibration to achieve about 88% smear density; these sizes have diametral ratios of about 40:10:1 and are blended in size fraction amounts of about 60% coarse, 18% medium, and 22% fine.

In addition to fabrication process advantages, irradiation test results available to date indicate that sphere-pac fuel performs at least as well as pellet fuel, and may in fact offer an advantage in significantly reducing mechanical and chemical interaction between the fuel and cladding.

From the standpoint of overall process complexity and economics, it should be noted that the normal feed for gel sphere preparation, heavy metal nitrate solution, is the usual

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product of fuel reprocessing, so that fabrication of gel spheres performs all the functions performed by both conversion and pellet fabrication in the case of pellet technology.

In view of the apparent and potential advantages of gel-sphere-pac fuel, an assessment of the state of the art of gel-sphere-pac technology was undertaken to provide a sound basis for further development. While considerable further development work is required, the flexibility of the gel-sphere-pac process in relation to both fabrication of advanced and alternative fuels and fuel performance suggests that continued development for LWR application is well justified.

EXECUTIVE SUMMARY

Recent interest in proliferation-resistant fuel cycles has focused attention on fuels that will require remote refabrication after reprocessing. The gel-sphere-pac process involves fewer process steps and fewer mechanically intensive steps than pellet technology; all operations deal with either liquids or microspheres, which are easily handled in a dust-free manner. For example, gel-sphere preparation replaces the powder-conversion step (carried out at the reprocessing plant for pellet flowsheets). However, the dense spheres, once prepared, are directly usable for loading fuel rods. In comparison, pellet flowsheets require powder pretreatment, pre-slugging, and pelletizing before the usable fuel form is obtained. These fabrication benefits will also lead to lower operator exposures during both fabrication itself and during maintenance.

In addition to these fabrication benefits, data available to date show that sphere-pac fuel may give superior performance in-reactor. 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. It should be noted that the normal feed for gel-sphere-pac, heavy metal nitrate solution, is the normal product of reprocessing, and therefore gel-sphere-pac performs all the functions performed by both conversion and refabrication in pellet technology.

Gel-sphere-pac technology involves two special characteristics: the preparation of truly spherical particles of high density in all necessary sizes, and loading these spheres into rods in an efficiently packed geometry by low- to medium-energy vibration. (Note that the latter operation distinguishes sphere-pac from vi-pac, which uses particles of any shape and very high-energy compaction.) Gel sphere preparation involves three major steps: preparation of a sol or of a special solution ("broth"), gelation of droplets of sol or broth to give semi-rigid spheres, and drying and sintering these spheres to a high density. Gelation may be accomplished by water extraction (suitable only for sols) or ammonia gelation (suitable for both sols and broth, but used almost exclusively with broths); ammonia gelation can be accomplished either externally, via ammonia gas and ammonium hydroxide, or internally via an added ammonia generator such as hexamethylentetramine. Sphere-pac requires three sizes of spheres to achieve a smear density approaching 88%; these sizes have diametral ratios of about 40:10:1. The preferred method at this time from a fabrication viewpoint is to incorporate all the fissile content in the two large sizes, which allows the fines to be made in a separate operation using only fertile isotopes — the so-called "fertile fines" method. However, the sphere-pac process is not limited to use of fertile fines, and all three sizes of spheres can have the same composition. If a lower density is acceptable, two sizes will yield about 85% smear density.

A discussion of development needs is conveniently organized along two standards: the scale of operation and the various functional systems involved. For processes aimed eventually at the design, construction, and successful operation of a commercial facility that requires remote (shielded hot cell) handling, the following sequence is both realistic and representative of the actual number of development stages required:

Cold Lab: to demonstrate process feasibility using nonradioactive stand-ins.

Hot Lab: to verify process feasibility using radioactive materials.

Cold Engineering: to demonstrate equipment concepts under non-radioactive conditions.

Hot Engineering: to verify equipment concepts under remote, radioactive conditions.

Cold Prototype: to demonstrate full-scale components, including integrated and/or remote operation for the more complex steps.

In general, cold lab work provides the basis for both hot lab and cold engineering work, while the latter two together provide the basis for both hot engineering and cold prototype work, while these two provide a solid basis for a commercial-scale facility. Fuel samples for irradiation testing would normally be produced during all stages of development. In the above sequence gel-sphere-pac development is largely through cold lab and is getting started on both hot lab and cold engineering. A small amount of hot engineering was done in the past and, because of criticality limitations, some components are already at prototype scale (but not at prototype sophistication). Some irradiation testing has been done, both in the U.S. and in Europe, with test rods and some full-length rods, with generally favorable results; additional tests are under way in the U.S. and abroad.

From a functional point of view, gel-sphere-pac development may be divided as follows:

gelation process; includes three options:
  - water extraction
  - internal chemical precipitation
  - external chemical precipitation

droplet formation
washing and drying
calcination and sintering
sphere characterization
waste treatment
sphere-pac loading of rods
inspection of loaded rods
scrap recycle

The gelation processes developed at ORNL during the 1960s were based on water extraction of sols of thoria, urania, plutonia, and various mixtures thereof, and were very successful for product microspheres up to about 600 μm in diameter (larger for some compositions). However, this process had difficulties with urania, particularly with sizes greater than 600 μm, and the chemical gelation processes developed in Europe are preferred. These processes use ammonia to cause a rapid gelation by the fast precipitation of ammonium diuranate, using various organic additives for gel support and/or other purposes. Both internal and external gelation can yield urania and urania-plutonia spheres over 1200 μm in diameter. Chemical gelation is also suitable for thoria-based compositions. From scouting tests at ORNL, we prefer internal chemical gelation over external gelation. Additional work must be done to optimize both compositions and conditions, to design and test engineering-scale equipment, and to carry out hot lab tests.

Droplet formation is well-understood and performed routinely at the lab scale for all required sizes. For the larger sizes, a pulsed laminar-flow nozzle is used, both here and in Europe. It provides excellent size control and acceptable throughputs; design and testing of remotely operable systems are still required. For the smallest size ("fines") a turbulent two-fluid nozzle is used and gives adequate throughput but a broader size spectrum than desired. The present approach is acceptable, but an improved method is desirable.

The requirements for washing and drying are reasonably well-understood and are being met successfully, but largely in batch operations. Continuous procedures need to be designed and tested. The requirements for the three sizes vary somewhat, particularly for the fines. During these steps the handling procedures change from hydraulic transport to gravity or pneumatic transport, and equipment amenable to this interface must be tested.

Calcining and sintering are being done successfully on a batch basis, yielding product about 98% of theoretical density. However, considerable development is still required to understand and optimize these processes for all the heavy metal compositions of interest. Scale-up will require equipment for continuous operation and/or larger batches, while providing the necessary atmosphere control, residence time, and uniformity.

Considerable technology has been developed for sphere characterization as part of the HTGR Fuel Recycle Program. Contact or glove box techniques have been developed for the determination of particle density, size, shape, composition, crushing strength, and microstructure. However, a need still exists for techniques applicable to the fines and for more rapid methods of chemical analysis.

No direct development work has been done on waste treatment, but the needs have been identified and reasonable processes are known to exist or are under development for other programs. The conventional wastes — such as discarded organic liquids, discarded equipment, and decontamination solutions — can be handled by methods used by other recycle programs. The major waste, ammonium nitrate, can be handled by either of two methods: catalyzed decomposition in molten salt or regeneration and recycle of ammonia and nitric acid. For organics such as urea and hexamethylenetetramine, the preferred treatment is internal recycle, but suitable processes still need to be developed.

The sphere-pac process for loading 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, and blending ratios and loading sequences to produce maximum smear densities and minimum loading times. Sphere-pac loading of commercial-length fuel rods remains to be demonstrated. Simultaneous loading of all three size fractions shows promise of overcoming the problem of excessive loading times for long rods. Much of the particle dispensing and blending technology developed for HTGR fuels is applicable.

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.

Compared with pellets, scrap recycle in gel-sphere-pac is a much smaller problem since sphere dimensions are not as critical as are pellet dimensions. Any defective spheres can be recycled after drying, before sintering to density, while dissolution is still relatively easy.

Very little effort to date has been directed toward planning and analysis of an integrated commercial refabrication plant based on gel-sphere-pac technology. Concepts for gel-sphere-pac processes and equipment are rapidly progressing to the point where meaningful evaluation can and should be performed.

A thorough irradiation test program needs to be planned and inaugurated as soon as possible, since performance is the crucial item in the final acceptance of gel-sphere-pac from both commercial and licensing aspects. In terms of total time, licensing will probably be the controlling factor, and performance data are needed.

Although not a part of this assessment, it should be mentioned that by the addition of carbon during the gel sphere fabrication step, carbide microspheres can be made for use as an advanced fuel in fast reactors. The gel-sphere process is also one of the preferred methods to make HTGR fuel kernels. Thus, the process is highly versatile and applicable to all ceramic-fueled reactors. In addition, pellets can be fabricated from calcined spheres; in addition to the technical benefits deriving therefrom, this approach has the benefit of yielding a fuel form that is already licensed. However, this report deals only with the fabrication of oxide sphere-pac fuel rods for thermal reactors.

1. INTRODUCTION

The objective of this report is to provide a current, comprehensive assessment of U.S. and foreign gel-sphere-pac technology pertinent to light-water reactor oxide fuels. The gel-sphere-pac route for fabrication of fuel rods is an alternate to the conventional pellet method. Gel-sphere-pac technology is not new but is currently receiving emphasis for a variety of reasons described later. With the gel-sphere-pac process, high density ceramic fuel spheres of controlled sizes are produced, and these are subsequently loaded, with the assistance of low-energy vibration, into the fuel rod cladding.

1.1 OVERVIEW

Gel-sphere technology is applicable to fuel rod fabrication in several ways, as indicated schematically in Fig. 1.1. Oxide spheres can be used directly for sphere-pac loading of both LWR and fast reactor fuel rods. By the addition of carbon during the sphere fabrication step, carbide microspheres can be made for use as an advanced fuel in fast reactors. The preceding are traditional applications of gel spheres. More recently, their possible use for the fabrication of pellets has been investigated; in addition to the technical benefits deriving therefrom, this approach has the benefit of yielding a fuel form that is already licensed. This report will deal only with the fabrication of oxide spheres and their incorporation into sphere-pac fuel rods. In addition to the applications shown in Fig. 1.1, both oxide and carbide spheres are suitable feed for HTGRs, in which they are coated with pyrolytic carbon and silicon carbide and then imbedded in a graphite matrix; this application requires spherical particles.

Gel-sphere preparation is based on three major steps: (1) preparation of a sol or of a special solution ("broth"), (2) gelation of droplets of sol or broth to give semirigid spheres, and (3) drying and sintering these spheres to a high density. Gelation may be accomplished by two methods: water extraction (suitable only for sols), and ammonia gelation (suitable for both sols and broths, but used almost exclusively with broths). Ammonia gelation can be accomplished either externally,

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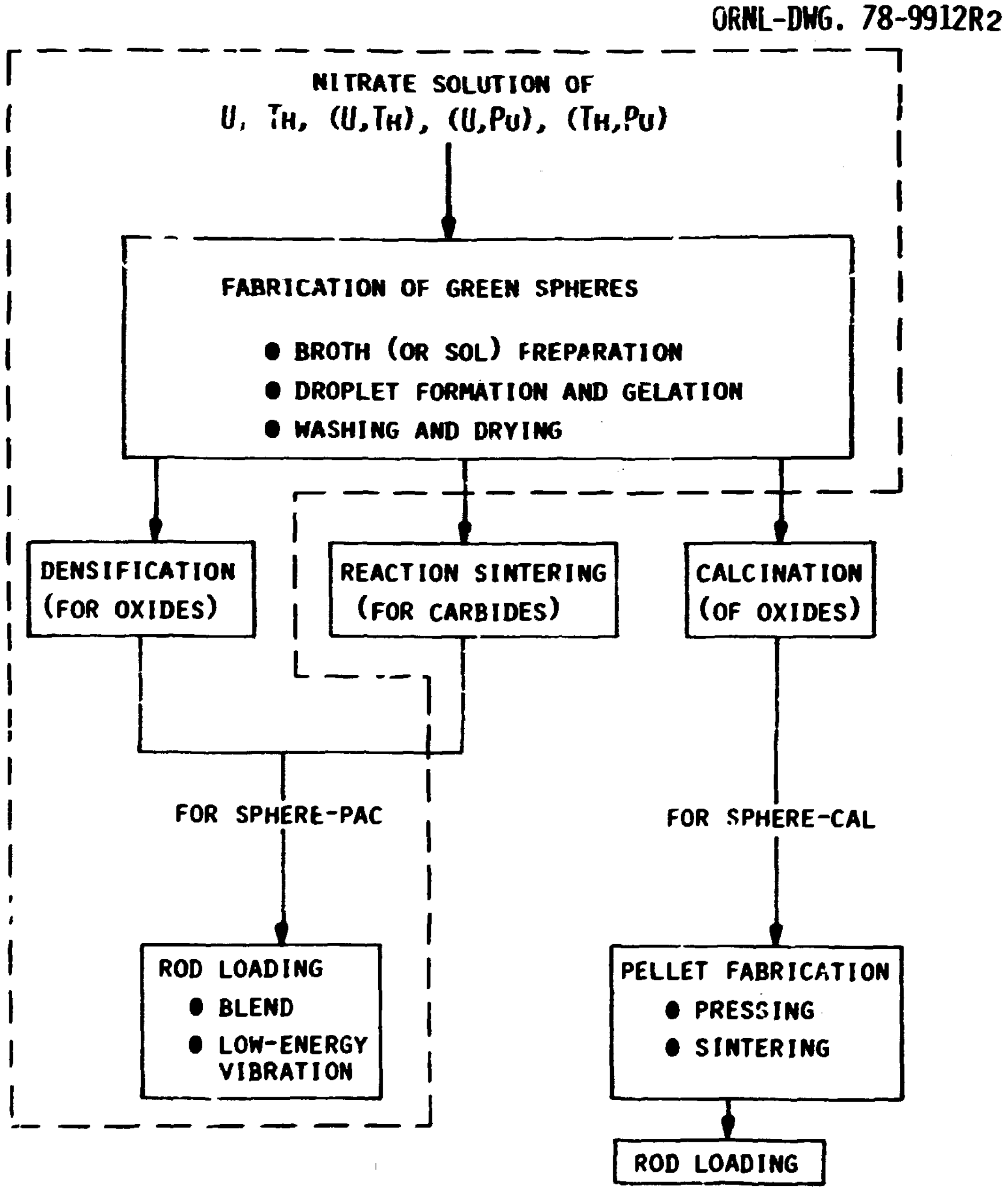

Fig. 1.1 Application of Gel-Sphere Technology to Fuel Rod Fabrication. The portion inside the dashed line is addressed in this report.

via ammonia gas and ammonium hydroxide, or internally via an added ammonia generator such as hexamethylenetetramine; internal gelation is followed by treatment with ammonium hydroxide to complete the reaction.

Sphere-pac requires three sizes of spheres to achieve about 88% smear density. These sizes must have diametral ratios of about 40:10:1. The actual diameters currently favored are 1200, 300, and 30–50 μm. The preferred method at this time is to incorporate all the fissile content in the two large sizes, which constitute about 80% of the total mass. This allows the fines to be made in a separate operation using only fertile isotopes — the so-called "fertile fines" method. However, the sphere-pac process is not limited to use of fertile fines, and if required for accountability or other reasons, all three sizes of spheres can have the same composition. If a lower density is acceptable, two sizes will yield about 85% smear density.

Together, the use of gel spheres and sphere-pac involves two special characteristics: (1) the preparation of truly spherical particles of high density in all necessary sizes, and (2) loading these spheres into rods in an efficiently packed geometry by low-energy vibration. A generalized equipment flowsheet is shown in Fig. 1.2.

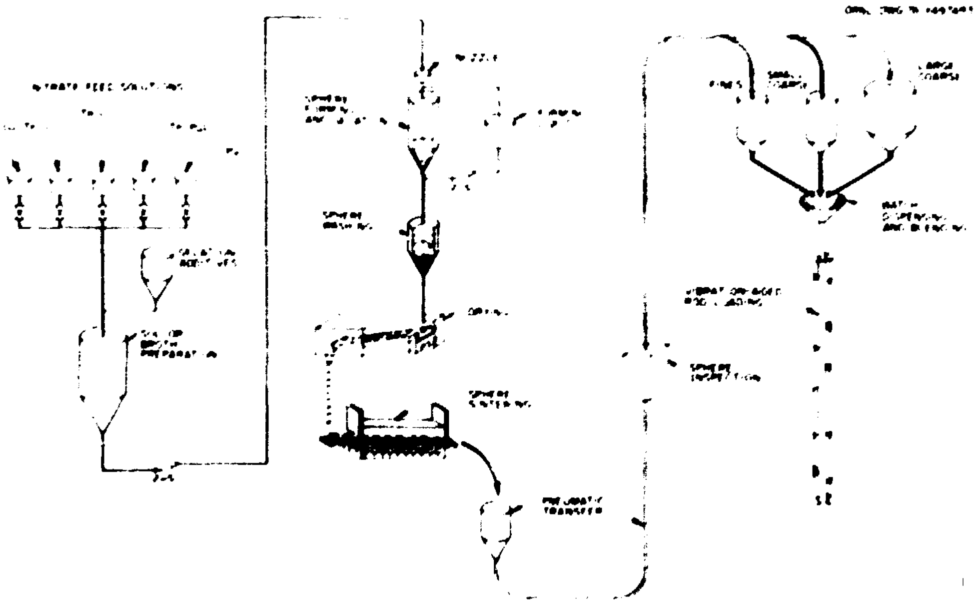

Fig. 1.2 Gel-Sphere-Pac Process

The original interest in gel-sphere-pac derived primarily from two factors: (1) the improved handling procedures possible with liquids and free-flowing spheres over the powder-pellet method (see Fig. 1.3) and (2) the versatility of the gel-sphere processes in being able to handle U, Th, Pu, and mixtures thereof.

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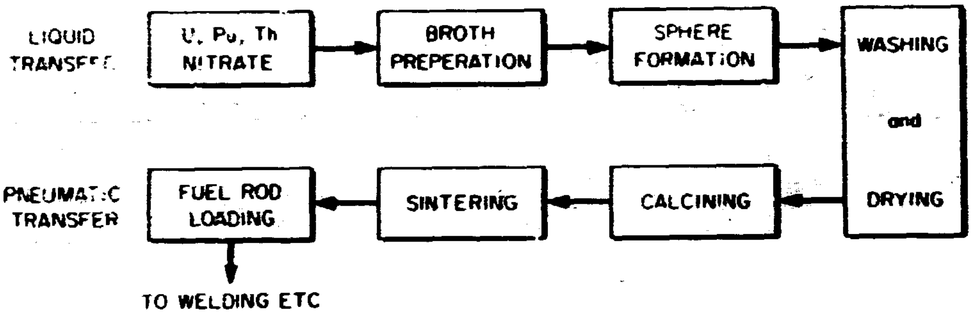

Fig. 1.3 Gel-Sphere-Pac Fabrication Employs Liquids and Free-Flowing Solids, which can be Handled in Closed-Pipe Systems.

Other fabrication benefits are: (3) the dust-free operations involved, which are cleaner and result in less operator exposure; (4) simpler mechanical operations, which are more amenable to remote operation and maintenance; (5) lower sintering temperature, because the small crystallites produced in the gels sinter more easily to a high density; and (6) easier conversion of mixtures to solid solutions than with powders.

In addition to the above fabrication benefits, sphere-pac also provides potential performance benefits in that less fuel-cladding interaction has been observed in experiments done so far.

1.2 HISTORICAL

The gel-sphere concept was invented by the catalyst industry over 20 years ago, while sphere-pac was conceived at ORNL sometime later. 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 particulate fuel for breeder reactors was terminated. The state of the technology at that time was thoroughly reported in program and topical reports, in symposia proceedings,[1-3] and in the completion report for the breeder fuel project referred to above.[4] At that time, U.S. attention focused on the preparation of urania sols that were gelled by water extraction, while European labs were looking at the chemical gelation of solutions of uranyl ion; sphere handling techniques were still relatively unsophisticated.

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 fuels for the High-Temperature Gas-Cooled Reactor. Extensive progress was made regarding sphere formation processes, control of sphere size, and sphere handling, transport, and inspection.[5,6] 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: (1) improvements in processes to produce large spheres of UO_2 by the use of uranium (VI), gel support via added organics, and chemical gelation by precipitation with ammonia; (2) continuation of irradiation testing; and (3) application of the carbide route to U,Pu for fast reactors. Most of the recent foreign work has not been reported in the open literature.

A related but distinctly different loading method called "vi-pac" has also been used. In this process irregular fragments or shards of ceramic fuel material are loaded into fuel rods and compacted by means of high-energy vibration. Shards were originally made by sol-gel processes applied to bulk materials (i.e., spheres were not formed). This approach was successfully used to fabricate 1000 fuel rods[7] but did not have the full benefits of sphere-pac — notable, ease of handling, dust-free operation, and low-energy packing. However, a major incentive, even at that time, was to avoid making pellets under remote conditions, and it was this requirement for thorium fuel cycles that prompted the early work in sol-gel technology.[8] Vi-pac fabrication is being pursued again using crushed high-density UO_2, but this work is directed to possible benefits in performance during irradiation in power reactors and will be supplanted by sphere-pac fuel when the spheres are available.[9] High-energy vibration has also been used with spheres where the smallest sizes were not free flowing, but again, the full benefits of sphere-pac were not realized, even though high densities were attained and good irradiation performance was achieved.[10]

1.3 PRESENT PROGRAMS

The renewed U.S. interest in gel-sphere-pac in 1977 came from two directions: the concern over nonproliferation-type flowsheets, which pointed toward fully remote refabrication, and the desire for improved fuel-cladding behavior to allow more severe thermal ramping during reactor operation.

This report was prepared with funding from the Department of Energy, Division of Nuclear Power Development under its Fuel Refabrication and Development (FRAD) Program, which is administered by Battelle Pacific Northwest Laboratories and is directed towards light-water reactors.[11] A similar study, but directed towards advanced (breeder) reactors, was also done at ORNL for DOE, Division of Reactor Research and Technology (RRT).[12] The FRAD program is supporting a major gel-sphere-pac development effort at ORNL, which has been under way since June 1977. RRT is supporting several smaller programs at ORNL, aimed at providing the basis for a gel-sphere-pac demonstration.

The HTGR Recycle Development Program,[6] which has supported work on the fabrication of spherical particles for many years, is currently funding work on the preparation of dense microspheres of mixed UO_2–UC_2 which will be required for the medium-enriched flowsheets proposed under various nonproliferation scenarios. Previously, HTGRs used highly enriched uranium for the fissile fraction, and the reference recycle flowsheet used a resin process to prepare these microspheres, which are a mixed oxide-carbide of intermediate density.

The Fuel Performance Improvement Program,[9] administered by Consumers Power Co. for DOE-NPD, is testing several alternative fuel forms, including sphere-pac. ORNL is providing dense urania microspheres to Exxon Nuclear Company, where fuel rods are being fabricated for irradiation in the Halden and Big Rock Point reactors.

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2. PREPARATION OF CERAMIC FUEL SPHERES BY GEL PROCESSES

Ceramic fuel sphere preparation by gel processes has been under development for almost 20 years. The concept known as the sol-gel process originated in the U.S., where active development was pursued until 1972. At that time the U.S. fast reactor program concentrated on pellet fuel and the government dropped support for sol-gel. However, several foreign countries continued gel-sphere preparation, are presently quite active in this area, and have made significant contributions to gel-sphere technology.

Throughout this gel-sphere development period three basic processes emerged, each dependent on a different approach to achieve sphere gelation. These processes are:

1. water extraction gelation — developed at ORNL in the U.S.,
2. external chemical gelation — developed at SNAM Progetti in Italy,
3. internal chemical gelation — developed at KEMA in the Netherlands.

The basic steps in each of these processes are generically the same. These are sol or broth preparation, sphere formation and gelation, washing (for internal and external gelation only), and drying, calcining, and sintering. However, as described in Sects. 2.1 through 2.3, different methods are used to accomplish each step. Water extraction gelation uses an organic alcohol to dehydrate droplets of sol until they solidify (gel). External chemical gelation uses either gaseous or dissolved ammonia to externally gel droplets of broth. Internal chemical gelation uses the formation of ammonia (as a decomposition product) to internally gel droplets of feed.

Water extraction gelation was developed for reactors requiring fuel spheres no larger than 600 μm. Very little development has been focused on the large sphere-pac size (>800 μm). However, this process appears impractical for such large spheres (i.e., 600 μm represents an upper limit for the applicability of this process). However, water extraction may have some advantages in preparing the fine (<100 μm) sphere-pac fraction. The other two processes (external and internal gelation), on the other hand, have been demonstrated to have advantages in preparing the large fraction. All the processes have been used to prepare the medium coarse (200–350 μm) sphere-pac fraction.

The following sections of this report describe in detail the three gel processes for preparing ceramic fuel spheres; the current status of each process flowsheet step is presented, equipment experience with scale-up and remote application is described, and the research and development needed to bring gel-sphere technology to a state where commercialization can be carried forth are presented. In these discussions you will note that water extraction is discussed in significantly greater detail than both internal and external gelation. This situation arises because the ORNL staff (having developed this process) has a much greater depth of knowledge of this process than could be acquired for the other two processes from the literature and personal communication.

2.1 WATER EXTRACTION GELATION — 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 (including compatible sol preparation procedures) were invented or developed at the Oak Ridge National Laboratory.[1,2] 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 addition, most of the development for the water extraction gelation process was directed at reactor concepts requiring fuel spheres no larger than 600 μm. This sphere size represents an upper limit for its applicability.

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 spheres;

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, while 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 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 our 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 microspheres 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.

2.1.1 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 may 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(IV), and uranium(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 by condensation;
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.

2.1.2 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 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.

To form good spheres, conditions must be selected so that mass transfer of the water in the organic liquid outside the drop is 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 is completed.

2.1.3 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 (ThO_2, UO_2, PuO_2), and most of this material (alcohol, H_2O, NO_3^-) is removed by volatilization below 220°C. The chemical gelation processes 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 the gel 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. Products containing uranium must be treated with H_2 at 1150°C (usually Ar-H_2 mixtures for safety) to complete the reduction to UO_2.

3. 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.

4. 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 in the gel makes drying of high-nitrate gels very difficult.

5. 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 using 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.

2.1.4 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. 2.1.1. Thoria sols have also been prepared by 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 at ORNL to prepare ThO_2 spheres use hydrothermal denitration in a rotary denitrator for sol preparation.[3,4] 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 the 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.

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[5] to produce dispersible ThO_2 at the rate of 45 kg/h (100 lb/h). 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 fluididized-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.

2.1.4.1 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.[6]

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 of distortion.[6] 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. Generally used still flow rates are 100 to 150 times the flow rate of the sol, so that the steady-state water concentration of the 2 EH is between 1.0 and 1.5 vol %.

2.1.4.2 Sphere Drying and Sintering

Drying and sintering of the ThO_2 spheres involve some complex physical and chemical changes. The density of the gel spheres is 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.[7] 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) down 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 U(VI) if present lower the autoignition temperatures and act as oxidizing agents, which can cause exothermic reactions even in the absence of air. The ThO_2 spheres prepared from hydrothermally denitrated ThO_2 powder are the least troublesome 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.

2.1.5 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. Thioxotropic 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) were the largest practical.

2.1.5.1 Preparation of Sols

To describe the preparation of UO_2 spheres, two one-week demonstration runs will be discussed.[8] 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[9,10] 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 lives 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 uranium 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.

2.1.5.2 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,[11] and the temperature of the 2EH was 50 to 80°C in the nonfluidized column (vs 25 to 35°C for the fluidized columns). 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 spheres 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[12] 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.

Heated 2EH is supplied to the top of the column, and the temperature decreases down the column as heat is lost to the surroundings. This temperature gradient is favorable since it gives rapid extraction of water at the top, where the sol is fluid, and slower extraction at the bottom, where gelation occurs. An 8.5-m (28-ft) column requires a 2EH temperature of 80°C to prepare 210-μm fired spheres from a 1 *M* UO_2 sol.

2.1.5.3 Drying and Sintering

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

<u>Drying</u>:

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;

<u>Sintering</u>:

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. From 0.5 to 1 g of steam was used 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 to minimize 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 was characteristic of the furnace; however, faster cooling, as high as 20°C/min or higher, would not affect the spheres. Use of an oxygen-free atmosphere was necessary during cooling because any O_2 present would oxidize the UO_2. The dense UO_2 spheres were 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.

2.1.5.4 Results and Material Balances

The size distributions of the calcined spheres produced during a demonstration run is shown in Table 2.1. The nonfluidized sphere-forming column was operated continuously. The production rate for the run was approximately 2.9 kg UO_2/d.

Table 2.1. 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	8556.2	1066.5	35.8	25.2
% of grand total	12.8	8.3	69.4	8.9	0.3	0.2
			86.8			

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[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.

Some of the chemical and physical properties of the calcined spheres are as follows: density, 97 to 100% of theoretical; 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 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 (see Fig. 2.1) were round, and cracking and surface imperfections did not represent a problem.

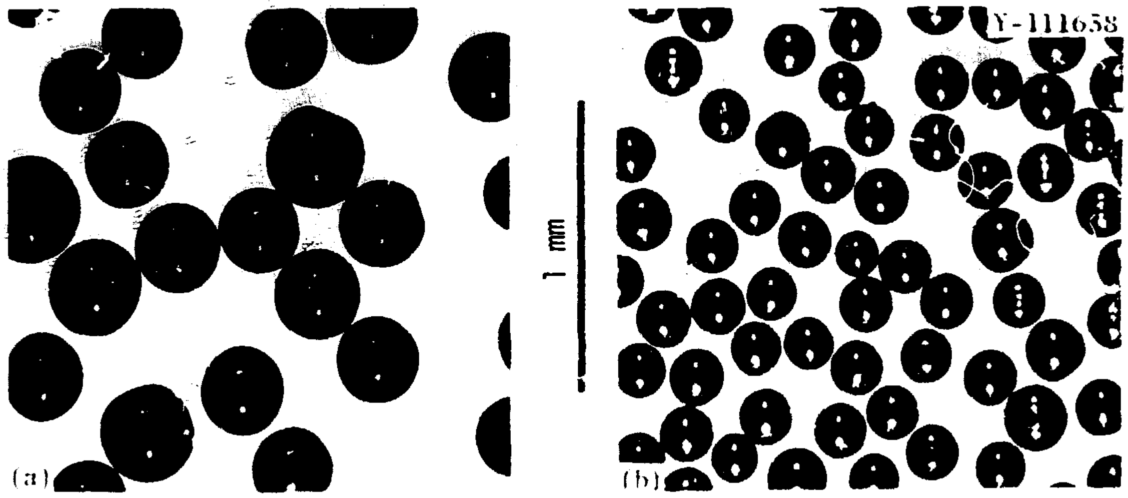

Fig. 2.1. Spheres of UO_2. (a) Gel spheres dried at 170°C in steam-argon. (b) Spheres calcined for 4 h at 1130°C in Ar-4% H_2.

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

2.1.5.5 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 a uniform reduction, and 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.

2.1.6 Application to $(Th,U)O_2$

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

1. Mix ThO_2 sol from hydrothermal denitration (Sect. 2.1.4) with UO_2 sols (Sect. 2.1.5). 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 greater 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. Method 3 is discussed in detail below.

2.1.6.1 Sol Preparation

The preparation of ThO_2-UO_3 sols by the amine extraction process[13,14] 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_2 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 d, 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.

2.1.6.2 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 gel. 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.

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 proper concentrations were not maintained during operation of the forming column, gel particles that are cracked, distorted, clustered, or surface-pitted are produced.

Past experience, largely involving the preparation of ThO_2 spheres, has shown that the periodic addition of surfactants to the 2EH gives satisfactory results for continuous operation of 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 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-μm-diam (sintered) size range.[6] This column and all the equipment in the column circuit can be readily adapted to remote operation.

2.1.6.3 Drying and Sintering

A steam atmosphere was used as the purge gas in the drying operation because it effectivly removed imbibed and sorbed organic materials and suppressed exothermic reactions.[7] Exothermic reactions of a magnitude sufficient to cause excessive breakage of the spheres occurred even with steam if a uniform temperature was 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.

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

The products had densities of 95 to 98% of theoretical, 20 to 40 ppm C, and O/U atom ratios of 2.001 to 2.020. The products were solid solutions of UO_2 in ThO_2, as determined by x-ray lattice parameter measurements. These gels had a good shrinkage pattern for ease of removal of the remaining volatiles. The density was only about 40% of theoretical at 850°C, and all the pores were 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.

2.1.6.4 Conclusions on $(Th,U)O_2$ 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. The column circuit is sufficiently developed to allow immediate adaptation.

2.1.7 Application to $(U,Pu)O_2$

All sols for preparing $(U,Pu)O_2$ spheres were made by blending UO_2 and PuO_2 sols. The U/Pu ratios were greater than 1 and the gelation and drying requirements were essentially those described for UO_2 sols in Sect. 2.1.5. 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 as 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 2.2 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 was 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 carried out in a single precipitation-filtration vessel 0.20 m (8 in.) in diameter with 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

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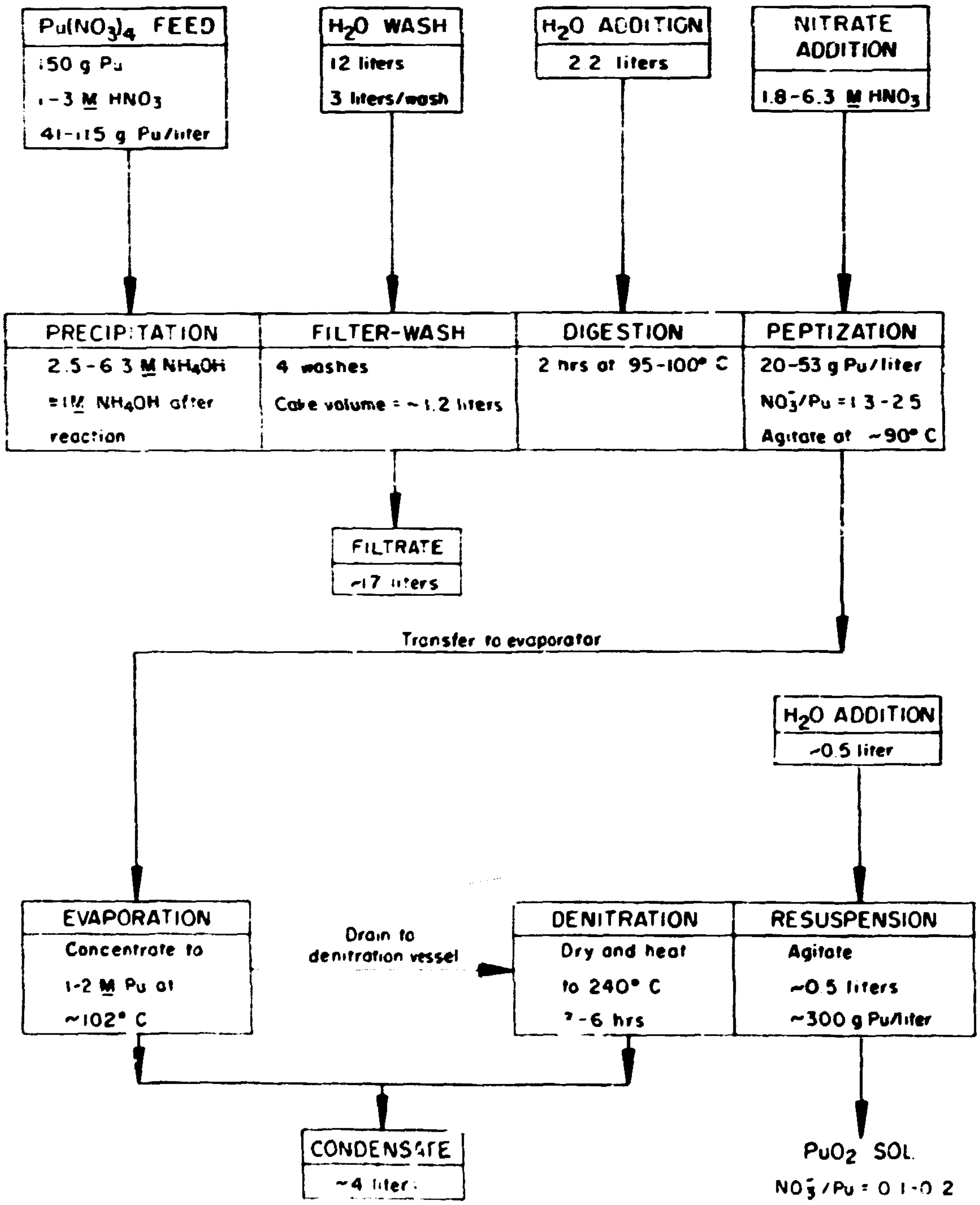

Fig. 2.2 Generalized Flowsheet for Preparing Plutonia Sol.

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 evolves 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. Though crystallite growth is desirable, the degree of agglomeration must be limited if a stable sol is to be obtained. Denitrated sol 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.

2.1.7.2 Solvent Extraction Preparation of PuO_2 sols

A solvent extraction process for preparing PuO_2 sols was developed.[15] The process (see Fig. 2.3) 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.

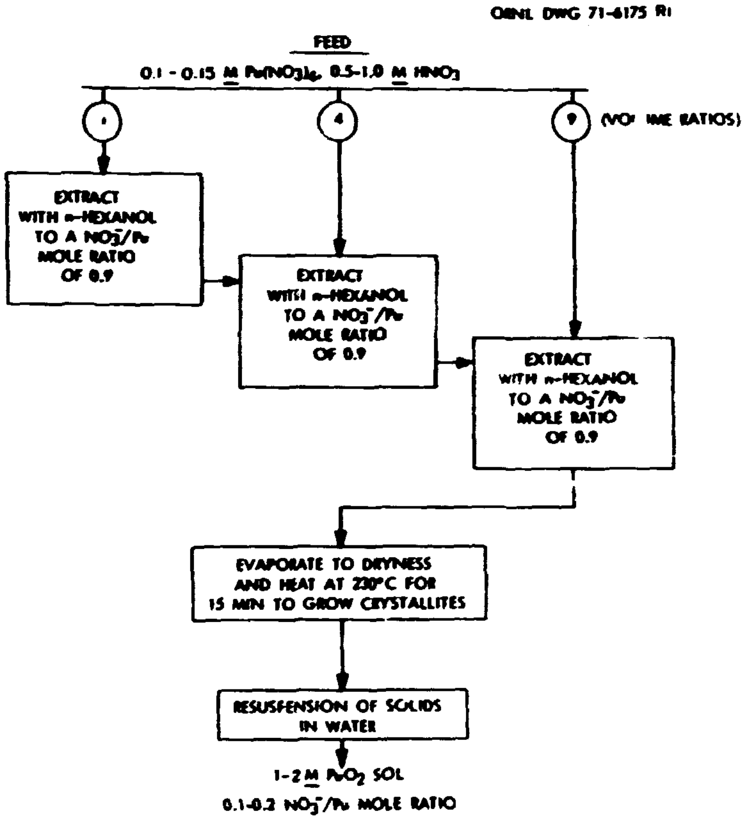

Fig. 2.3. Solvent Extraction Process for the Preparation of Low-Nitrate Plutonia Sol.

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. 2.3, 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 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 be either 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.[15]

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 upon 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.

Although these experiments were perfomed 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.

2.2 EXTERNAL CHEMICAL 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[16,17] in 1970. The distinguishing feature of this method is that a water-soluble organic polymer is added to a heavy metal solution or sol. The polymer supports the particle spherical shape while ammonia diffuses into the gel bead and precipitates the heavy metal. One of the most attractive features of the original method was that no pretreatment of uranium solutions was required. The necessary chemicals were simply added to the uranium solution and the spheres gelled. A simplified flowsheet for the external chemical gelation processes is shown in Fig. 2.4. Figure 2.5 illustrates the process flowsheet developed for continuous production using the SNAM process.

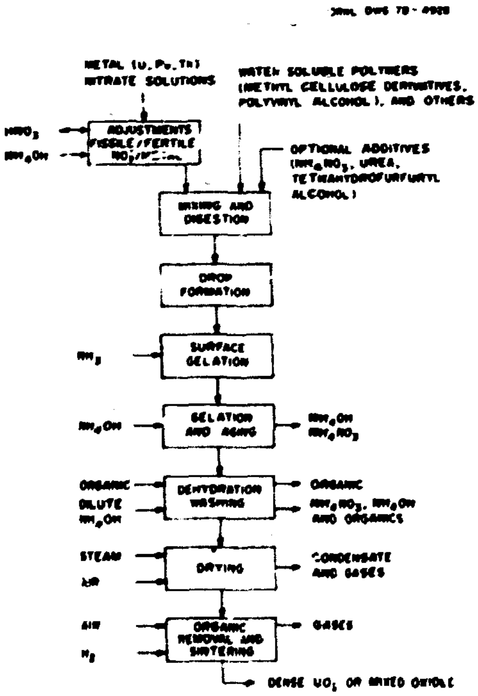

Fig. 2.4. Simplified Flowsheet for External Chemical Gelation Process.

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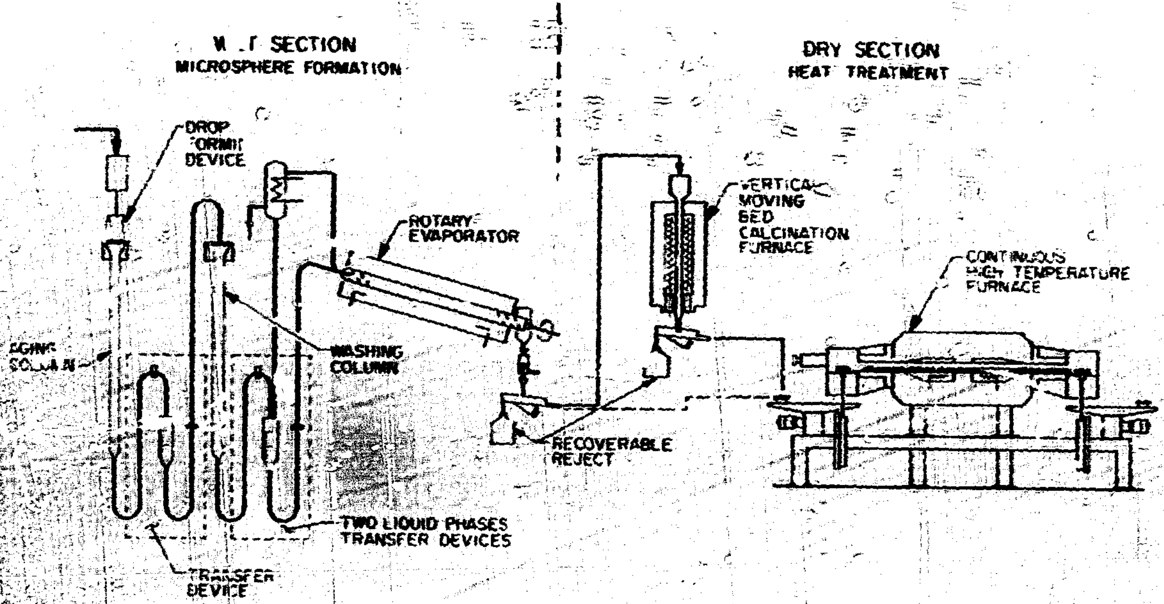

Fig. 2.5. Flowsheet of the SNAM Process. Based on G. Brambilla et al., pp. 191–209 in *Symposium on Sol-Gel Processes and Reactor Fuel Cycles*, CONF-700502 (May 1970).

Although the Italians developed the SNAM process, people at HOBEG* and KFA-Jülich in Germany and at Harwell in Great Britain use or used modified SNAM processes.[18–23] Figures 2.6 and 2.7 illustrate the process flowsheets developed by KFA for continuous production of thorium-containing spheres. Workers at KEMA in the Netherlands also used an external gelation method but had difficulty producing particles greater than 100 μm in diameter.[24–26] Thus they prefer their internal gelation process. In addition, KFA people are working toward elmination of the water-soluble organic polymers.[22,23] Workers at General Atomic Company (GA) in the United States use a proprietary external gelation process for sphere preparation.[27]

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*Hochtemperaturreaktor-Brennlement Gesellschaft.

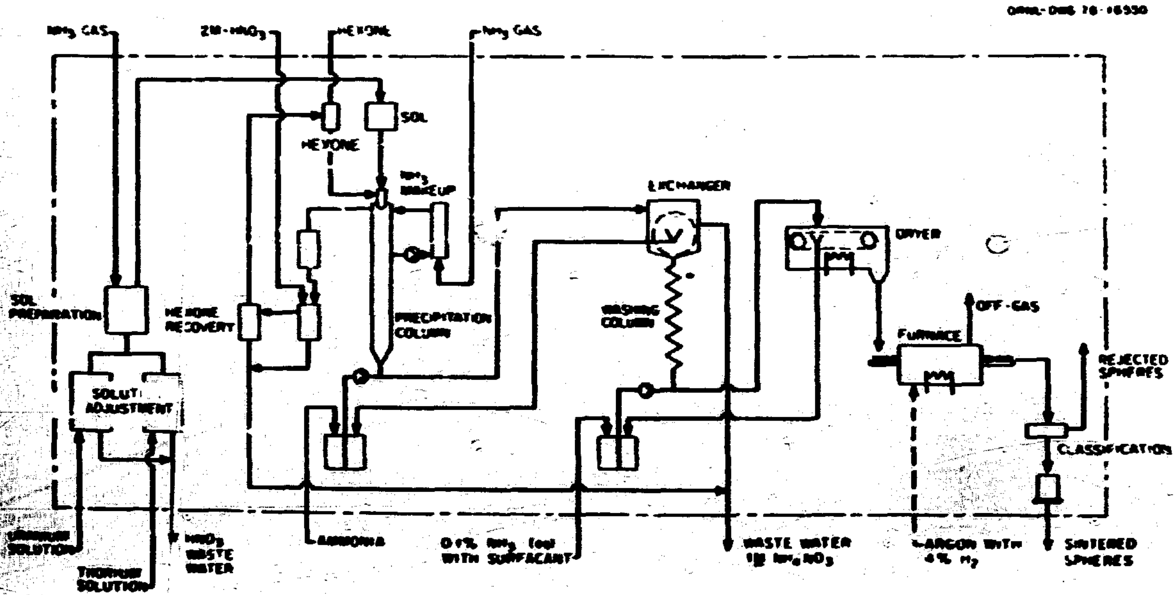

Fig. 2.6. Flowsheet of the KFA Precipitation Process Using Hexone. Based on E. Zimmer et al., *Trans. Am. Nucl. Soc.* 20: 591–93 (1975).

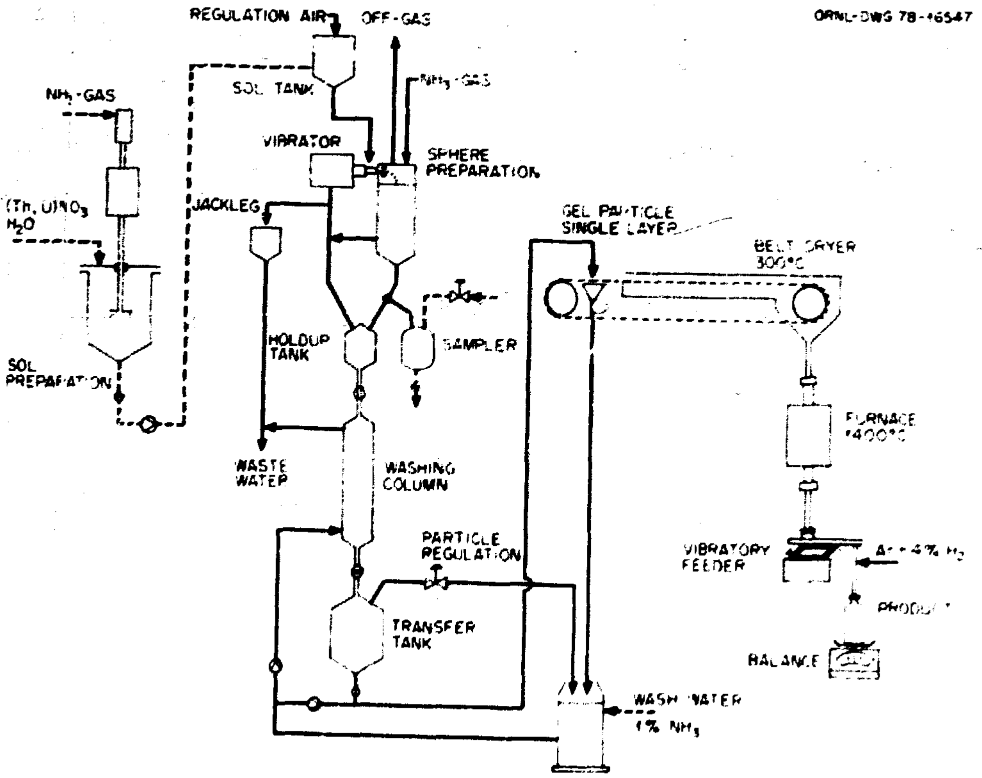

Fig. 2.7. Flowsheet of the KFA Precipitation Process Without Hexone. Based on H. D. Ringel and E. Zimmer, *Trans. Am. Nucl. Soc.* 27: 292–93 (1977).

The SNAM-type process development status was stated in the conclusions of a 1970 report:[17]

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.

The spherical shape is formed by dripping the sol or broth from a capillary, or 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 developed a foam technique.[28] 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,[22,29,30] but the Italians[29] 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,[31,32] special calcining to decompose the organic compounds (porosity is essential for escape of decomposition gases),[17,18,20–23,33–36] dissolution of these compounds during washing,[23] or, as mentioned above, elimination of the organic compounds from the process.[22,23]

Although other users have produced fires with their variation of the SNAM process, the Italians used the CNEN method to produce fines.[37–39] 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.[37–39]

2.2.1 Sol and Broth Preparation

As mentioned above, no pretreatment was required for preparing the uranium broth. However, the thorium was supplied as a sol and the plutonium as Pu(IV) polymer, although 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 is 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[40] 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 modifer 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 it 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 (TFHA), formamide, urea, ammonium 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 THFA, the Germans have done most of their work using PVA and various additives including urea and THFA, 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.[17,18,41]

2.2.2 Sphere Formation 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.[16] 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.[22,28] 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.[20,22,31,32,42] 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.[22,23,36] 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 last report[36] 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.[31,32,42] 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.[20–22]

The Italians used azeotropic distillation to dehydrate their beads after washing with water.[16,17] Carbon tetrachloride was recommended because of its nonflammability. This method of dehydrating was also designed for continuous production in pilot plants with capacities up to 30 kg/d.[17,43] The Italians preferred this method because it gave the beads a more open porous structure, important in calcining. Also, no sticking occurred while 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 organic liquid from the azeotropic distillation before calcination, although the spheres are clearly "let free" of the organic.[17] 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 that air drying and vacuum drying were satisfactory for combining dehydration and drying.

Workers at KFA have developed a belt drier for continuously drying (and dehydrating) the spheres in a monolayer at 250 to 300°C in air.[20,22,23,31,32,36,42] 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. After drying, reabsorption can be so rapid that spheres may absorb water and burst on cooling. Therefore, while the spheres are at 160°C their water content must be equilibrated 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 burst problem.

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.[20–22] The NUKEM method took several hours to dry the spheres of isopropanol.

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.[16,17,33,34] Harwell calcined in CO_2 at 50°C/h to 800 to 850°C (held for 4 h).[18,41] HOBEG calcined in air at 300°C. The NUKEM process calcined at 300°C for 5 h in air. 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 to 2500°C. The heating rates used ranged from 100 to 400°C/h. These sintering conditions led to greater than 95% of theoretical density (TD) for the particles.

Both SNAM and NUKEM processes used air in sintering thoria particles.[16,20] The KFA spheres could achieve 99% TD in 10 min at 1000°C but were sintered at 1300°C for several hours to produce a more stable product.[31,32,36]

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.[16,43] 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%.[16] Narrow size ranges of ±3% are obtained for average diameters of 150 to 1000 µm.[16,17,33] Batches of kilogram size have been produced in laboratory studies, while several hundred kilograms have been produced in a continuous pilot plant.[17,35] Shape separation is done after drying and after sintering on the continuous system, with less than 1% rejects in each case.[17]

Harwell reported[35] 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 were given for $(Th,U)O_2$ spheres and will be given in Sect. 2.2.8.

The Thoria sol for the KFA process is prepared by treating $Th(NO_3)_4$ with ammonia gas.[20,22,23,32,36,42] 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 at 99% TD. The laboratory-scale unit using this process produced 250 drops per second or 0.5 kg Th/h (based on 475- m-diam kernels).

In the process developed later by KFA, the sol was formed in much the same way. However, 2 to 3 *M* ThO_2 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% TD have been produced.

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 kernels. 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 dense (9.7–9.9 Mg/m^3) ThO_2 spheres 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.

The GA process for ThO_2 includes preparation of a dispersible ThO_2 powder, addition of a gelling agent, and sphere-forming and gelling in a gaseous ammonia column.[27] The dispersible ThO_2 is prepared by feeding a 2 *M* $Th(NO_3)_4$ solution into a fluidized-bed reactor at 400 to 500°C. The ThO_2 is collected and dispersed in dilute HNO_3 solution to form a 3.5 *M* sol. Following gelling, the spheres are collected in a 3% NH_4OH solution and then washed in a three-stage countercurrent wash column. The washed spheres are dried on a continuous belt with infrared heat, then sintered to 1100 to 1300°C to high-density (95 to 99% TD). Over 5000 kg of ThO_2 200 to 850 μm in diameter has been produced by this process.

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 THFA; 5 to 10 kg/m^3 Methocel, and 0.2 to 1 *M* HNO_3 (free).[16,17,33,43] The THFA 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% TD. Particles of 98.5% TD 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[41] gave the following two examples for producing UO_2 spheres. A broth was made containing 80 g $UO_2(NO_3)_2 \cdot 6H_2O$, 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 gelating 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[22] 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 spheres.

The HOBEG broth was composed of uranyl nitrate, PVA, other additives (including THFA)[21–23] 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% TD.

General Atomic, using a proprietary process, prepares UO_2 spheres by addition of complexing and gelling agents to uranium solutions, which are formed and gelled in a gaseous ammonia column.[27] The gelled spheres are collected in a 10% NH_4OH solution. They are then washed in a six-stage countercurrent column, and the water in the washed spheres is extracted in a four-stage alcohol column. They are then dried in a batch microwave dryer followed by low-temperature calcining to 600°C in a fluidized-bed reactor. Finally, the UO_2 spheres are sintered in a fluidized-bed reactor to 1700°C. Spheres between 200 and 350 μm have been demonstrated.

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 used in the same process discussed previously. A reducing atmosphere is used for sintering since uranium is present.

The Harwell process using Dextran was given in more detail in the following for mixed-oxide spheres.[35] "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-diam jet with ammonium hydroxide gave 3- to 4-mm-diam 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.[20] 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 in 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/d of spheres.

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.[21,22] 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 to 1700°C to 97 to 99% TD. The dense kernels 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 polymetric form by denitrating $Pu(NO_3)_4$ by solvent extraction.[16,39,43] 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 per cent 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.[17,34]

The SNAM process has been reported to have problems with making good sintered spheres containing plutonium.[22,23,29] 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.[41] 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), heated to 800°C in CO_2 at a rate of 50°/h, and held for 4 h. The calcined spheres (90% TD) 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% TD. 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 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 in diameter (std dev 2 μm) and coarse particles of 800 to 1100 μm. The goal is to achieve 100% yield.

2.2.10 Summary of Pilot Plants

The facilities discussed above can be used to produce more than one oxide sphere. The SNAM process has been carried farthest in its development to commercial scale, with designs for pilot plants up to 30 kg/d 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, but 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 2.2.

Table 2.2. 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	34
SNAM	Casaccia, Rome, CNEN	PuO_2, $(U,Pu)O_2$	3	34
SNAM	Springfields, BNFL	UO_2	20	34
KFA	KFA, Jülich	ThO_2, $(Th,U)O_2$	12	36
Harwell	Harwell, Berks. AERE	UO_2, PuO_2, $(U,Pu)O_2$	17	23
HOBEG	HOBEG, Hanover	UO_2, ThO_2, $(Th,U)O_2$	18	21
NUKEM		ThO_2, $(Th,U)O_2$	60–100	20
GA	San Diego, Calif.	ThO_2	240	27
GA	San Diego, Calif.	UO_2	24	27

2.3 INTERNAL CHEMICAL GELATION — J. M. Begovich

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 (often termed the KEMA* process) generally requires an acid deficient solution of the heavy metal corresponding to the oxide being prepared (see Fig. 2.8 for a simplified flowsheet). An ammonia donor solution, 3 *M* in urea and hexamethylenetetramine (HMTA), is mixed with the concentrated (∿3 *M*) heavy metal solution, with all solutions at 0°C or below. The resultant reaction mixture is pumped through a dispersion device that forms spheres, which

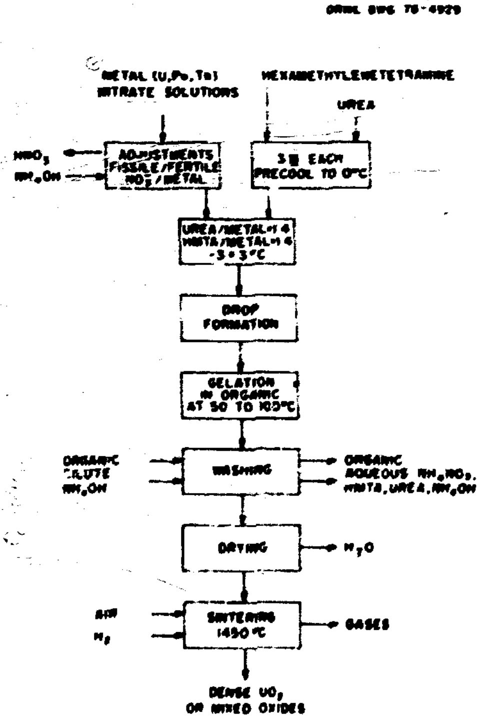

Fig. 2.8. Simplified Flowsheet for the Internal Chemical Gelation Process.

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*Keuring van Electrotechnische Materialen at Arnhem in the Netherlands.

are then gelled in a hot organic medium. The organic medium is then washed off with suitable solvent (e.g., CCl_4), and the spheres are washed with ammonia (NH_4OH). The spheres are then air dried, calcined, and sintered in a reducing atmosphere to 99% TD.

2.3.1 Broth Preparation for UO_2

The 3 *M* acid-deficient uranyl nitrate (ADUN) solution can be prepared[44] 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.

For method (1), moderate heating can increase the dissolution rate, but too high a temperature should be avoided since $UC_3 \cdot 0.8H_2O$ 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 a low temperature (–5 to 0°C) to reduce the decomposition rate of HMTA,
2. addition of urea to complex the uranyl ion (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). 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 at ECN Petten,[22] the urea and HMTA solution, kept at −5°C, was mixed with the ADUN solution, which was kept at about 2°C. The volume (and molar) ratio was 1.4 to obtain a broth with a uranium molar concentration of 1.25 and a temperature of −3°C. With this reaction mixture the as-formed gelled spheres undergo a linear shrinkage factor of 3.2 in being processed to sintered spheres of theoretical density. Thus, if final diameters of 1200 μm are desired, the initial gel spheres must have diameters of 3800 μm. This initial droplet diameter can be reduced if the broth has a higher uranium concentration.

Possible methods to achieve a high uranium concentration in the reaction mixture 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 ratio of HMTA and urea to uranium can be varied[45–48] 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.

2.3.2 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. In the hot liquid, the rate of HMTA decomposition overcomes the urea-uranyl ion complex and causes the drops to gel.[44] The role of the urea than 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.

Three sizes of spheres are required for Sphere-Pac fuel fabrication: large (800–1500 μm in diameter), medium (100–400 μm in diameter), and fine (10–70 μm in diameter). Formation of each of these size fractions is discussed below.

2.3.2.1 Production of Large Spheres[44]

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,[23] 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. Droplets formed this way had a size distribution with a standard deviation of 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 (bp) of 87°C, it is used 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 hard, smooth gel spheres and a good sintered product. However, the best product was produced in TCE. Use of either TCE or perc is advantageous since both are volatile enough for easy removal from the spheres. Chloride contamination of the final product does not appear to be a problem. A disadvantage of the perc is its relatively high density — the uranium concentration of the reaction mixture 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 Wurenlingen, Switzerland, as the organic gelation medium.[48] 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 allows gelation 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.

2.3.2.2 Production of Medium-Size Spheres[44]

To produce 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 aryl-substituted branched aliphatic hydrocarbons) at 80 to 90°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 a spinnerette was used.[23] A straight paraffin oil was used for this size fraction to give a low enough density to allow settling of the gelled particles.

The system used for the lar . size fraction could also likely be used for the medium spheres. Multiple nozzles may be required to obtain the necessary production rate, but vibrated two-fluid nozzles should be able to form the proper size droplets very uniformly.

2.3.2.3 Production of Fines[22,44]

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, which gave the proper size but with wide size distribution. 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. This is the method that has been used at ORNL.

2.3.3 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 ammonia.[22,23] 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.[23] 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.[23] Alternatively, CCl_4 could be used[48] to remove the organic before washing with NH_4OH. Enough NH_4OH was used[44] 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 the washing is monitored for completeness by conductivity measurements.[48]

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.[22] 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.

2.3.4 Drying

Following washing, the spheres are dried in air at temperatures ranging from room temperature to 170°C. KEMA[44] dried its spheres at 70 to 80°C. In the continuous process line at Petten the spheres were separated from the wash liquid and loaded onto trays, which then were placed in a moving belt dryer. 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 we have found it very convenient to dry in either of two ways: (1) overnight in a covered container in an oven, or (2) overnight, using vacuum to pull room temperature air through the bed. If the spheres survive the drying stage intact, they will normally not crack during the remaining steps. The rate of drying must be limited to allow the water time to escape the spheres.

2.3.5 Calcining and Sintering

The available information on calcining spheres made by the KEMA process is somewhat confusing. In a 1973 paper, Kanij et al.[44] states that they calcined in air at 450°C to remove the volatile organics. The heating rate was 200 to 300°C/h. They then 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. However, a 1970 paper[49] mentioned no calcining step; the spheres were transferred directly from air drying into an oxygen-free, dry mixture of N_2—20% H_2 at 1400°C.

Recent information indicates still another procedure in use at KEMA.[22,23] After drying, the spheres are heated to 500°C in a mixture of nitrogen and hydrogen. Then spheres are sintered in the reducing atmosphere of nitrogen and hydrogen at 1600°C, although 1500°C may be high enough. It was found to be important to avoid formation of U_3O_8 during calcining since this leads to porous UO_2.

Although KEMA has apparently decided to go directly to a reducing atmosphere after drying, in the continuous process at Petten an air calcination step at 350°C was used 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, with a design rate of 4 kg UO_2/h and 20 kg UO_2/shift.

2.3.6 Application to UO_2

Using the KEMA process, Kanij et al.[44] produced smooth spherical particles of 99% TD as measured with mercury at atmospheric pressure. 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 in diameter) 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 medium and fine fractions produced has not been disclosed; however, enough of each was produced to load fuel rods for irradiation testing.[22]

The Hydrolysis Process,[20,47,50] 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% TD. Intermediate sized spheres 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 spheres after being calcined and sintered in hydrogen at 1200°C to 1700°C had diameters of 210 ± 30 μm and 98% TD.

The Transuranium Institute at Karlsruhe has also made 100- to 1000-μm-diam UO_2 spheres using the general KEMA process.[45,46] The broth 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 the ratio of HMTA to urea was changed much 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 spheres were dried either in air at room temperature or under vacuum at elevated temperature with no apparent difference to the final product. The spheres were then sintered and reduced 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% TD were obtained with a carbon content of less than 200 ppm. If the spheres were sintered to a temperature of only 1200°C, densities were 96 to 98% TD. Also, UO_2 spheres have been prepared by iron-curtain countries[51] using the internal gelation process.

2.3.7 Application to Other Oxides

Apparently the internal gelation process has never been applied to ThO_2 and only briefly applied to $(Th,U)O_2$ at KEMA.[49] 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.

The Dutch planned to use the same chemistry for uranium-plutonium mixtures that they used for pure urania.[22,23] They did enough work with plutonium at Petten to allow its inclusion in their patents. Plutonium was added to the ADUN used for the large 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, Jülich, hydrolysis process was modified[47] for application to the production of $(U,Pu)O_2$ spheres over the size range of 100 to 1000 µm. The experimental work was actually performed at EIR in Wurenlingen, Switzerland. The process was similar to that described by EIR.[48] 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 with a single-phase structure were generally obtained. 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.[52] Uranium and plutonium nitrate solutions were mixed in the ratio desired and denitrated by the addition of formaldehyde. After urea and HMTA were 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% TD with less than 2% being rejected as scrap. The standard deviation for the 1000 μm size was 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.[45] 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 a NO_3^-/Pu molar ratio of 1.5. After a few hours of heating at 90°C and stirring, a dark green sol was fomed 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% TD, with carbon contents of about 40 ppm. The process was capable of producing spheres with diameters ranging from 60 to 1500 μm.

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2.4 APPLICATION OF DROP FORMATION PROCEDURES TO MEET GEL-SPHERE-PAC REQUIREMENTS — P. A. Haas

For a given feed lot the amount of metal oxide in a product sphere is determined by the size of the sol or broth drop before gelation. Formation of the drops is important to the yield since oversize and undersize spheres constitute the principal off-specification material. The average drop diameter must be predictable and controllable so that the specified fired sphere size can be produced from sols or broths with different properties.

The capacities needed for development systems and production plants are generally in the range from 0.1 to 10 kg/h of product spheres. 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 feed through small orifices or capillaries. The formation of drops from these feed streams can result from several different mechanisms, the four most useful of which will be discussed separately below.

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

2.4.1 Drop Weight Mechanism

The slow formation of a drop from a wetted capillary 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 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 orifice.

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 capillary tip, d will be the outside diameter of the capillary 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 capillaries 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 to give a drop of 1.26 times the original diameter.

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 and 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.[53] 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 vibration energy inputs. 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 (problem 6). 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 match that of 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 (effective d) 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 an effective diameter smaller 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 capillary or to the liquid feed stream to the jet. The effects of the vibration are observed with a strobescopic light of the same frequency. The arrangement most commonly used at ORNL is shown as Fig. 2.9. A simpler nozzle

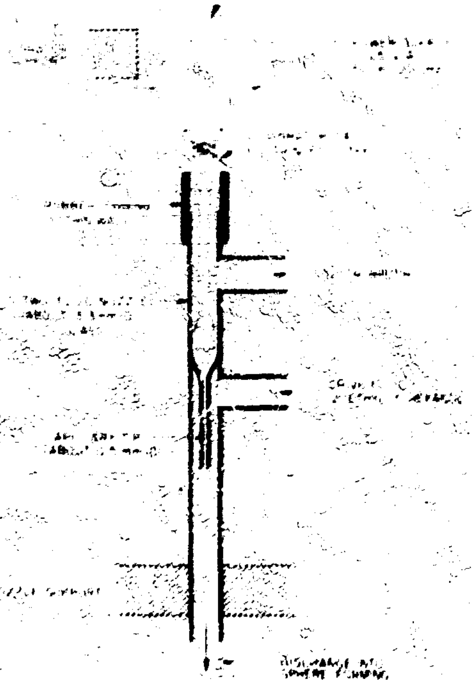

Fig. 2.9. Two-Fluid Nozzle with Vibration.

for forming drops in gas without a drive fluid is shown as Fig. 2.10. A single vibrator or a single drive fluid flow can serve multiple jets. However, jets are usually supplied by individually metered flows of sol

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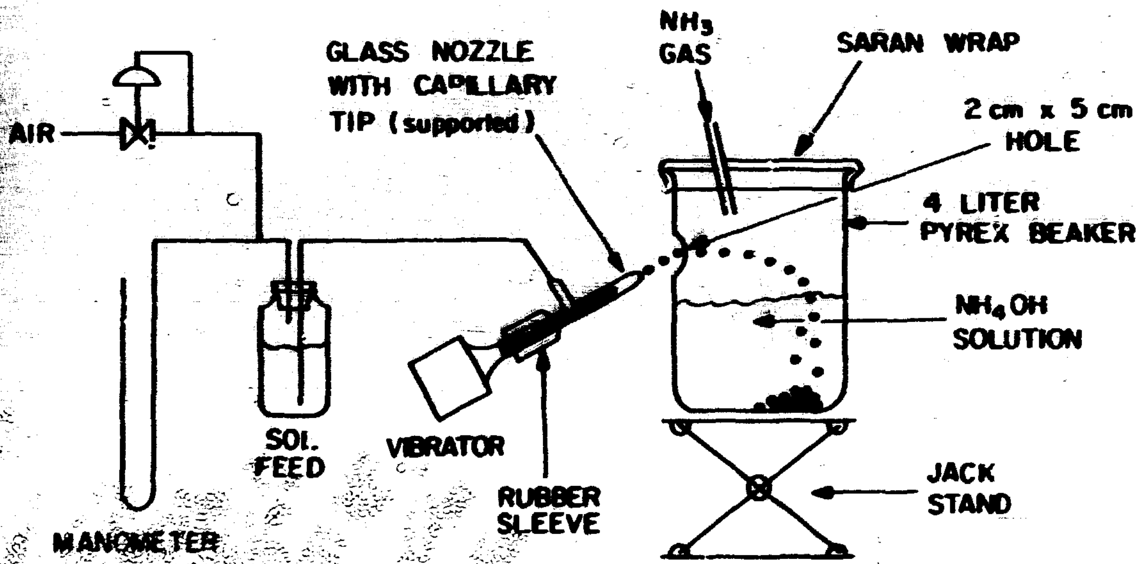

Fig. 2.10. Droplet Formation in Gas Without a Drive Fluid.

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:

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 shown in Fig. 2.10 by coupling it rigidly to the vibrator (axial motion).
4. move the capillary from which the jet discharges transverse to the axis [Fig. 2.11(b)];
5. apply an ac electrostatic potential to the jet [Fig. 2.11(d)].

All these can give a uniform breakup at frequencies near the natural frequency of jet breakup and are less effective as the difference from the natural frequency increases. The arrangement shown in Fig. 2.9 is

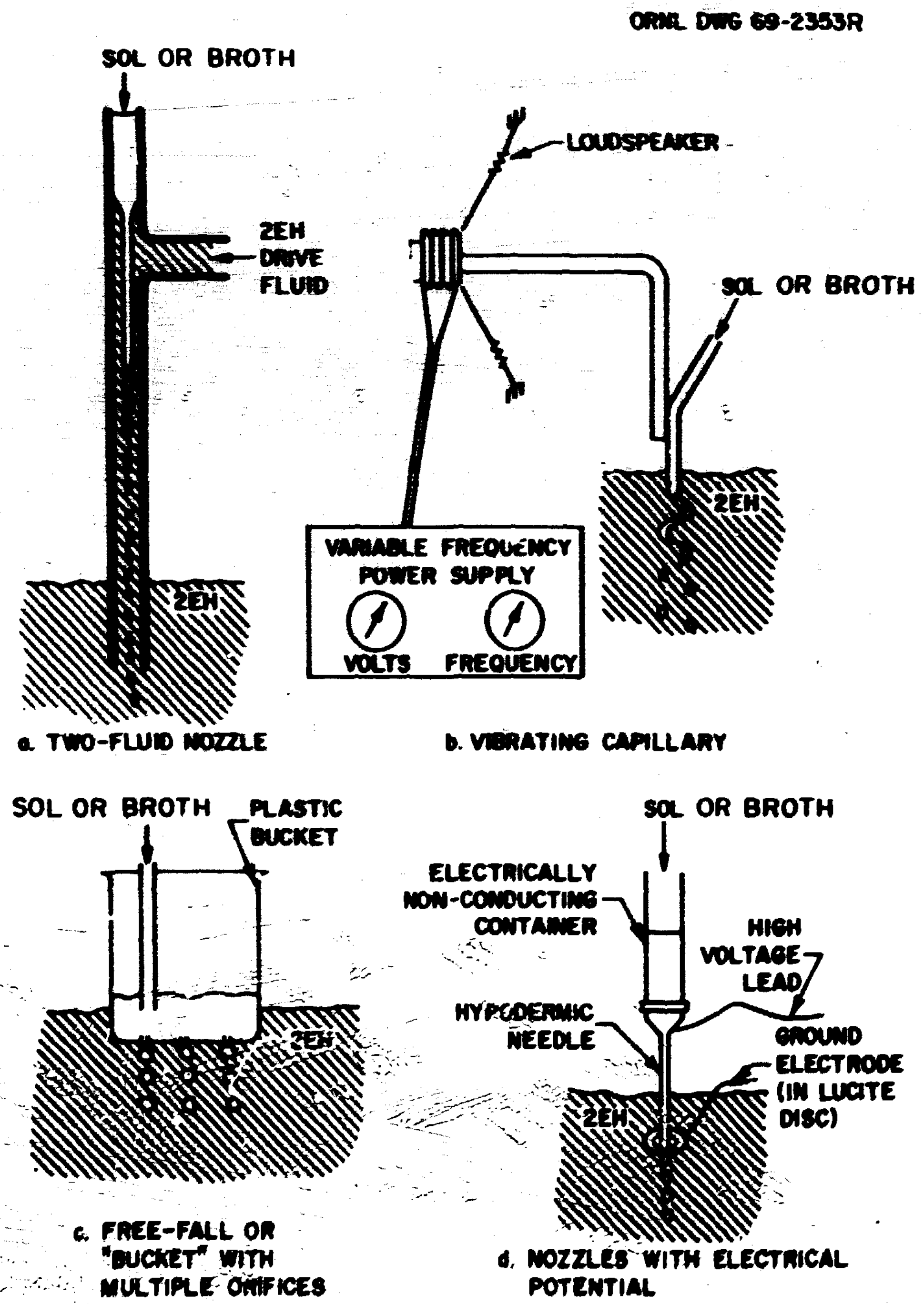

Fig. 2.12. Devices for Dispersing Sol or Broth as Drops in 2-Ethyl-1-Hexanol (2EH).

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 [Figs. 2.10, 2.11(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 (Fig. 2.10), the diameter of the jet is equal to the diameter of the capillary 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 feed flow rate. The centerline velocity for laminar flow is twice the average velocity. The natural frequency of breakup corresponds to jet lengths of 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 feed flow rate.

2.4.4 Turbulent Breakup in Two-Fluid Nozzles

Practical throughput 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, and may even be preferred, 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 calcining.

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 (i.e., channel inside diameter and fluid velocity). The average diameter is controlled by regulating 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 gives an advantage over spray nozzles or spinning disk atomizers in gas.

Results and correlations were recently reported by Karabelas[54] 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 had used for our data. Therefore, we now prefer the following relationship:

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

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 we use organic-broth interfacial tensions as follows to predict the drop sizes:

45 mN/m for TCE
15 mN/m for 2 EH
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).[11] From visual observations it appears that the differences are

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	39	26	19	∿14
Two-fluid nozzle (turbulent flow)	76	28	11	∿ 4	< 2

even greater at $0.2d_{50}$; however, we do not have numerical measurements at the small diameters. 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. 2.12.

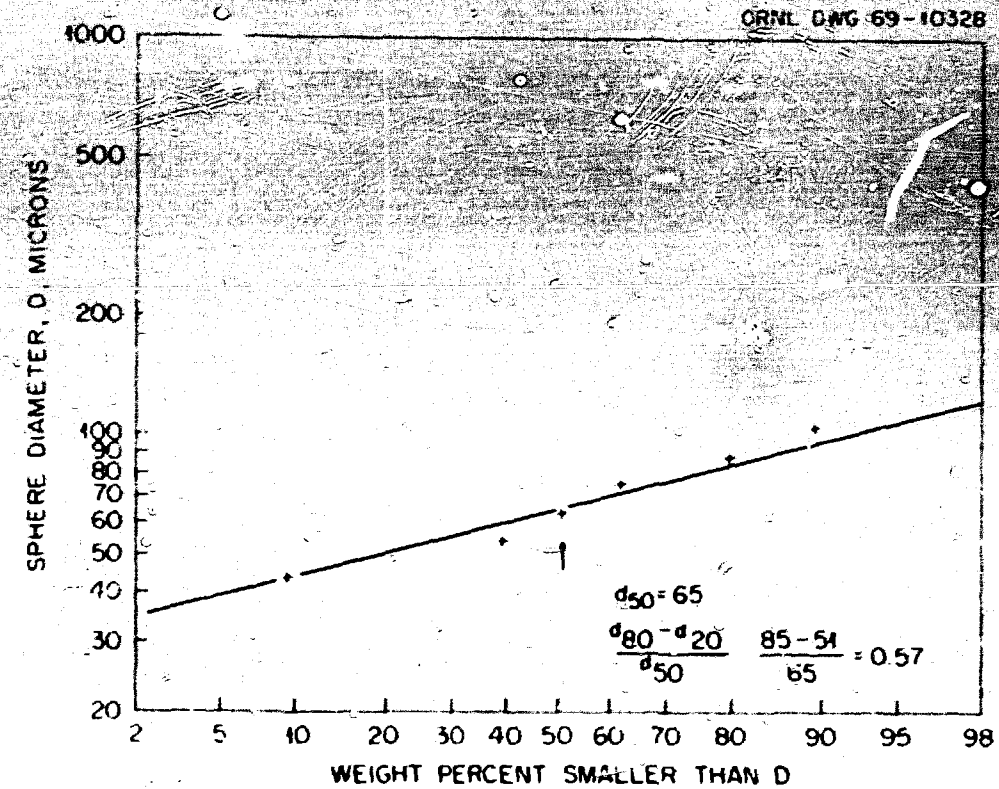

Fig. 2.12. Size Distribution of a Sample of ThO_2 Spheres Prepared by Nonlaminar Flow Dispersion of a Two-Fluid Nozzle.

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 require 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 ($\ngtr 600$ preferred) to avoid undesirable turbulent effects at the sol capillary tip. Because 2EH is less viscous and less dense than trichloroethylene (TCE) or tetrachloroethylene, use of 2EH allows about 20 times the velocity and 20 times the capacity at the same Reynolds number.

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

1. Large product spheres (above 600 μm in diameter) 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. Laboratory preparation of uniform 100-μm-diam product is practical, but production-scale operation is not. The calculated capacities per nozzle are 7 to 150 g U/h for 150-μm spheres.

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

5. For a turbulent nozzle, 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.

Table 2.5. Calculation of Allowable Nozzle Flow Rates

Diameter, µm		Drive Fluid ID (mm)	Dense UO₂ Sphere Diameter (µm)	Calculated Nozzle Capacities for Laminar Flow					
				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[a]	Sol Capillary			Sol Capacity (liters/h)	Capacity[b] (g U/h)	Velocity (m/s)	Capacity[b] (g U/h)	Velocity (m/s)	Capacity[b] (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 a solution concentration of 300 kg U/m³ (g/liter).

[b] These are conservative calculated values, which, in practice, were found to be low by a factor of at least 5. (For 2EH, the calculated and experimental values are in reasonable agreement.) Note also that for the smallest sizes (75 and 38 µm), a multistage turbulent nozzle is used, which has a very high capacity.

2.5 GEL-SPHERE CALCINATION AND SINTERING — A. E. Pasto

This section describes the various heat treatment techniques applied to assure high-density chemically acceptable oxide 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, in the case of materials containing uranium or plutonium, to produce the desired oxygen-to-metal ratio. Inasmuch as sintering and reduction ordinarily occur simultaneously, these latter two steps will be considered as one operation.

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.

2.5.1 Phenomenological Considerations

As indicated in preceeding sections, the "recipes" for producing dense spheres 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 requires a "shotgun" approach. In this approach as many variables as possible are evaluated and whatever works is adopted. What has happened during calcination and sintering is assessed 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 in the spheres during heat treatment. These are as follows:

Elimination of volatiles (H_2O, NH_3, NO_3^-, organic compounds)
Crystallite rearrangement
Crystal growth
Phase changes (e.g., $UO_3 \rightarrow U_3O_8 \rightarrow UO_2$)
Initial-stage sintering
Final-stage sintering

These 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[20,50,55,56] between 80 and 220°C (physically combined) and 350 and 450°C (chemically combined) for UO_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.[14,56] 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[57] 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 on sintering. 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 has been studied for ThO_2 by Bannister[58] and for UO_2 by Suzuki et al.,[59,60] Landsperský et al.,[57,61] and Breschi et al.[62] Bannister found that for ThO_2 gel produced by the

ORNL water-extraction technique, the first 4% of the linear shrinkage was due solely to elimination of volatiles. After this, the remainder of the shrinkage was controlled by grain boundary diffusion of thorium. Crystallite 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 300 to 600°C, the material was completely transformed to UO_2, in agreement with other work[34] 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 homogenous product.

Landsperský's preliminary investigations covered UO_2 produced by the KEMA process and KFA-Jülich's H-Process. Calcining in air led to removal of most volatiles in the range 200 to 250°C, which was considered to be critical range of 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 to 450°C. 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.[55] 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.[60]

In more detail, Landsperský et al.[57,63] further investigated KEMA and H-Process UO_2. Drying in air at both room temperature and 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 too much above 500°C converted UO_3 to U_3O_8.

Landsperský's sintering study[63] on the same materials in Ar–4% H_2 elucidated an important point. With spheres that had been air dried to 220°C, then sintered in Ar–4% H_2, 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 that 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[34,50,64] have used this technique to prepare sintered microspheres 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, crystallite 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 mass transfer process, usually diffusion of the ions 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.

Summarizing this section, densification of particular fuel spheres is a process not amenable to calculation or even prediction. The many variables in processing before sintering may lead to numerous structures and chemical constitutents being present. The optimal sintering routine must be developed for each material variation. Primary sintering process variables are drying and calcination temperatures, heating rates, and atmospheres. Primary preparation process variables include amount and type of additives remaining after washing, crystallite size of the gel, and structure of the crystallites and their attendant pore volume and shape. The "recipes" presented for obtaining high-density spheres in previous sections were determined by trial-and-error techniques guided by consideration of the described phenomena.

Inasmuch as the sintering "recipes" for the various processes have been presented previously, they will not be reiterated here.

2.5.2 Continuous Processing

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 at ORNL for remote use.[65] For large-throughput operation, a continuous vertical tube moving-bed calciner was developed by ORNL.[66] 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 of the moving charge was that interparticle sticking, a potential problem particularly with fines, could be avoided. A similar device was used in a SNAM process pilot plant.[17,43]

The KEMA process has been scaled up to pilot-plant operation.[55] 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[20] for $(U,Th)O_2$ by HOBEG and KFA in their production plant, turning out 4 kg heavy metal per hour.

The SNAM[17,43] 8-kg/d pilot plant used a moving-bed calciner (as noted above) followed by a continuous-throughput horizontal sintering furnace (pusher-type). Apparently particle sticking was not a problem during sintering. Thus, it appears that large batches can be produced on a semicontinuous or continuous basis by use of available technology.

2.6 PRODUCT SPHERE CHARACTERIZATION — A. E. Pasto

Characterization of the sintered spheres is necessary to ensure that product specifications are met. Sphere quality must be verified for composition, impurities, density, sphericity, oxygen-to-metal ratio, gas content, microstructure, strength, and size. Development of technique for characterizing $(U,Pu)O_2$ coarse and fine spheres has been pursued previously at ORNL.[67] Results of this five-year fuel development program are available to help guide current work. Further discussion of product properties needing characterization and, where applicable, methods for determining these is presented below.

2.6.1 Density

Attaining the high smear density required in LWR rods with sphere-pac fuel requires spheres that are nearly theoretically dense. The fuel density value that needs to be determined is the sphere bulk density. This is readily determined on spheres larger than tens of micrometers in diameter by immersion in mercury at near atmospheric pressure, since at this pressure pores larger than about 12 μm in diameter will be penetrated. For smaller spheres, the interparticle pores may be smaller than 12 μm, so that elevated pressures are required to penetrate them with the mercury.

Other techniques include immersion in water or other fluids. However, care must be exercised in the use of such techniques since open pores of nanometer size can be penetrated and falsely high sphere bulk density values obtained if such porosity is present.

Another technique for sphere density determination involves 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 spheres can be continuously removed, measured, and returned to the line, yielding density and size data simultaneously.

2.6.2 Size and Shape

Sphere size may be measured by several techniques, the choice depending on the expected use of data obtained. Since precise size and size distribution data are not critical for rod loading requirements, size is probably best measured by continuously screening the materials as they leave the sintering furnace. This assures size range control of the product suitable for sphere-pac loading. However, for more precise size and distribution data, to provide feedback to the sphere forming operation, other techniques are desirable. The best techniques yield instantaneous measurements on individual particles chosen at random from a given process step, and return them to the stream. Such a device, using a light-blockage technique, has been developed at ORNL.[68] It is readily applicable to the large and medium spheres currently being produced, but may not be useful for fine spheres (<75 μm). With this technique individual particles are dropped through a tube, past a light beam shown in Fig. 2.13. The shadow created by the particle is

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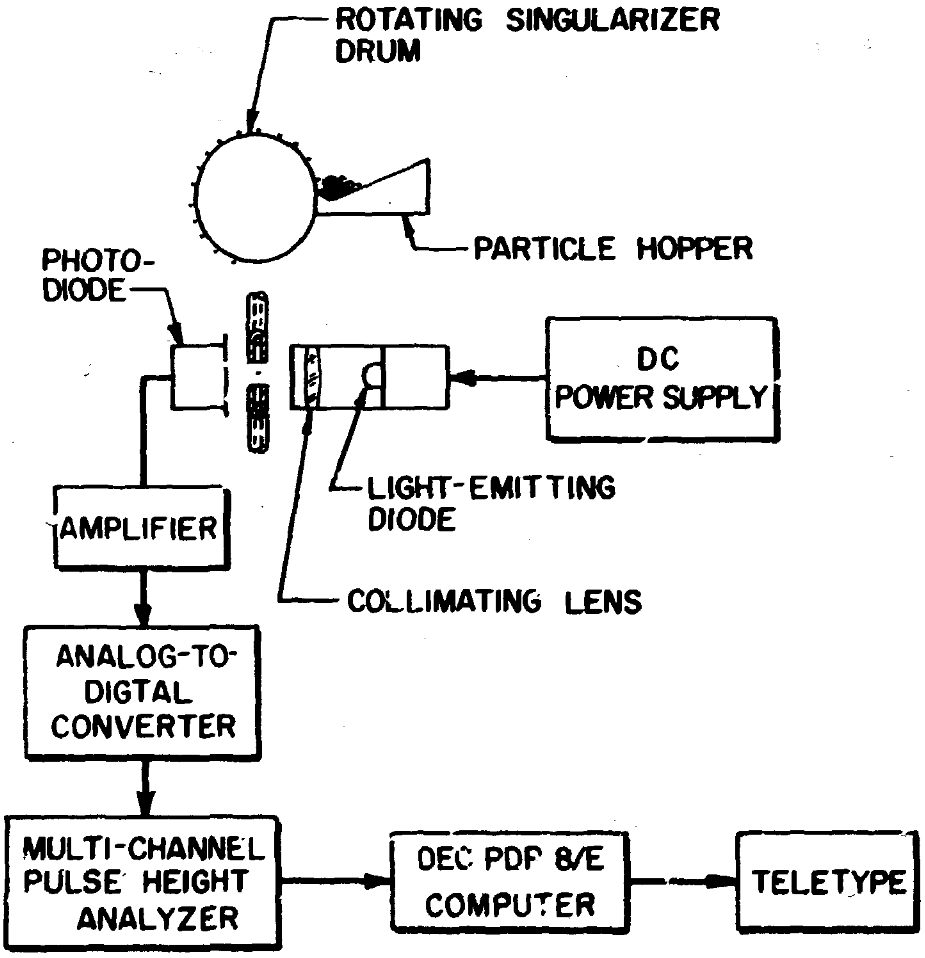

Fig. 2.13. Electronic Data Collection System for the Particle Size Analyzer.

detected by a photodiode. The drop in the detector's output is converted to a voltage gain, amplified, digitized, and stored as a single count in one channel of a multichannel pulse height analyzer. Particles are singularized by a rotating evacuated drum and analyzed at rates up to 20/s with a resolution of 0.5-2.0 µm on the diameter. After the sample is accumulated, the data are transferred automatically to a computer, which generates diameter and volume distribution and calculates the means and standard deviations. Since each particle in the sample is sized, the confidence intervals around the means are small. The device is calibrated with a set of high-precision stainless steel spheres (AFBMA Grade 10), with traceability to the NBS established through ORNL secondary standards. The accumulated spheres, having passed through the device, may then be transferred pneumatically to a weighing station. Mean density of the sample may be derived from the weight and the mean volume.

This device may also be outfitted with another beam and photodiode, at right angles to the first, and comparison of the signals will allow a shape (diameter ratio) factor to be obtained.

More complete size and shape analysis, but not on a continuous basis, may be performed by commercially available image analysis devices. These may use either the spheres themselves or photo-micrographs or radiographs as the image former. Size may be calculated by linear dimension (along several axes), projected surface area, or perimeter measurement. Shape analysis is simple with this type of equipment. These are essentially microscopes, which are also useful for the fine fraction.

2.6.3 Chemistry

Standard techniques for chemical analysis of nuclear fuel materials have been developed, especially for pellet fuel. These can be applied in general to gel-derived fuel, since it is also a sintered solid material. A good starting point is the specification ANSI/ASTM C 776 "Standard Specification for Sintered Uranium Dioxide Pellets" and its prescribed methods, ANSI/ASTM C 696 "Standard Methods for Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear-Grade Uranium

Dioxide Powders and Pellets." The pellet specification has sections on physical characteristics that require modification. Also, it and the methods will have to be modified to account for the various fuel compositions: $(U,Th)O_2$, $(U,Pu)O_2$, $(Th,Pu)O_2$.

2.6.4 Strength

Transfer of sphere-pac fuel and loading it into commercial-length rods will stress the spheres so much 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[69] involves use of a steel holder plate drilled with 64 flat-bottomed holes into which individual spheres are placed. A pin with flat ends is then put into one hole and load is applied with an Instron machine. 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 spheres is simply poured onto it, the plate is tilted, and automatically only one sphere is loaded per hole. The plate can then be x-radiographed to determine individual sphere size. When mated to the holder and inverted, spheres 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.

2.6.5 Microstructure

Particle microstructure is determined ceramographically either through standard mounting and polishing and optical or microprobe examination or fracturing and electron microscopic examination. Several papers[59,62,67,70] have been published illustrating the use of these techniques.

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. The effect of microstructure, if any, on irradiation performance will need to be determined by irradiation testing. Also, the effects of surface roughness and microcracks on the efficiency of sphere packing during rod loading needs to be evaluated.

2.7 CRITERIA FOR PROCESS SELECTION AND SCALE-UP — P. A. Haas

The first requirement for process selection is to specify the product composition and particle size. While the sol-gel and gel-precipitation processes are each usually demonstrated for a range of compositions and sizes of product spheres, the relative practicality of the different processes is very dependent on the product size and composition. Scale-up or process capacity is also important to process selection. Some operations that are convenient and easy on a laboratory scale are difficult to scale up to large capacities. Sphere-pac fabrication has its greatest promise for remote operations, and the remote application must be considered as a criterion for process selection. This subject is discussed in Sect. 2.8.

The objective of this section is to apply the above criteria for process selection to the gel-sphere preparation. The sizes and compositions are determined by the requirements for sphere-pac fabrication and the application to thermal reactors. The capacities of demonstration plants are equivalent to 10 to 100 kg/h with multiple fabrication lines for large capacities.

2.7.1 Scale-Up of Sphere Fabrication

A Sphere-Pac fabrication facility for thermal reactors must provide the large (800—1500 μm average diameter), medium (200—350 μm average diameter), and fines (<100 μm average diameter) of dense UO_2, $(U,Pu)O_2$, or thorium based fuel. The internal gelation process using hexamethylenetetramine has been most completely demonstrated for all these sizes with UO_2 or UO_2-PuO_2, but the fines were difficult to prepare. Gel-supported precipitation or external gelation processes using water-soluble polymers are simpler than internal gelation from the standpoints of feed stability and the use of aqueous ammonia instead of a liquid organic forming medium. However, the suitability of external gelation processes for the large size and the fines is less certain. Therefore external gelation processes remain second choices until the preparation of large UO_2 spheres is demonstrated. Gelation by water extraction is not practical for large UO_2 spheres but remains a backup process for the fines.

The schematic flowsheets for internal gelation (Fig. 2.3, p. 61) and external gelation (Fig. 2.4, p. 45) 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.

2.7.2 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:

1. the NO_3^-/U mole ratio should not exceed 1.6, while solvent extraction purification processes usually produce a value greater than 2;
2. the feed constitutents 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, it is dissolved in warm HNO_3 or $UO_2(NO_3)_2$ solutions. If all the feed is $UO_2(NO_3)_2 \cdot X HNO_3$ 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.[71] 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 replaceable, as an occasional failure with solidification throughout these components is possible.

2.7.3 Sphere Formation and Gelation

Drop formation technology was reviewed in Sect. 2.4. 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 strong enough to survive the impact at the liquid 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 medium size. A 1 Mg/d plant would require about 30 kg/h for the large size and 10 kg/h for each of the two smaller sizes. The capacity of a single drop-forming nozzle for either large 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 medium size, the capacity of a single feed system and nozzle is about 0.2 kg heavy metal per hour. The internal gelation pilot plant in the Netherlands used a spinerette disperser for large capacities, but using it 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.

2.7.4 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 is a batch operation. The minimum holdup time during washing is 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.

2.7.5 Drying

External gelation processes have required careful control of drying conditions, with use of a single layer 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.

2.7.6 Sintering

Development of sintering conditions and procedures is in progress. Operation of high-temperature furnaces with hydrogen in a remotely operated facility imposes major engineering design problems (see Sect. 2.8). However, the same requirements occur for all ceramic fuels (pellets as well as sphere-pac), and the gel spheres probably sinter at lower temperatures than those necessary for pellets. Therefore, scale-up of sintering is probably not a major factor in process selection.

2.8 REMOTE APPLICATIONS — C. C. Haws

Following the review of criteria for process selection and scale-up, a review of remote experience is pertinent since this is the least developed of all fuel fabrication areas. While no direct remote experience is available on external and internal gelation, an extensive water extraction sol-gel program was conducted at ORNL 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 mixture 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.

2.8.1 Significant Engineering Scale Demonstrations

The first sol-gel hot demonstration processing a high-level alpha and high-energy gamma emitter was the Kilorod program.[4] The facility was designated 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* were prepared at a rate of 10 kg/d, then crushed and loaded into about 1000 fuel rods by vibratory packing. Reactor chemical and physical specifications were met by both the shards and the fuel rods.

Personnel exposure levels were maintained below permissable limits.[72] 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 approximately 10% that to the operator on an individual basis.

An isotopic heat-source program based upon sol-gel technology was conducted in the late 1960s at ORNL.[73] 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 the hot-cell pilot plant at 150 g/d, using ^{239}Pu

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

as a stand-in, were successful. Extreme radiolytic effects from the ^{238}Pu, even through considered in the design, made operation of the unit for its intended purpose impractical, so operation and the program were discontinued. The success of ^{239}Pu operations is of interest to the thermal reactor program. A high-purity ^{238}Pu isotope is not considered as a feed material in the thermal reactor program.

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.[74] 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 hot 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.

The operational and engineering experience gained in the above demonstrations, although limited, provide confidence in the successful execution of similar efforts in the thermal reactor program.

2.3.2 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. The transuranium (TRU) operation at ORNL possesses many conceptually desirable features. 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 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 or modules especially designed for removal, or 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 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.

2.8.3 Identification of 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, problems 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 immediate removal and replacement to continue operation. This can arise from any of a number of minor process instabilities. For this reason, design of the feeding system would necessarily provide for quick replacement. Removed needles would be either discarded or thoroughly cleaned, dried, and inspected to make certain that they were in operable condition before being returned to the operation. Since this is a tedious task for manipulator operations, an 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 contol scrap recycle. Early detection of maloperation (i.e., off-size or misshapen droplets) would also be required. Means of detecting and correcting other 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 provided with TV viewing (which is less desirable). The buildup of impurities in the recycling solvent must be monitored to prevent maloperation, 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 scrap disposal. 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 so 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 demand the construction and operation of a cold prototype if the hot operation is to be successful. The functional testing of individual equipment pieces should begin shortly after the equivalent of the start of Title II engineering. As individual pieces are proved, complete systems should be assembled and tested in cold mechanical mockups. Testing must be continuously pursued through in-place testing in the pre-hot operation of the completed pilot plant. 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.

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3. FABRICATION OF FUEL RODS BY SPHERE-PAC TECHNIQUES

The sphere-pac process is one of two principal techniques (the other is vi-pac) through which an assemblage of small particles can be loaded to high density in a nuclear fuel rod. The techniques are similar in that neither requires the critical pellet preparation inherent in the conventional fabrication process, and both depend on vibrational agitation of the cladding to compact a particle bed. Feed particles are usually spheres produced by a gelation process or angular shards prepared from sintered, fused, electrodeposited, or pneumatically impacted oxides.[1] A number of variations on 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 applied during densification of the fuel rod. The term vi-pac (an abbreviation for vibratory compaction) will be used to describe other forms of the vibratory loading process. Sphere-pac is the significantly more attractive of these packing options since dust problems and packing time and energy are minimized by the free-flowing nature of the spherical feed material.

3.1 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.

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The simplest studies involve only one size of sphere. White and Walton[4] described 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 with a theoretical packing density of 69.80%, (4) face-centered cubic, and (5) hexagonal close-packed for which the theoretical packing densities are identical at 74.05%.

Experimental work with single-sized spherical particles indicates that measured packing densities of only about 62.5% of theoretical density are usually obtained.[5] This density arises, most probably, from a mixture of orthorhombic and double-nested packing arrangements, since the cubic and hexagonal close-packed 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, a regular arrangement of void space is also present. Smaller sized spheres could be mixed into the batch to fill these voids and thus increase the density. Conversely, a number of much larger spheres could be added to the original batch. In this situation, one large sphere 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, his occurs with a mixture of about 70 vol % coarse and 30% fine material.[5,6]

The two sphere size fractions may be combined and blended before packing or they may be sequentially packed by infiltrating the smaller spheres through interstitial spaces in 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 minimum 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 planar interstitial void present amid a triangle of three closely packed same-size spheres can be best filled by a sphere 0.154 (~1/7) times the diameter of the others. The precise density achieved by binary packing will thus depend on the relative sizes of the fractions, but will not exceed a limiting density of 86% of theoretical.[5] Experimentally Babcock and Wilcox have prepared fuel rods with 82% of theoretical density using two sizes of spheres.[7] The sphere sizes used in that study were not reported.

When spheres of two sizes with a diameter ratio less than 7 are used, they must be blended together before or during 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 of 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 for production of acceptable fuel rods if smear densitities greater than about 82% are required.

However, a mixture of three differently sized sphere fractions will provide suitable densities. Possible techniques that can be used to pack three sizes of spheres into a container include: (1) preblending of the three sizes, (2) sequential infiltration of the three sizes, and (3) a combination of these processes, which involves infiltration of the smallest spheres 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 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 fraction 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 densitities 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 9[illegible].5%. According to these estimates, ternary packing arrangement should produce nuclear fuel elements.

3.2 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 the best size ratios, relative size fraction amounts, and 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 spheres with 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 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. 3.1) are described in the following excerpt.[8]

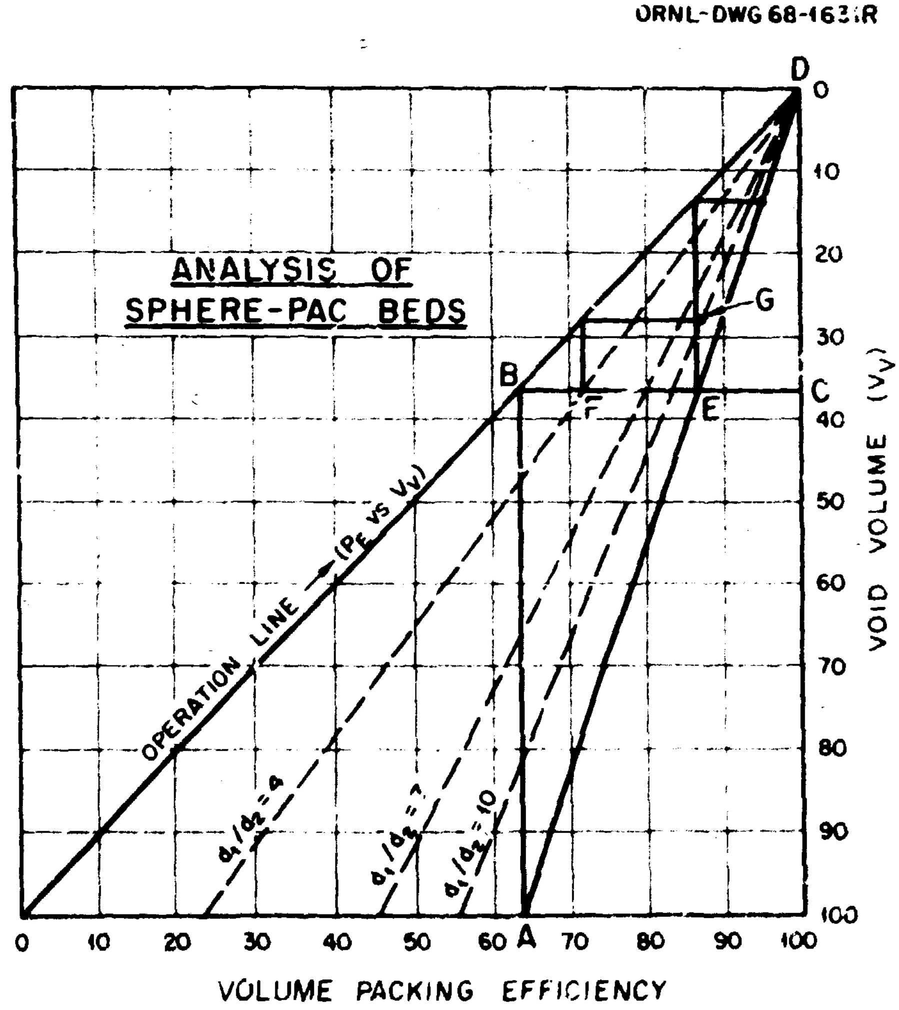

Fig. 3.1. ORNL Analysis of Sphere-Pac Beds.

> . . . 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 of 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 density 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 spheres 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 up to 84% 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 Gelensberg, AG, in which seven plutonium-uranium-bearing rods were loaded. Smear densities up to 76.6% were obtained with two size fractions, apparently by infiltration of small spheres (125–200 μm) into a bed of 800- to 1110-μm-diam coarse spheres. He also reported that three rods loaded with 1000- to 1250-μm coarse spheres 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).

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

Similar success have been reported in Italy,[18] where oxide spheres of 707 to 840 and 70 to 100 μm in diameter 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 loading methods, each employing three sizes of spheres, have been developed to achieve smear densities above 85%; they are: (1) double or sequential infiltration and (2) a blended binary bed with single infiltration. The third option, a ternary blend approach, was not mentioned in experimental literature for sphere-pac, but the Dutch workers are known to have employed this method successfully.[19] Though ternary blending of angular particles is the usual practice for vi-pac fuel fabrication, a mixture of spheres of large diameter ratio tends to segregate during transfer operations. This poses a difficult problem with the ternary blend approach to sphere-pac. Thus selection of a process approach for further sphere-pac development will be based on the following considerations. The sequential infiltration method would appear to be too slow for commerical application and will not be considered further. The blended binary bed and single infiltration technique, though slower than ternary blending, is attractive for high smear density with reasonable loading time. The ternary blending approach, while posing a sphere size segregation problem and possible slight density penalty relative to the fines infiltration route, is attractive from the standpoint of very rapid loading. Therefore, both these latter techniques are candidates for further development.

3.3 LOADING EQUIPMENT AND METHODS — R. R. Suchomel

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

The equipment to be used for rod loading obviously depends on the sophistication of the technology available. Primitive packing studies can easily be performed with only a section of cladding, a supply of different sized spheres, and some device to compact or vibrate the bed. To pack rods to optimum density with good reproducibility, other items such as a follower rod, hold-down screen in the case of fines infiltration, and sphere blenders 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 of the end plugs. Advancement to an automatic or remotely operable system would require the addition of components needed for sphere transfer, lot blending, 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 only equipment items required for performing loading tests and fabricating irradiation specimens.

3.3.1 Vibrational Input

The input of vibration is basic to the sphere-pac process, and 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 for either 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 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[20] 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 eletromechanical vibrator was used inside a glove box. The vibrator was tilted 45° to supply both lateral and axial vibration to the vertical fuel rod.[21]

A similar glove box system was set up at Argonne National Laboratory.[22] Accelerations up to 15*g* were measured during fuel rod vibration from a 60-Hz electromagnetic vibrator. The Swiss sphere-pac program[23] 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, 2.5*g*; 49 Hz, 12*g*; and 56 Hz, 21*g*. Another type of pneumatic vibrator has been used for compaction studies; it 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 20,000*g*, was incorporated into a vi-pac loading machine at ORNL.[24]

A third type, the electrodynamic vibrator, is often used for particle compaction. It is more versatile, providing frequency sweep capability and imparting 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 have been extensively used for vi-pac loading and occasionally for sphere-pac work. A recent application to a modified 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 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 continous sweep between 250 and 750 Hz. Applied accelerations of 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% 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[25–28] 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[29] indicates that ultrasonic frequencies were less effective in producing densely packed fuel rods then were sonic frequencies in the range of 20 to 5000 Hz.

Naruki[30] proposed an optimum vi-pac loading process that involved several stepwise increases in acceleration. For compaction, a constant sweep between 300 and 3000 Hz was maintained for 15 min with accelerations of 40*g* and 60*g*.

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 stand-points. However, a larger electrodynamic shaker may be required to successfully load long fuel rods or obtain high throughput rates.

3.3.2. Fuel Sphere Blending and Loading

Fuel spheres must be properly sized before being loaded into fuel rods. Sphere preparation techniques are expected to yield material with adequate size control without screening except for normal scalping. If necessary, nonspherical particles could be adequately removed by passing the spheres over a shape separation table.[31,32]

Vi-pac fuel fabrication requires that all particle types be blended before rod loading since infiltration is impractical for such nonspherical material. A blending operation will also be required for sphere-pac loading, either for the two coarse components or for all three components, depending on the loading technique employed. 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 weighted 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 conveyers 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[29] 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.

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.

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[22] 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 spheres have been loaded into the rod, they must be restrained to prevent segregation during compaction. The technique employing a binary coarse blend with single infiltration requires that the blended coarse bed be restrained during infiltration of the fines. Both Ayer and Soppett[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.[8,10,19] A load of up to 4 kg can be applied to the follower rod to restrain the upper segment of the bed.

3.3.3 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.[24] 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.

3.3.4 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 included: (1) fuel rod outgassing (if necessary), (2) placement of plenum spring or other retaining device, 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.[33] outgassed sphere-pac fuel rods 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. A rod could be outgassed by heating and evacuating it and then allowing it to backfill with dry helium. Pechin[34] 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 or other restraining devices. 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 or to isolate a rigid spacer. 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.[21]

The procedure used for welding the top end plug should be identical for both pellet and sphere-pac fuel. Welding technology is well advanced; for example, Zircaloy is readily welded by tungsten inert-gas (TIG) or magnetic force welding (MFW) techniques.[35] Atmosphere control is, of course, important during welding, to prevent contamination and possible corrosion during irradiation. An automatic machine for welding fuel rod end-caps has been developed.[36]

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.

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

The quality control inspection of nuclear fuel during fabrication is an important part of the manufacturing process[37-39] and aids in assuring that the fuel rod will operate successfully in a reactor environment. Final steps in sphere-pac fuel rod fabrication include the determination of fuel density, fuel uniformity, enrichment, assay, and fuel column height.

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

In many respects the quality assurance tests are independent of whether the fuel rod is loaded with pellets or spheres.[40] Thus most techniques currently in use by fuel manufacturers and laboratories to perform the necessary inspections can be applied to sphere-pac fuel rods. While some inspections, such as gamma scan and heavy metal assay, are amenable to remote performance,[8] most of the measurement devices currently in use will require significant development to enable the inspection to be performed economically with acceptable precision, accuracy, and speed in a remote environment.

3.4.1 Dimensional Inspection

Conventional methods are available for inspecting rod length, diameter, wall thickness, ovality, and camber both before and after loading. Fuel loading method (particles versus pellets) will have little influence on inspections that are performed on the empty tubing. However, postloading dimensional inspections such as end-cap concentricity and final visual inspection will require development of remote techniques.

3.4.2 Density, Homogeneity, Assay, and Fuel Column Length

Gamma ray attenuation has been used to determine density profiles along sphere-pac loaded fuel rods at ORNL.[41] A ^{60}Co radioisotope source and NaI(Tl) detector were used to scan rods loaded with a number of different (Th,U)O_2 fuels. Under the (Th,^{233}U)O_2 (Kilorod) project at ORNL,[42] rods containing $^{233}UO_2$ fuel were inspected in a hot-cell environment. Results obtained encourage further development of such a device for application to sphere-pac fuels.

A gamma scanning device currently under development provides feedback control to the fuel sphere volumetric dispensers used for loading the rod. The device will function as a 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. Remote methods for weighing the fuel charge to determine the smear density must be evaluted with regard to compatibility with the loading technique and with accountability requirements. The basic development requirements relate to capabilities for remote operation.

The total heavy metal concentration and distribution can be determined by multiple gamma attenuation methods. These methods have been applied to HTGR fuels and can be applied to sphere-pac-loaded fuel.[43,44] The uranium and plutonium content and distribution can be determined by x-ray densitometry.[45] The technique can also be applied to thorium. The Th, U, and Pu distribution in fuel pins could be determined by applying multiple gamma ray attenuation with a selective K-edge absorption method.[46] This method has been shown to work in a high radiation environment, and is applied to HTGR fuel rods and reprocessing streams.

High-speed fuel rod enrichment scanners, such as the system used by the Babcock and Wilcox fabrication facility to scan fuel rods loaded with pellets for commerical nuclear power reactors,[47] could be applied to sphere-pac fuel. Active scanning devices are also used by the General Electric Wilmington Nuclear Fuel Manufacturing Operation,[48] and other fuel rod producers use similar scanning systems.[49] Such devices use a ^{252}Cf neutron source to induce fission in the fuel. The loaded fuel rod is transported through the irradiation assembly, and the delayed fission gamma rays are detected a few seconds after irradiation. In this way the fissile distribution along the fuel rod and the total assay of the rod are determined. Spatial resolution to 3 mm is possible, and fuel rods up to 4 m in length can be scanned within minutes. Attached to such devices are gamma ray attenuation units, which determine fuel column density and enrichment using ^{137}Cs radioisotope sources and NaI(Tl) detectors. Such units are also used to determine fuel column length within the rod. Fuel rod scanners are commercially available.[50]

Other systems, which use passive gamma counting, have also been developed and are also used by manufacturing facilities to monitor fuel distribution along fuel rods. These systems can be used to measure ^{239}Pu, ^{235}U, ^{238}U, or Th distribution.[51]

Selection of the proper method for rod inspection depends on the radiation environment. For refabricated thorium-based or spiked fuels of high gamma activity, the delayed fission gamma ray method for determining the distribution of the fissile material along a fuel rod may not be applicable because of interference of radiation from the fuel itself. In such cases the detection of prompt fission neutrons from the irradiated sample may be used.[52] Experiments are under way to test the method by using an existing prompt neutron assay device at ORNL.

In summary, the basic methods used for determining fuel density, uniformity, enrichment, assay, and column length can be applied to sphere-pac fuel rods. Gamma ray attentuation methods for density and uniformity measurements are applicable in high radiation environments. The density, uniformity, and fission product distribution in irradiated fuel rods are currently being measured at a number of facilities.[53] The best method for each determination depends on the fuel isotopic composition, density, and radiation environment. Depending on these factors, commercially available scanning systems may be usable for some applications. Others may be satisfied by alternate methods currently under development in the HTGR and FBR programs, including the use of optimized neutron spectra for fuel irradiation with prompt neutron detection and multiple gamma irradiation with selective K-edge absorption.

3.4.3 Impurity Analysis

Whether sphere-pac rods are loaded with outgassed fuel under a contained high-quality atmosphere or loaded in air and subsequently outgassed, the application of conventional methods for determining moisture content and gas release from sphere-pac fuel rods requires further evaluation. Mass spectrometer analysis of samples of outgassed fuel spheres before loading and control of the rod loading environment may be the most practical method to measure and control contamination. Destructive analysis of small sample rods to verify proper pressurization and impurity content may be required for verification of the technique.

3.4.4 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.

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

At present sphere-pac fuel rods are loaded only 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 commerical facility will require extensive engineering development. Application of sphere-pac to a remote operation 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 require further development for commerical or remote operations. A flowsheet describing a typical fuel rod fabrication process employing the coarse blend-fines infiltration sphere-pac process is shown in Fig. 3.2. This flowsheet identifies the processing steps required during fuel rod fabrication, and is applicable to either a contact or remote production operation.

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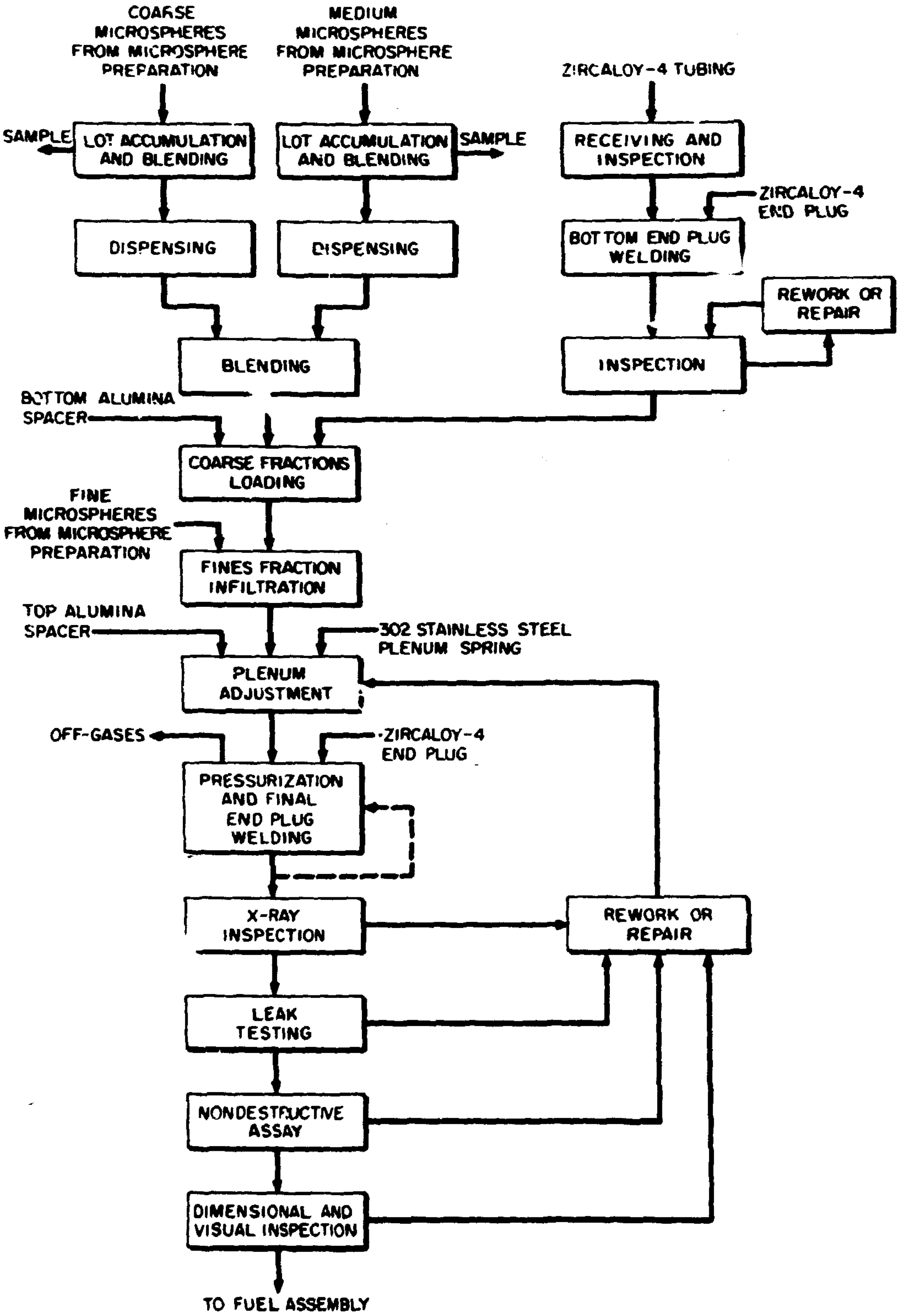

Fig. 3.2. Typical Flowsheet for Fuel Rod Fabrication Using the Sphere-Pac Process.

3.5.1 Sphere-Pac Loading

A review of sphere-pac technology indicates that the major problems in scale-up of the loading process lie in obtaining acceptably short loading time and high enough fuel density. According to work to date with the coarse blend—fines infiltration loading method, an hour or more may be required to completely load a commerical-length fuel column. Nearly all this time is taken up by the fines infiltration step. Such a processing time would make 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 commerical sphere-pac operation might be a 5-min loading time to fill and compact a full-length fuel rod. To meet this time limit will require much more rapid fines infiltration or ternary blending.

Infiltration times could be dramatically decreased through feeding of alternating layers of blended coarse and fine spheres into the rod. A small amount of blended coarse would be put into the cladding followed by an amount of fines, calculated to exactly infiltrate this segment of coarse bed. Additional layers would be added until the desired fuel column height is obtained. With this approach the fines fraction would have to infiltrate only a short section of the bed rather than the entire fuel column. As the alternating layers are made smaller, the process approaches the case in which all three size fractions are preblended before being loaded into the rod. Literature reports indicate that through the use of preblending, long 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.

If the fines infiltration route proves to have a significant advantage in density or uniformity, and minimum rod loading time is found to be about an hour, 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 by simultaneously loading and compacting 12 rods in a 1-h batch processing step. Large electrodynamic vibrators are commercially available to handle payloads of such size.

However, recent ORNL results with the ternary blend sphere-pac process look very promising for achieving both high density and short loading time. In early experiments with this method, 1.8-m (6-ft) rods were loaded to greater than 88% packing density in 6 min. The procedure used was simultaneous feeding of the three size fractions into the rod in 3 min, followed by a 3-min compaction using a pair of pueumatic vibrators. With the controlled feeders and blenders now being developed, the ternary blend sphere-pac process now appears the most likely route to achieving the high smear density and short loading time needed for commerical application.

3.5.2 Fuel Handling

Pneumatic conveying is the preferred method for transporting the dried calcined or sintered gel spheres between and within the processing systems. This type of conveying takes advantage of the free-flowing character of the gel sphere fuel and provides great flexibility in routing of transfer lines, thereby easing restrictions on the placement of process equipment, an important aspect in remote fabrication. Also, a pneumatic conveying system is amenable to high throughput and remote operation. Flow indicators, pressure monitors, and hopper level indicators allow ready determination of operating parameters and provide feedback for efficient operation. 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 pressures [0.1 MPa (<15 psi)] and moderate flow [5 liters/s(<10 scfm)]. Cyclone separators provide essentially total recovery of spheres, including fines, from the conveying gas. In addition, 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 has been acquired under the HTGR Fuel Recycle Development Program at ORNL on pneumatic conveying of nuclear fuel spheres.[59] This program has also involved the development of auxiliary sphere handling equipment, such as samplers,[55] weighers, and level sensors. The equipment has been developed with the ultimate goal of total remote operation, as required by the ^{233}U fuel cycle.

The first handling step shown in Fig. 3.2 is the lot accumulation and blending of the two larger size fractions to prepare large lots of feed stocks for subsequent loading. Lot blending of individual size fractions can be done with commercially available V-blenders. A sample would be extracted from each blended lot to determine sphere size distribution, mean diameter, and average density. A passive sampler, developed for remote use in HTGR fuel refabrication, has been demonstrated to extract reproducible representative sample from batches of spheres.[55] These spheres are similar in size to the larger sizes required for sphere-pac work. The sampler consists of a sequence of conical splitters. At each stage, spheres are poured over the apex of a cone and divided into eight streams, which are then recombined into two flows of equal volume, one of which is directed out of the device while the second feeds the next stage. After two stages, the sample consists of one-fourth of the total batch; after five stages, it is 1/32; and after ten stages, it is 1/1024 of the inital supply. The number of stages can easily be changed to provide the desired sample size.

From the lot accumulation and blending equipment, spheres pass to dispensing devices. The dispensers meter out the precise 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 meter the quantities of fissile, fertile, and shim particles needed for production of HTGR fuel rods and have been shown to dispense very accurate and reproducible portions. They are mechanically simple, each consisting of two pinch valves or a pinch valve and a plug valve. The entire unit is removable for service or replacement.

These dispensers feed a blender, which must homogeneously mix the spheres and load them into the cladding. No devices suitable for blending spheres at large diameter ratio are available commercially.

However, a number of blenders have been devised and successfully used in laboratory sphere-pac experiments employing concepts such as conveyor mixing and vibratory feeding. A continuous ring blender based on a cone splitter, which has been developed for fabrication of HTGR fuel rods, shows promise of being scalable to the size needed to fill LWR fuel rods. These techniques should be readily adaptable to a remote operation.

3.6 REMOTE APPLICATION — R. R. Suchomel

Two of the major difficulties of any remote operation involve material handling and equipment maintenance. Since the sphere-pac process is not as mechanically intensive as the pellet fabrication method, equipment maintenance should be simpler. However, much of the engineering work that will be required for a remote system will be focused on equipment items not specific to the sphere-pac process. For example, sophisticated welding equipment will be needed to secure the top end plug, and precise weighing devices will be required to accurately determine the amount of fuel in a loaded rod; these equipment items are equally applicable to both pellet and particulate fuel rods.

The flowsheet in Fig. 3.2 shows that many fabrication steps are common to all fuel forms. Once the fuel is loaded and the end plugs are in place, sphere-pac rods are handled no differently from pellet rods. Equipment items specific to fabrication of sphere-pac fuel rods will be those needed for fuel handling before and while the fuel is loaded into the cladding.

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

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4. IRRADIATION PERFORMANCE OF SPHERE-PAC FUELS FOR THERMAL REACTORS

J. A. Horak

For sphere-pac (SP) oxide fuels — UO_2, $(U,Pu)O_2$, and $(Th,U)O_2$ — to be considered as viable alternatives to pellet fuels, they must exhibit irradiation performance equal or superior to that of pellet fuels under LWR operating conditions. The most important operating parameters are linear heat rating, burnup, and fuel effects on the cladding.

This section presents the information obtained to date on the above three parameters for sphere-pac fuels irradiated in thermal neutron reactors, along with limited relevant data from irradiation of fast reactor fuels. Indications are that sphere-pac oxide fuels will perform as well as or better than pellet fuels under LWR operating conditions. Some of the reasons for the good irradiation performance of the sphere-pac fuel are (1) higher gap conductance for sphere-pac fuels than for pellet fuels, (2) less fission product chemical interaction with the Zircaloy cladding, and (3) less fuel-cladding mechanical interaction than for pellet fuels.

4.1 IRRADIATION OF THERMAL REACTOR FUELS

4.1.1 Studies at ECN, Petten, Netherlands

The major LWR sphere-pac irradiation test program has been conducted by workers at the Netherlands Energy Research Foundation (ECN). They 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 a well-instrumented pressurized loop, and in the HBWR. Two complete assemblies containing 36 fuel rods per assembly are being irradiated in the Dodewaard Reactor. Each assembly contains 35 sphere-pac fuel rods and one pellet fuel rod.

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Table 4.1 summarizes the ECN irradiation program on sphere-pac fuels for LWRs.[1] The status of the ECN experiments as of February 1978 is as follows:[2]

B-71, -72, and -73	Report issued[3]
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 4.1. 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[a]	2	70	4	86	U-sphere pac
B-73[a]	2	70	10	88	U-sphere pac
B-71[a]	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

[a] See ref. 3.

Table 4.2 contains some of the important details for the R-109 experiment irradiations conducted in the HFR.[4] 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 sphere-pac fuel rod, some postirradiation examination (PIE) has been conducted, and the heat ratings are calculated from calorimeters in the HFR loop, which should provide reliable values. The only other experiment 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 315) 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 comparative data that are available. The information from the complete subassembly experiments B-202 and B-203 will be very important to the current program. Tables 4.3 and 4.4 contain fabrication data for the fuel rods in the R-109

Table 4.2. Main Data of the Irradiation Experiments on Plutonium Recycle Sphere-Pac Fuels

Experiment	Fuel Rod	Smear Density (% T.D.)	Pressure of He Filling Gas (MPa)	Maximum[a] Linear Heat Rating (kW/m)	Maximum[a] Burnup (% FIMA)	Fuel Type
R-109/1	306	84	0.1	62	1.16	(U,Pu)O_2 sphere-pac
	307	84	0.1	62	0.20	(U,Pu)O_2 sphere-pac
	308	84	2.5	60	1.07	(U,Pu)O_2 sphere-pac
	309	84	2.5	62	1.22	(U,Pu)O_2 sphere-pac
R-109/2	302	88	0.1	60	0.53	UO_2 sphere-pac
	314	88	0.1	60	0.51	UO_2 pellets
	317	88	0.1	60	0.51	(U,Pu)O_2 sphere-pac
R-109/3	303	87	2.5	62	0.54	UO_2 sphere-pac
	315	88	2.5	62	0.54	UO_2 pellets
	318	88	2.5	62	0.52	(U,Pu)O_2 sphere-pac

[a] The maxima of the linear heat rating and of the burnup were calculated from loop calorimetry data. (This table supplied through the courtesy of ECN.)

Table 4.3. Fuel Rod Fabrication Data for the R-109 Experiments[a]

Bundle Rod	Fuel Composition[b]	Fuel Type[c]	^{235}U in U (at. %)	Pu in Oxide		av H Content (ppm)	Column Weight (g)	Column Length (mm)	Smear Density			Gas Volume, cm^3 STP		Helium Filler (MPa)
				av (wt %)	Variation (% of av)				(Mg/m^3)	(% TD)	Variation (% of av)	Inter-particle	Plenum	
R-109-1														
306	$(U,Pu)O_2$	Sphere	0,72	1,37	+13, -15	0,9	326	523	9,18	83,7	+0,7, -1,6	5,8	2,8	0,1
307	$(U,Pu)O_2$	Sphere	0,72	1,37	+10, -11	0,9	325	519	9,22	84,1	+0,5, -1,1	5,6	3,0	0,1
308	$(U,Pu)O_2$	Sphere	0,72	1,37	+11, -9	0,9	327	527	9,13	83,3	+0,5, -2,5	6,0	2,4	2,5
309	$(U,Pu)O_2$	Sphere	0,72	1,37	+11, -12	0,9	324	518	9,21	84,0	+0,5, -0,8	5,6	3,1	2,5
R-109-2														
302	UO_2	Sphere	3,16			0,9	327	500	9,62	87,8	+1,4, -2,3	4,1	3,3	0,1
314	UO_2	Pellet	3,16			1,2	328	502	9,60	87,6	+0,8, -0,9	4,2	[illegible]	0,1
317	$(U,Pu)O_2$	Sphere	0,72	1,43	+8, -10	0,8	319	487	9,63	87,9	+1,4, -2,4	4,0	4,5	0,1
R-109-3														
303	UO_2	Sphere	3,16			0,9	323	498	9,56	87,2	+1,5, -2,5	4,3	3,8	2,5
315	UO_2	Pellet	3,16			1,2	330	505	9,61	87,7	+0,8, -0,9	4,2	3,1	2,5
318	$(U,Pu)O_2$	Sphere	0,72	1,43	+10, -12	0,8	318	488	9,60	87,6	+1,6, -2,0	4,1	4,9	2,5

[a] From A.V.D. Linde and J.H.N. Verheugen, ECN-77-056 (May 1977). Ref. 5.

[b] $(U,Pu)O_2$ present only as large spheres, 1050 µm. UO_2 115 µm and <38 µm.

[c] Sphere = vibratorily compacted mixture of three fractions. Pellets are dished at both ends, 9.11 mm in diameter, 11 to 12 mm long, density 10.26 Mg/m^3 UO_2, dish volume 19 mm^3 per pellet.

Table 4.4. Nonfuel Data for Fuel Rods in R-109 Experiments[a]

Cladding material	Zircaloy-4, stress relieved 4 h at 540°C
ID, mm	9.30 ± 0.01
OD, mm	10.75 ± 0.04
surface treatment	outer, pickled; inner, sandblasted
Insulation pellet material	UO_2 with 0.72 at. % ^{235}U in U
diam, mm	9.17
length, mm	10; flat ends
Plenum spring material	Inconel X750
Plenum volume, cm^3 STP	0.56

[a] From ref. 5.

experiment.[5] Table 4.5 gives the makeup of the sphere-pac rods. The UO_2 columns in rods 314 and 315 consist of 45 pellets each. The dishes at both ends of these pellets have a diameter of 8.1 mm and a depth of 0.31 mm. Rods 306, 307, 308, and 309 contain an insulation pellet only at the bottom end of the fuel column. All other rods have insulation pellets at both ends of the fuel column.

Irradiation of the rods in the HFR pressurized water loop was with the outer surface of the Zircaloy-4 as pickled and degreased and the inner surface sand blasted. Table 4.6 contains the pre- and postirradiation diameter measurements for experiments R-109-2 and R-109-3. The diameter increases are small, and there is no observable difference between the performance of sphere-pac and pellet fuel rods. Table 4.7 contains the rod and fuel column length measurements for experiment R-109. Again, the length changes are small, and there is no observable difference between sphere-pac and pellet fuel rods. Table 4.8 contains the fission gas release data[5,6] for fuel rods in experiments R-109-2 and -3. For sphere-pac rod 302 the fission gas release is about equal to that of pellet rod 314. In general the release from sphere-pac fuel and pellet fuel was similar for low-burnup rods and low-density pellets irradiated at maximum linear heat ratings of about 60 kW/m in test reactor with a relatively large number of scrams and power setbacks.

Table 4.5. Makeup of Sphere-Pac Rods in ECN Experiment R-109[a]

Fuel Rods	Fraction	Content (wt %)	Sphere diam (μm)	Fuel Material
306–309	large	61.5	1050	$(U,Pu)O_2$
	medium	18.5	115	UO_2
	fine	20.0	<38	UO_2
317–318	large	65	1100	$(U,Pu)O_2$
	medium	19	115	UO_2
	fine	16	<15	UO_2
302–303	large	60	1100	UO_2
	medium	20	100	UO_2
	fine	20	<20	UO_2

[a] From ref. 5.

Table 4.6. Pre- and Postirradiation Average Fuel Pin Diameters for Experiments R-109-2 and R-109-3[a]

Fuel Rod	Type	Location	Diameter, mm		Diameter Decrease (μm)
			Before Irradiation	After Irradiation	
302	Sphere pac	0°	10.739	10.716	23
		90°	10.733	10.707	26
314	Pellet	0°	10.742	10.720	22
		90°	10.745	10.720	25
317	Sphere pac	0°	10.749	10.733	16
		90°	10.739	10.701	38
303	Sphere pac	0°	10.740	10.730	10
		90°	10.750	10.740	10
315	Pellet	0°	10.760	10.747	13
		90°	10.750	10.740	10
318	Sphere pac	0°	10.720	10.720	0
		90°	10.740	10.730	10

[a] From refs. 5, 6.

Table 4.7. Fuel Rod and Fuel Column Length Measurements for the R-109 Experiments[a]

Fuel Rod[b]	Length, mm		Length Increase	
	Before Irradiation	After Irradiation	(mm)	(%)
		Fuel Rod Length Measurements		
306	614.65	615.38	0.73 ± 0.06	0.12
307	614.65	615.11	0.46 ± 0.06	0.08
308	614.65	615.09	0.44 ± 0.06	0.07
309	614.65	615.32	0.67 ± 0.06	0.11
302	614.65	614.93	0.28 ± 0.06	0.05
314	614.70	615.17	0.47 ± 0.06	0.08
317	614.90	615.20	0.30 ± 0.06	0.05
303	614.65	615.29	0.64 ± 0.06	0.10
315	614.65	615.01	0.36 ± 0.06	0.06
318	614.65	615.32	0.67 ± 0.06	0.11
		Fuel Column Length Measurements		
306	523	520.7	−2.3	−0.4
307	519	519.2	−1.8	−0.4
308	527	525.2	−1.8	−0.4
309	518	515.8	−2.2	−0.4
302	499.8	500.7	0.9	0.2
314	501.8	499.7	−2.1	−0.4
317	486.8	487.1	0.3	0.1
303	498.0	492.1	−5.9	−1.2
315	504.5	503.7	−0.8	−0.2
318	487.8	486.9	−0.9	−0.2

[a] From ref. 5.

[b] All are sphere-pac but 314 and 315, which are pellet rods.

Table [illegible]. Fission Gas Release Information for Several Fuel Rods in Experiments [illegible] and [illegible]

	[illegible]					
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
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	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
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[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

[illegible]

[illegible]

[illegible]

Figure [illegible] shows the bottom portion (0–35 mm) of fuel rod [illegible] after operation at a maximum linear heat rating of [illegible] kW/m to [illegible] MWd/kg metal. The maximum power generation occurs over the region from about [illegible] to [illegible] mm above the bottom of the enriched fuel column. The maximum linear heat rating from the structure shown in Fig. [illegible] was about [illegible] kW/m during the irradiation. The most important information shown in Fig. [illegible] is the 1-mm-wide annulus of unrestructured particles between the restructured $(U,Pu)O_2$ and the cladding. A partially restructured region [illegible].7 mm wide is evidenced by the outlines of the large $(U,Pu)O_2$ particles and intermediate-size (115-μm-diam) [illegible]O_2 particles. The partially restructured region behaves like the restructured region, as evidenced by the location of the cool-down crack surrounding the restructured and partially restructured fuel. All the sphere-pac fuel rods observed have at least a 1-mm annulus of unrestructured particles between the restructured fuel and the cladding. This annulus and its importance are discussed in detail later, together with the figures showing the cross sections through several fuel rods at higher power ratings and also during the presentation of the data from power ramping studies.

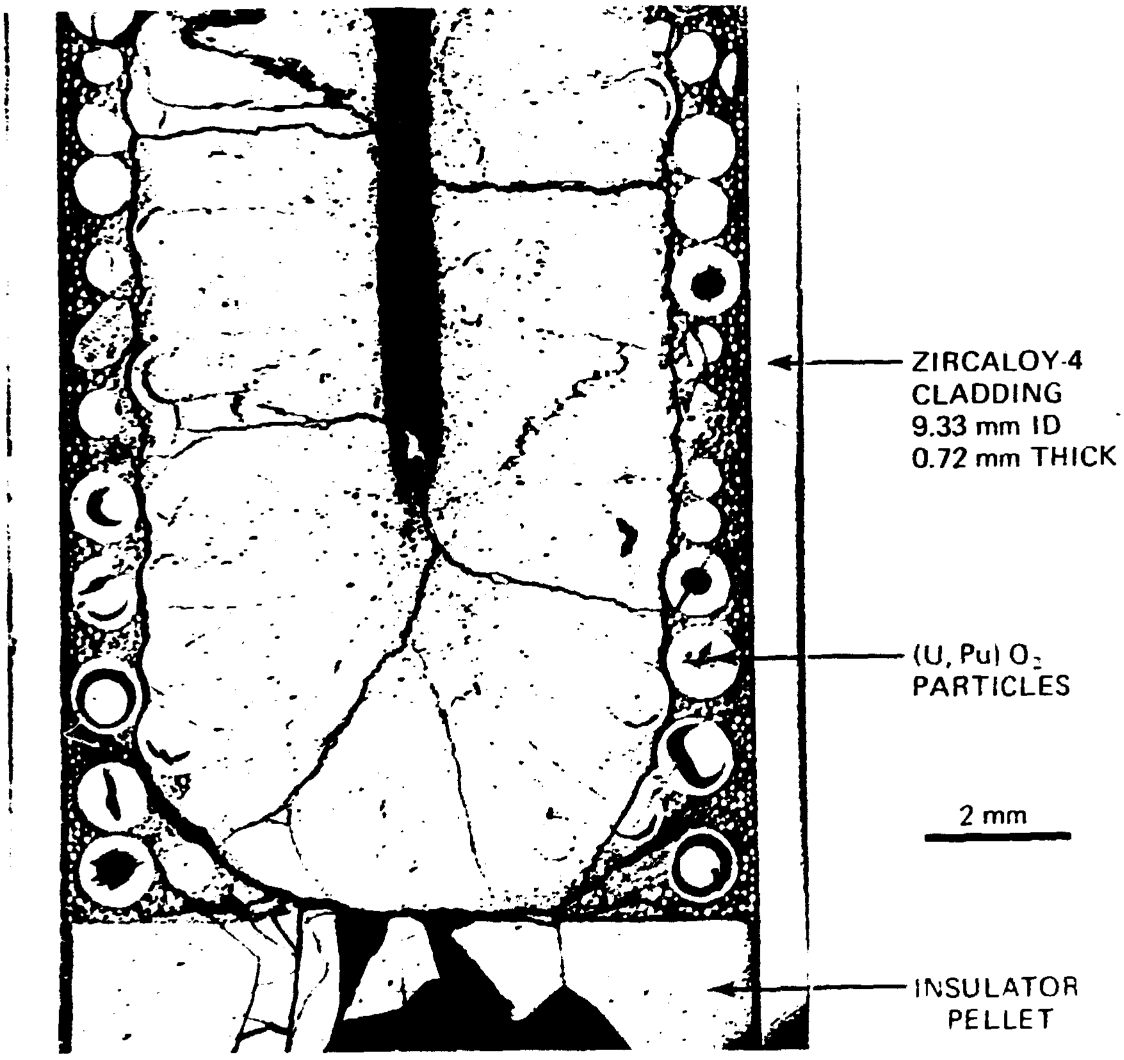

Fig. 4.1. Longitudinal Section Through (U,Pu)O_2 Fuel Rod 3[illegible] at ~39 mm from Bottom of Rod. Note annulus of unrestructured particles about 1 mm between the restructured fuel and cladding. Axial void is [illegible].7 mm in diameter. Plutonium is only in large spheres (1000 μm diam); note the poor as-manufactured quality of several of these particles. The smaller UO_2 particles (115 μm and 38 μm in diameter) have not relocated during the irradiation and handling. Reproduced with permission from ref. 5.

There is evidence that the width of the unrestructured annulus is larger for the fuel rods prepressurized with 2.5 MPa (25 atm) helium fuel (fuel rod 309) than for the fuel rods filled with only 0.1 MPa (1 atm) helium (fuel rod 306).[5] This effect would appear to be worth investigation in any irradiation experiments planned in the current program.

Figure 4.2 contains two transverse micrographs of rod 306.[4] Figure 4.2(a) shows the structure at 361 mm from the bottom end of the fuel rod, where the maximum linear heat rating was 47.0 kW/m (14.3 kW/ft). The unrestructured annulus is at least 1 mm wide and the partially restructured region is about 1 mm thick. From the partially restructured region to the central void the structure looks identical to that of pellet fuel, showing columnar grains, lenticular voids, and radial cracks. Some of the medium and smaller diameter UO_2 particles have fallen out during polishing and etching, since they were present in the as-cut sample and in the partially polished sample.[4]

Figure 4.2(b) shows the transverse microstructure of rod 306 at 414 mm from the bottom of the fuel rod, where the maximum linear power was 37.0 kW/m (11.3 kW/ft). The unrestructured annulus is 3 times as wide as in Fig. 4.2(a), and the partially restructured region is also very large. Both Fig. 4.2(a) and (b) are for linear powers that would be at the upper end of the operating range for commercial LWRs. Again, as in Fig. 4.2(a) some of the medium and small UO_2 particles fell out during polishing and etching.

Note that Figs. 4.1 and 4.2 show no evidence of fuel or fission product interaction with the Zircaloy-4 cladding.

Figure 4.3 shows the transverse microstructure of sphere-pac UO_2 fuel rod 302 at six different distances from the bottom of the rod; the companion UO_2 pellet fuel, rod 314, has not yet been examined.[4] For rod 302 the maximum power generation was 58.0 W/m (15.2 kW/ft), which occurred over the region from about 200 to 240 mm from the bottom of the rod. This location is shown in Fig. 4.3(b). Even at this power rating the unrestructured zone is about 1.3 mm thick. A very clear circumferential cool-down crack is seen at this distance inside the cladding. The partially restructured region in Fig. 4.3(b) is rather narrow and the restructured region behaves exactly like pellet fuel.

Interestingly, Fig. 4.3(a), where the fuel operated at a maximum power of about 40 kW/m, exhibits a larger central void than does Fig. 4.3(b). The reality of this and potential significance to commercial LWR operations need to be examined further.

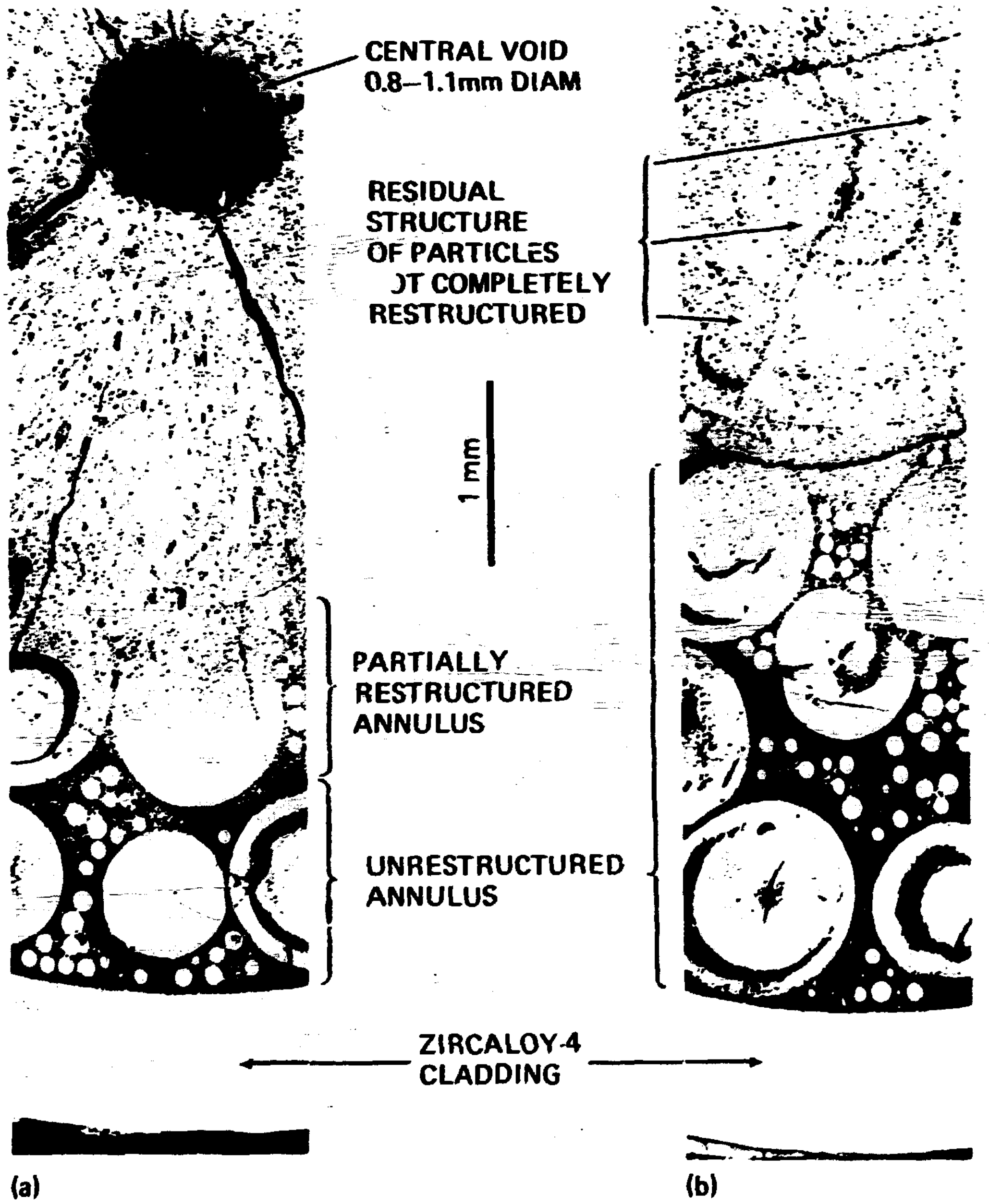

Fig. 4.2. Transverse Microstructures of Rod 306 at Two Different Distances (Hence Two Different Maximum Power Levels) from the Bottom of the Fuel Rod. The unrestructured annulus is very large, and there is no evidence of interaction of fuel and/or fission products with the Zircaloy-4 cladding. (a) 361 mm from bottom of fuel rod; about 47 kW/m. (b) 414 mm from bottom of fuel rod; about 37 kW/m. Reproduced with permission from ref. 4.

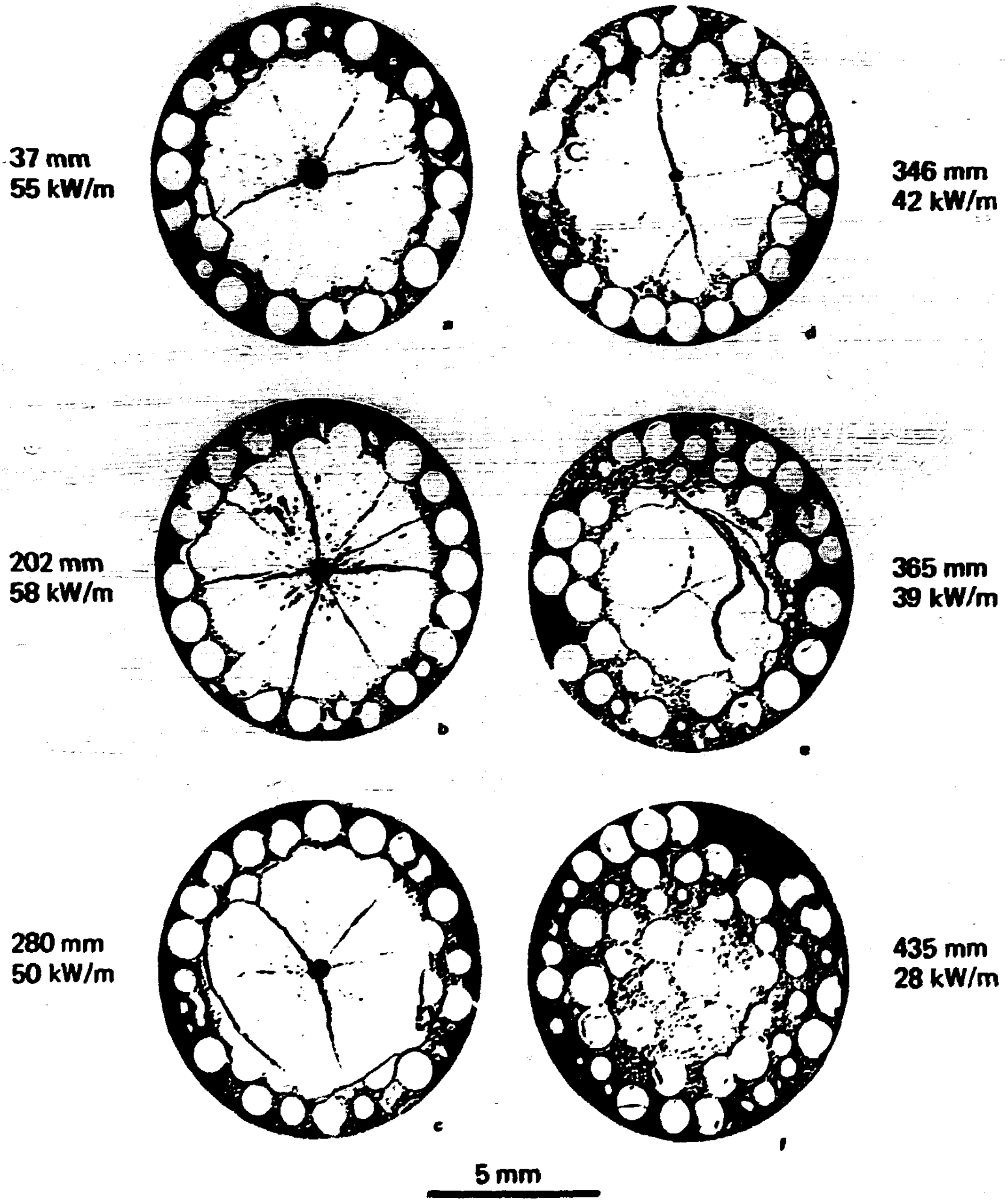

Fig. 4.5. Transverse Microstructure of Fuel Rod 302 at Six Different Elevations (and Power Levels). The elevations from the bottom of the rod and the associated maximum power level are indicated next to each micrograph. Reproduced with permission from ref. 4.

The positions of the microstructures from the bottom of the fuel rod and the associated maximum power levels are shown in Figs. 4.3(a) through (f) and are self-explanatory. The lower the power level the less the volume of restructured material and the smaller (usually) the axial void on proceeding from Fig. 4.3(a) through (f). Again, there is no evidence of any fuel or fission product interaction with the cladding.

Unfortunately, the burnup levels achieved in fuel rods 302 and 314 (≈4 MWd/kg metal) are considerably below those of interest for commercial LWR operation. This is a portion of the irradiation test program that will have to be pursued. However, even at the highest burnups (≈11 MWd/kg metal) achieved in the ECN work and the very high power levels at which the fuel operated (≥62 kW/m, 19 kW/ft) the unrestructured annulus is still 1 mm wide. One would not expect to operate commercial LWR fuel at these high power levels.

Figure 4.4 shows the cross section of Fig. 4.3(b) enlarged an additional 5 times. This was the region of maximum power generation in fuel rod 302. The unrestructured annulus is clearly larger than 1 mm, and the partially restructured region is about 1 mm wide. The structure in the restructured volume of the fuel appears to be identical to that of pellet fuel. The columnar grains, lenticular voids, and central void are clearly visible. Again there is complete absence of any interaction between fuel or fission products and the cladding.

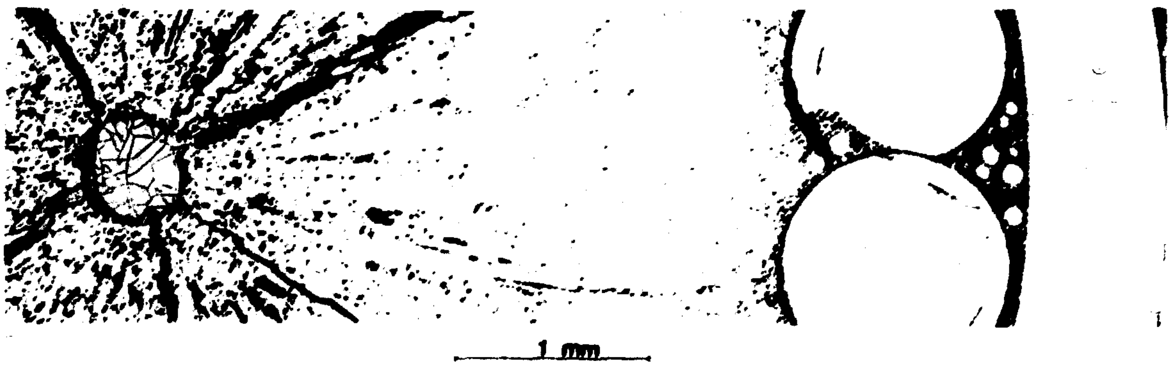

Fig. 4.4. Further Enlargement of a Portion of Fig. 4.3(b). The region shown above is the 4 o'clock position (i.e., 120° from the top) of Fig. 4.3(b). The unrestructured, partially restructured, and restructured regions are clearly visible. Note also that no fuel or fission product interaction with the cladding has occurred. Reproduced with permission from ref. 4.

Transverse cracking occurs in the sphere-pac fuels at intervals along fuel columns operated at higher temperatures. These have been observed clearly by neutron radiography at Petten[6] and at Risö.[7] They have been less clearly observed by gamma ray scanning at Petten.[6] The cracks are rather regularly spaced, and the sections between cracks have a height-to-diameter ratio slightly greater than 1. Apparently sufficient sintering occurs in the central portion of the fuel to cause the fuel column to crack as a result of thermal strains during cool-down.

The unrestructured annulus, which is always present in the sphere-pac fuel even at the highest power ratings of 66 kW/m (20 kW/ft), should provide two important benefits to the irradiation performance of LWR fuel elements. The first benefit is a lower stress exerted by the fuel on the cladding than that in pellet fuel rods. The second benefit is that the unrestructured annulus eliminates the "short circuit" for fission product transport to the cladding. In the unrestructured annulus the spherical, or at least nearly spherical, particles can move vertically under a moderate stress. Hence, during fuel expansion that accompanies increases in reactor power level the stress exerted on the cladding by the fuel is mitigated by vertical movement of the spheres.

Important evidence of this has been obtained by Sens and Majoor.[1] 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 rods had the same helium pressure, smear density, and cladding. The rods were identical in all parameters except that one contained sphere-pac fuel and the other contained pellet fuel. Figure 4.5 shows the length increases for both fuel rods upon increasing the power level. The strain produced in the fuel rod containing pellets was more than twice the strain produced in the rod containing sphere-pac fuel. 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 by motion of the

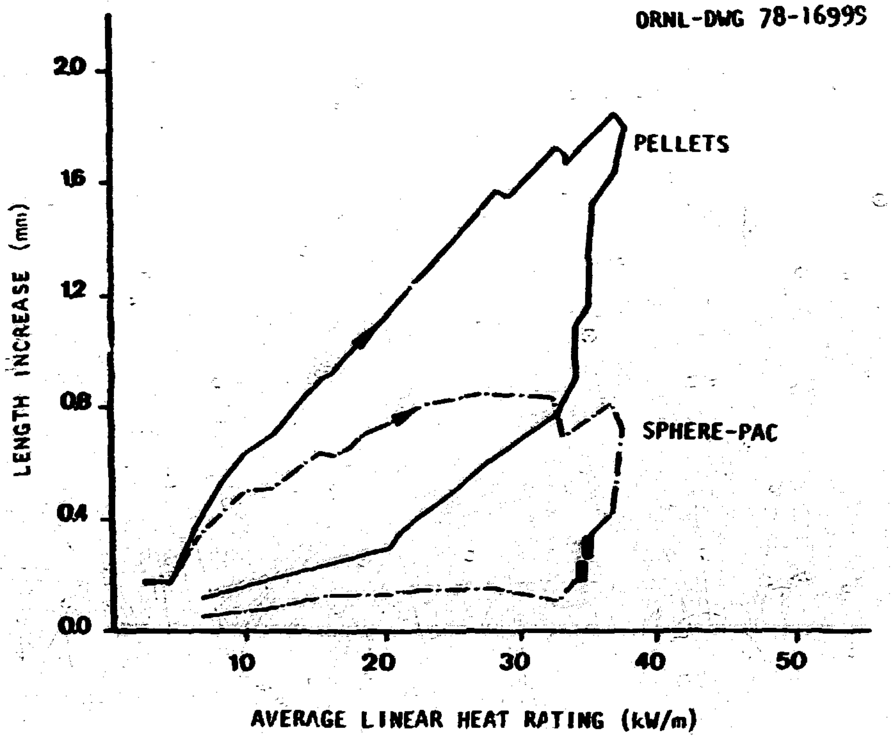

Fig. 4.5. Length Increases in Pellet and Sphere-Pac UO_2 Fuel Rod on Increasing the Linear Power from Zero to Almost 40 kW/m. The resultant strain in the pellet rod is more than twice that in the sphere-pac rod. Based on ref. 1.

unrestructured spheres at the periphery of the fuel column. This should reduce the radial as well as axial strains in the cladding.

Cladding failures that are observed in LWR fuel almost always occur at an interface between pellets or at a location where a radial crack in the pellet reaches the cladding. The localized stresses in the cladding are greatest at these two locations. The presence of the annulus of unrestructured particles in the sphere-pac fuel rod eliminates both the above mechanisms for producing high localized stresses in the cladding; this should result in improved fuel element performance and decreased cladding failures.

4.1.2 Studies at Risö, Denmark

Knudsen and co-workers[7] 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 rod was made with pellet fuel and the other was made with sphere-pac fuel. The rods were first irradiated in the HBWR to 29.6 MWd/kg metal at linear powers over the range 28—44 kW/m. The overpower studies were conducted in the DR3 reactor at Risö. The rods were ramped at rates of 5 to 6 kW/m min from about 35 kW/m to failure. The HOTCAKE and WAFER-1 modeling codes were used to analyze the strains produced during the ramping studies. Knudsen et al. concluded "that the performance of the sphere-pac rod at high burnup was not essentially different from that of the pellet rod." They stated that modeling codes could not distinguish between pellet and sphere-pac fuel. This had already been assumed by us since no one has yet attempted to employ the properties of sphere-pac fuels in the LWR modeling codes. Therefore, their results can be used to qualitatively indicate that sphere-pac fuels behave the same as pellet fuels for the burnup and linear heat ratings achieved in their studies.

4.1.3 Studies at KFA, Jülich, FRG

From 1965 to 1968 Kerforschungsanlage (KFA) at Jülich, FRG, had an irradiation test program on sphere-pac fuels for use in a Heavy Water Breeder Reactor (HWBR).[2] The program was discontinued when interest in the HBWR diminished in the late 1960s. Reports have been written on the 14 irradiations that were conducted in seven separate experimental assemblies. The fuel and fertile species were 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 % 630—1000-μm-diam and 25% 33—100-μm-diam spheres. The rods had smear densities of 81—82% and were 276 mm long for irradiation in the FRJ-2 Reactor at Jülich. The cladding was Zircaloy-4; no rods containing pellet fuel were irradiated in that program.

A portion of the KFA program included two irradiations containing 14 fuel rods, 4 of which were taken to high burnup. Pertinent information on these four rods is given in Table 4.9. The cladding of rods RBE-35, -36, and -37 was autoclaved before loading.

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.

Table 4.9. High-Burnup Sphere-Pac Fuel Rods Irradiated by KFA Jülich

Experiment	Rod	Cladding Dimensions, mm		Burnup MWd/kg(Th+U)	Max Linear Power (kW/m)
		OD	Wall		
LV9.3-E-31	RBE-35	11.77	0.62	44.7	56
LV9.3-E-31	RBE-36	11.77	0.62	45.2	57
LV9.2-E-32	RBE-37	10.75	0.72	49.8	58
LV9.2-E-32	RBE-38	10.75	0.72	50.3	60

After irradiation the 14 fuel rods showed no evidence of interaction of the fuel or fission products with the cladding. The maximum cladding diametral increases were 0.02 to 0.05 mm. 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 46–47% for RBE-35 and -36 and 41–51% 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 of the fuel.[2] The magnitude of the difference and the absolute concentrations were not provided.[2] Higher ^{233}U concentrations in the outer regions of the fuel are most probably due to flux depression across the fuel rod. The higher thermal neutron flux in the outer region of the fuel resulted in a higher conversion of ^{232}Th to ^{233}U in this region.

Although the experimental program has not been active since 1970, Kraftwerkunion (KWU) has sold an HWR to Argentina, and interest in the LWR and HWBR programs may be revived. An assembly of 12 fuel rods has been fabricated and is ready for insertion into a reactor that would provide relevant information for assessing the performance of sphere-pac fuels in LWRs or HWRs.

4.1.4 Studies at CNEN, Rome, Italy

In the Italian fuel development program 16 sphere-pac fuel rods somewhat relevant to LWR fissile contents were irradiated in the RS-1 swimming pool reactor.[8] Two fuel rods of solid solution $U_{0.982}Pu_{0.018}O_2$* containing 450–500-μm and <37-μm-diam spheres to produce a smear density of 80%, clad with Zircaloy-2, were irradiated in the Halden BHWR (experiment IFA-124). After irradiation 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 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. 4.6, which was prepared from radial cross section ceramographs at many locations along the rod. The restructuring and central void profile offer direct evidence that particles did not fall down the central void from the top of the fuel column during irradiation. The central void was closed at the top and bottom of the fuel column; the particles that were observed in the central void during postirradiation examination of sphere-pac fuels were transported there during ceramographic preparation of the fuel rod.

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*The original conference proceedings have a mistake in Table 1 on p. 377 indicating the fuel to be $U_{0.982}Pu_{0.18}O_2$ instead of the composition given above.

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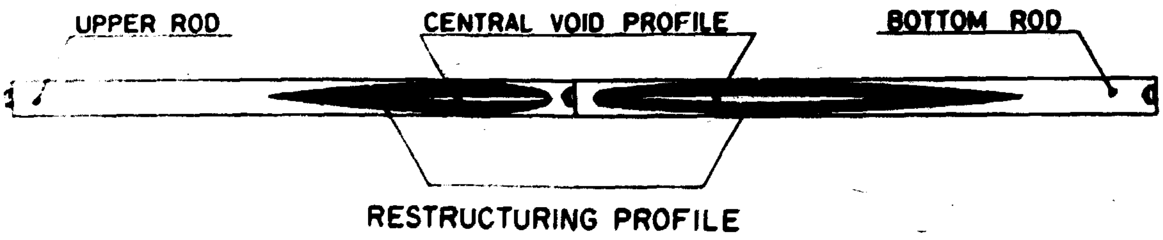


Fig. 4.6. Central Void and Restructuring Profiles in Two Fuel Rods of $U_{0.982}Pu_{0.018}O_2$ Irradiated in the Halden Reactor at a Maximum Power of 52.0 kW/m to 0.5 MWd/kg Heavy Metal. The reactor control rods were inserted from the left in the figure, producing a shorter restructured zone in the upper fuel rod. From A. Cervellati et al., pp. 324–413, CONF-700502.

Restructuring of the particles was observed to within approximately the outer 1 mm of the fuel. This is consistent with the Petten results reported earlier. Restructuring had occured in all regions of the 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.[8] This phenomenon has been observed in other fuel rods where poor hydrogen and moisture control existed during fabrication of the fuel or during loading or helium filling of the fuel rod.[6,9,10]

The second experiment in the Italian fuel development program (SDK-2) contained six rods of $U_{0.95}Pu_{0.05}O_2$ in vi-pac and pellet form that were to be irradiated under representative BWR operating conditions. Particle sizes of 710 to 840 μm mixed with fines of 25 to 88 μm were used to provide a smear density of 80%. No further information on SDK-2 is given in reference 8.

The Italians[8] irradiated an additional 15 sphere-pac fuel rods of FBR fissile contents (i.e., 10–18% Pu). All the postirradiation examination data and ceramography are consistent with the data in Figs. 4.1 through 4.6 of this presentation.

4.1.5 Assessment of Tests to Date

The failure of Zircaloy cladding in water-cooled reactors is predominately by stress-corrosion cracking (SCC) due to fission product attack at the grain boundaries of the regions of highly localized stresses.[9,11–13] To date, at least Cs, I, and Cd have been identified and several others have been suggested[9] as corrosive chemical species involved in the SCC of Zircaloys. The unrestructured annulus that exists at the periphery of sphere-pac fuel rods should reduce fission product transport to the cladding and decrease cladding failures.

With the unrestructured annulus present no pellet-pellet interfaces or radial pellet cracks are available to provide the fission products a rapid transport path to the cladding. The fission products will still move rapidly in the central restructured region through the radial cracks, but these cracks terminate in the unrestructured and partially restructured annuli. From there out to the cladding, a straight line distance from 1 to

2 mm, the fission products must move by some type of random walk process through the packed spheres to reach the cladding. The actual distance that must be traversed is some multiple of the 1 to 2 mm since the packing of different size spheres eliminates a straight-line path to the cladding.

For SCC to occur both stresses and a corrosive chemical environment are needed. The presence of the unsintered annulus reduces both the probability of producing highly localized stresses in the cladding and the concentration of corrosive fission products to reach the cladding. Since these characteristics of sphere-pac fuel mitigate the apparent causes of SCC, sphere-pac LWR fuel rods should perform at least as well as pellet fuels.

4.2 THERMAL REACTOR IRRADIATIONS OF FAST REACTOR OXIDE FUELS

There have been several irradiations of fast reactor $(U,Pu)O_2$ fuel rods in thermal reactors. Several of these irradiations have been instrumented, and the information obtained provides a significant contribution to understanding the irradiation performance of sphere-pac oxide fuels. In-reactor temperature measurements are valuable in determining fuel restructuring temperatures and kinetics and effective gap conductances for both pellet and sphere-pac oxide fuels. The gas pressure measurements are used to determine fission gas release rates, total fission gas release, and oxygen buildup rates during irradiation. Combining temperature and pressure measurements provides information on fuel thermal conductivity and gap conductance as functions of fission gas release.

The information presented in this section should be utilized only for relative comparison between pellet and sphere-pac fuel. The absolute information should not be directly related to LWR applications because of (1) use of stainless steel rather than Zircaloy cladding, (2) generally higher linear heat ratings than experienced by LWR fuels, and (3) significant differences in radial fission rate profiles for the high-fissile-content fuel compared with LWR fuel in a thermal neutron environment.

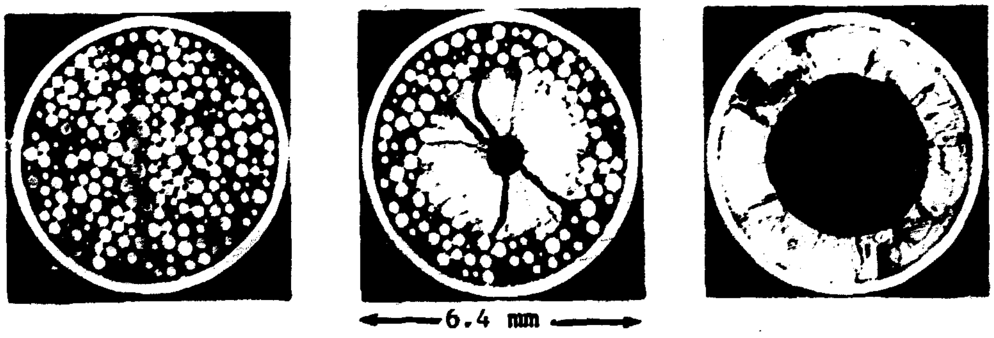
4.2.1 Studies at ORNL

To assess the performance of sphere-pac 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. Two sphere sizes (300–600-μm-diam and <44-μm-diam) were used to produce smear densities of 84%. The compositions of sphere-pac fuel studied[14] were $UO_{2.02}$ (20% enriched), $^{235}U_{0.80}Pu_{0.20}O_2$, and $^{238}U_{0.85}Pu_{0.15}O_{1.97}$. Table 4.10 and Fig. 4.7 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 for maximum fuel temperatures above 1650°C.[15] This has also been noted by Lahr,[16,17] who observed the initiation of restructuring of (U,Pu)O_2 fuel within 2 min after

Table 4.10. 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. 4.7.



ROD A ROD B ROD C

Fig. 4.7. 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 (35 kW/ft) (Table 4.10) there is a small annulus of nonrestructured spheres between the restructured fuel and the cladding.

beginning of irradiation in $(U,Pu)O_2$ operated at linear power levels from 63.0 to 69.4 kW/m (19.2–21.2 kW/ft). The results shown in Fig. 4.7 and those of Lahr illustrate that restructuring begins very early in the life of the fuel element. The early initiation of sintering and restructuring in sphere-pac and pellet UO_2-PuO_2 fast breeder fuels have also been confirmed by thermocoupled irradiations in the ORR.[18]

Table 4.11 lists the conditions and Fig. 4.8 shows the transverse microstructures of two sphere-pac fuel rods and one pellet fuel rod irradiated in the ETR.[19,20] For the urania-plutonia sphere-pac fuel operated at 65.5 kW/m (20 kW/ft), a large annulus of unrestructured spheres is adjacent to the cladding. For the hyperstoichiometric urania sphere-pac fuel operated at 72 kW/m (22 kW/ft) the annulus is much smaller, but most of the radial cracks are terminated at the inner side of the annulus. For the stoichiometric urania pellet fuel operated at 85 kW/m (26 kW/ft) the radial cracks prop-agate to the cladding. Figure 4.8 illustrates that the central void diameter is larger for higher linear power and lower fuel rod smear density. Because of the differences in fissile atom density and composition of the fuel shown in Fig. 4.8 the comparisons are only qualitative.

Only one of the ETR irradiations of urania-plutonia was taken to high burnups: 8.7 to 11.3 at. % at linear heat ratings of 29.0 and 33.0 kW/m (8.8 and 10.1 kW/ft), respectively.[21] These fuels had an unrestructured annulus of particles at least 0.6 mm thick between the

Table 4.11. 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	6.0	44	82	460
B	$UO_{2.02}$	72.0	5.5	44	73	470
C[b]	$UO_{2.00}$	85.0	5.7	47	84	540

[a] Transverse cross sections shown in Fig. 4.8.

[b] Pellet fuel.

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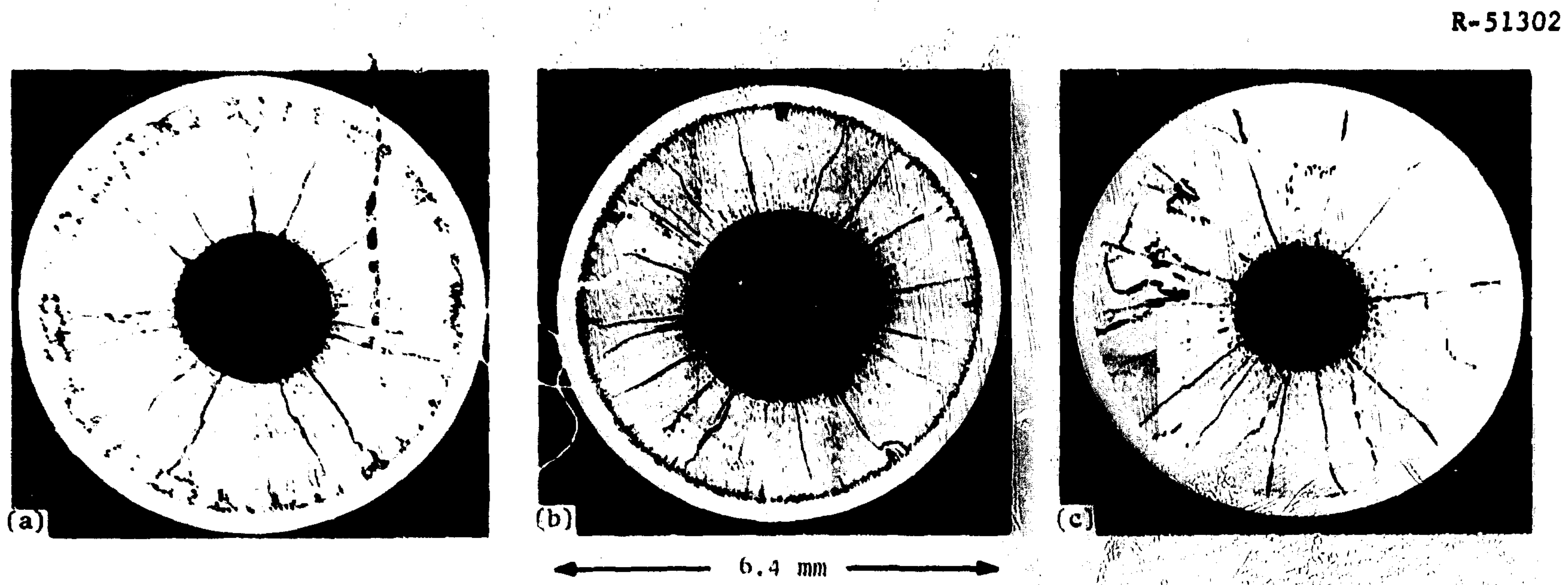

sphere-pac
Rod A

sphere-pac
Rod B

pellet
Rod C

Fig. 4.8. Transverse Cross Sections of Sphere-Pac and Pellet Fuel Rods Operated at High Linear Powers to Burnups of 5.5 to 6.0%. (See Table 4.11.)

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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 in the same tests at 36.5 kW/m (11.2 kW/ft) to 13.8% burnup the fission gas release was 96%.

To determine restructuring kinetics and effective gap conductances for sphere-pac fuel, three capsules containing the six fuel rods described in Table 4.12 were irradiated in instrumented capsules in the ORR.[14] Eight thermocouples were located at the longitudinal center of each fuel rod to measure fuel temperature and cladding temperature at three locations. Radial heat flow from the center of the fuel rod to the outer capsule wall was measured with four additional thermocouples in the capsule wall. The transverse cross sections of two sphere-pac fuel rods and one pellet fuel rod are shown in Fig. 4.9.

The sphere-pac rod in SG-2 that operated at a central temperature of 1500°C showed only slight restructuring in the central half of the fuel. In the cooler outer annulus of the fuel some of the particles were lost during ceramographic preparation of the samples; this also occurred in the cooler outer region of the sphere-pac fuel rod in SG-3. The higher maximum temperature of 2000°C experienced by the sphere-pac rod in SG-3 resulted in complete restructuring in the central half of the fuel. Considerable restructuring also occurred in the pellet fuel that 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 outer cladding temperature being 75°C higher in the sphere-pac rod than in the pellet rod.

The 12 thermocouples at the longitudinal center of each fuel rod provided data needed 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[10] showed a gap conductance for $U_{0.80}Pu_{0.20}O_{1.99}$ pellet fuel of 7.3 kW/m^2 °C and for sphere-pac fuel, 19.3 kW/m^2 °C. Figure 4.10 shows the transverse fuel temperature profile for the sphere-pac and pellet fuels irradiated in ORR capsule SG-3. Because of the lower gap conductance for the pellet fuel its surface temperature was higher than that of the sphere-pac fuel.

Table 4.12. Fuel Parameters and Operating Conditions for Instrumented ORR Irradiations of $(U,Pu)O_2$

Capsule	Fuel Rod[a]	Fuel Parameters			Operating Conditions			
		Form	Composition	Smear[b] Density (% of Theoretical)	Total Time (h)	Maximum[c] Temperature (°C)	Time at Maximum Temperature (h)	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 (0.375 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.

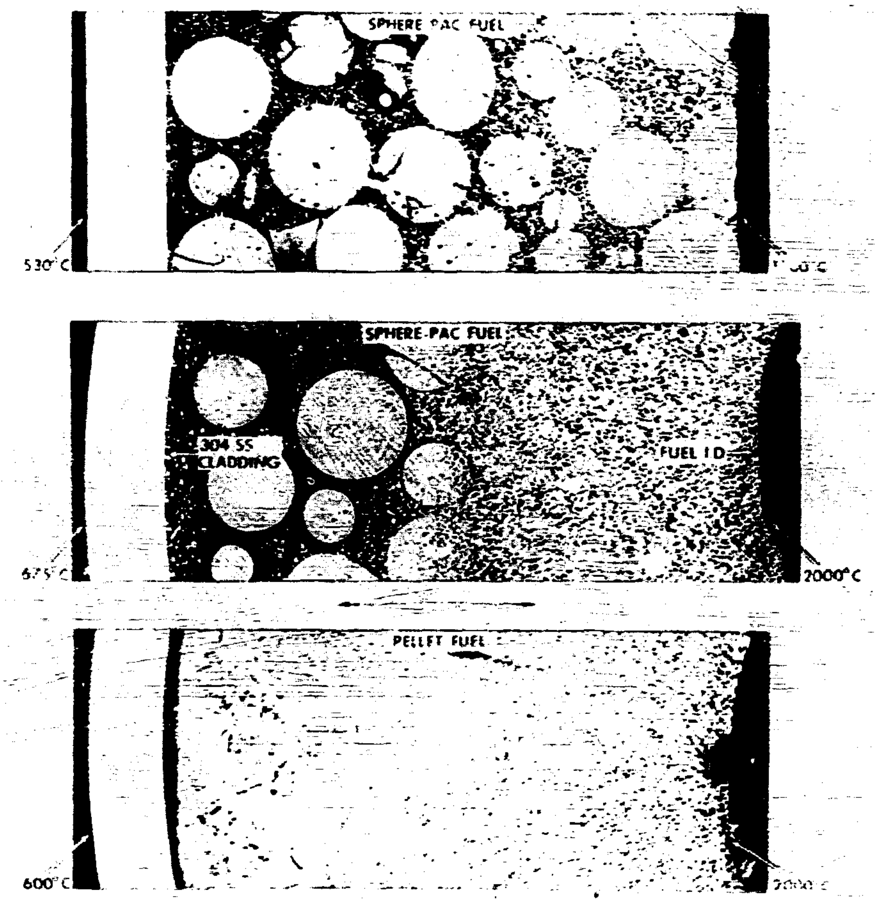

Fig. 4.9. Transverse Cross Sections of Sphere-Pac and Pellet Fuel Rods After Short-Time Irradiation in ORR to About 0.5% Burnup. Irradiation conditions and other information are given in Table 4.12. Top, rod 3; middle, rod 5; bottom, rod 6.

Figure 4.11 shows longitudinal fuel-cladding interfaces for sphere-pac and pellet fuel rods that operated[10,22] at the same cladding inner surface temperature in ORR capsule SG-3. No detectable cladding attack occurred in the sphere-pac rod. However, attack to a significant depth of the cladding was apparent in the pellet rod near the pellet interfaces.

In addition, two instrumented capsules, each containing four urania-plutonia rods, were irradiated[10] 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, its operating conditions, and performance is given in Table 4.13. The most important information obtained in this irradiation is shown in Figs. 4.12 and 4.13. In Fig. 4.12 melting appears to have occurred in the central

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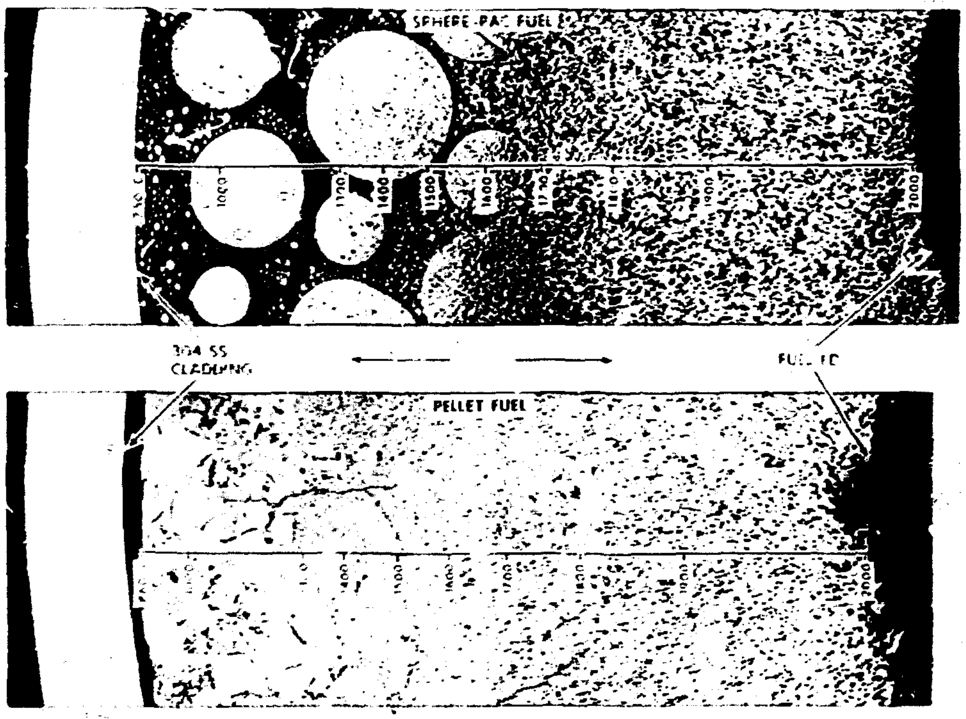

Fig. 4.10. Transverse Temperature Profile for $U_{0.80}Pu_{0.20}O_{1.98}$ Sphere-Pac and Pellet Fuel Irradiated in Instrumented ORR Capsule SG-3. The temperatures on the extreme left are the fuel surface temperatures. (From ref. 10.)

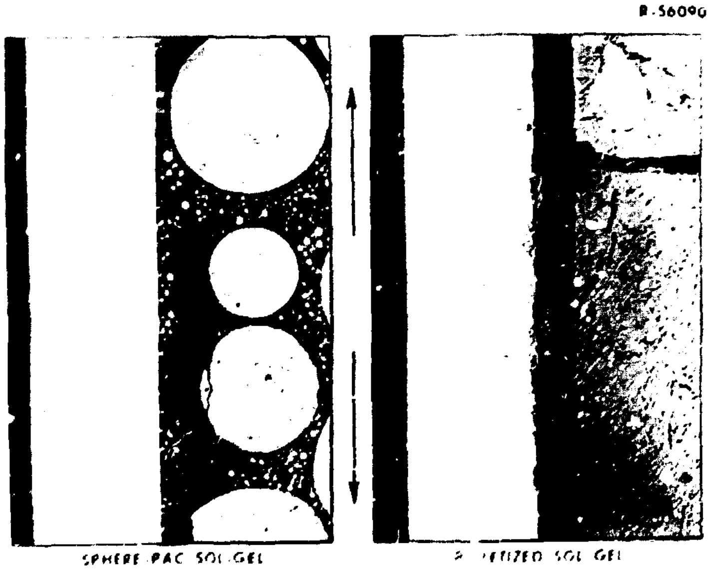

Fig. 4.11. Absence of Fuel-Cladding Chemical Interaction for Sphere-Pac $U_{0.80}Pu_{0.20}O_{1.98}$ Fuel Irradiated in ORR Capsule SG-3. Type 304 stainless steel cladding inner surface was above 650°C for 430 h in sphere-pac rod (left) and for 265 h in pellet rod (right).

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Table 4.13. Fuel Rod Parameters for Instrumented ETR Capsule 121 Containing $U_{0.80}Pu_{0.20}O_{1.98}$[a]

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

[a] From ref. 10.

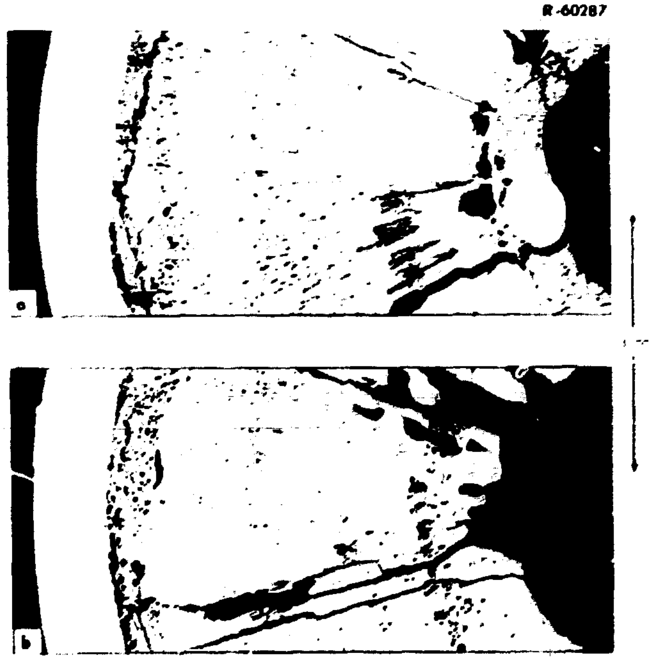

Fig. 4.12. Transverse Cross Section Through Two Pellet Rods Irradiated in ETR Instrumented Capsule 121. Melting or near melting has occurred near the center, and the fuel and cladding have interacted chemically. (a) 121-1. (b) 121-2. From ref. 10.

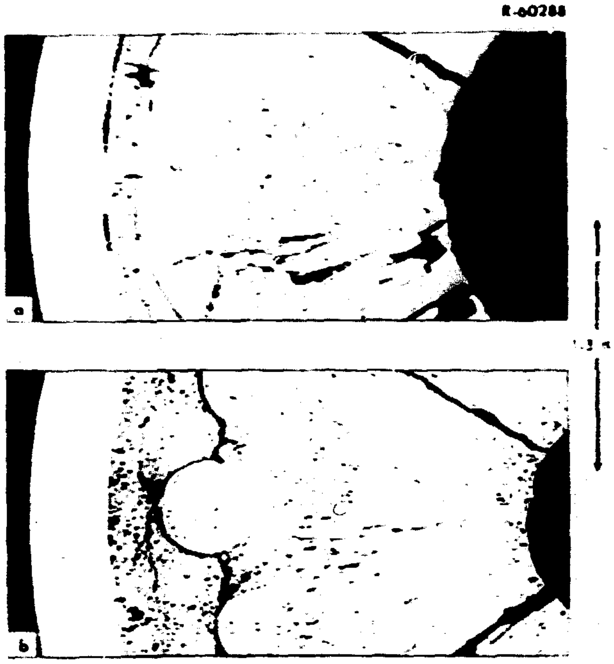

Fig. 4.13. Transverse Cross Section Through Two Sphere-Pac Fuel Rods Irradiated in ETR Instrumented Capsule 121. Large radial cracks terminate at the outer edge of the restructured region. No detectable chemical interaction has occurred between the fuel and the cladding; however, the cladding appears to be adherent to the fuel at the center and bottom of rod 121-3. (a) 121-3. (b) 121-4. From ref. 10.

region of the pellet fuel. The small white spots in the columnar grain region and in the equiaxed grain region further out are unoxidized metallic fission products. Large radial cracks propagate to the inner side of the cladding, and the fuel and cladding have interacted chemically. Figure 4.13 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. This is surprising since the measured peak cladding inner temperature was 605°C, quite low for restructuring and/or mass transport by vaporization-condensation. In rod 121-3 the fuel appears to adhere to the cladding in at least two locations. The circumferential cool-down crack follows the outline of the unrestructured or partially restructured spheres. The large radial cracks do not propagate to the cladding but are terminated at the outer edge of the restructured region.

4.2.2 Studies at Karlsruhe, FRG

In addition to the fuel development work at KFA for the German thermal reactor program, 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.[16,17] The plutonium contents ranged from 9.29 to 21.5%, which is the fissile content of fast reactor fuels. Two size fractions of particles were used: 800 to 1100-μm (U,Pu)O_2 and 125 to 200-μm UO_2, to obtain reported smear densities of 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 fuels 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 for fast reactors. Also, alloy 1.4988 is not used in thermal reactors, and the upper end of the average cladding temperatures is too high for LWRs. Of the eight fuel rods irradiated, only one had an average cladding temperature less than 350°C.

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*Alloy 1.4988 is similar to ASTM type 316 stainless steel with a nominal composition of 67 wt % Fe, 16 wt % Cr, 14 wt % Ni, 1.3 wt % Mo, 1.1 wt % Mn, and 0.7 wt % V and low limits on impurities C, Si, P, S, Co, Cu, N, Ta, and Nb.

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5. STATUS AND RECOMMENDED FUTURE WORK

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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 commercial application can be realized. Areas requiring additional work are discussed below. Much of the overall technology required for design, construction, and operation of a commerical 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 1977. This work is funded at ORNL by the Department of Energy Division of Nuclear Power Development as a part of the Fuel Refabrication and Development Program, which is administered by Battelle Pacific Northwest Laboratories, and through the Reactor Research and Technology Division.

5.1 SOL AND BROTH PREPARATION

5.1.1 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 exits 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 to 1500 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, and the latter will probably require it. 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 and mixed (U,Pu) and (Th,U) oxide spheres, but with the older sol-gel flowsheets. Considerable experience exits in Europe for preparation of (U,Pu) oxide and carbide spheres by a broth-type process.

5.1.2 Future Work

It is important to evaluate European broth-type processes for preparing large spheres and to select a process for further development. Scouting tests of known internal and external chemical gelation processes must be conducted. Subsequently, flowsheets must be developed for selected processes as necessary to meet U.S. fuel cycle requirements. Critical parameters must be explored over a wide range to provide good process definition and control.

All uranium-plutonium processes now in use start with a pure plutonium nitrate solution. Therefore, particular emphasis should be placed on developing techniques for utilizing co-processed uranium-plutonium. Similarly, little or no work on Th-Pu gel-sphere processes has been conducted in Europe. Therefore, particular emphasis must be placed here also if on-going reactor design and fuel cycle studies indicate that these are desirable fuels. The influence of potential spikes and low-decontamination flowsheets on fuel fabrication technology is a virtual unknown and must be evaluated for both pellet and sphere-pac fuels.

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 also be determined.

Another major need is in the area of fine (<75-μm-diam) sphere preparation. European programs have had difficulty in preparing this size material. The initial work with true sols shows promise here, since the slower gelation rate could be an asset for this application.

As is true for most steps in the gel-sphere-pac process, there is need to progress through the normally accepted stages of development 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 that radiolysis will not be a problem (or to define the allowable limits) for both the processes and the equipment. Additionally, cold development at engineering and prototype 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.

5.2 FORMING AND WASHING OF GEL SPHERES

5.2.1 Status

The status of sphere forming and washing is basically the same as that discussed for sol preparation. Several designs of pulsed droplet generators capable of producing essentially single-size large or medium spheres have been operated. Multi-needle units have also been operated with throughputs of 10 kg/h. Gel 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.

5.2.2 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. A process must be selected for disposing of or treating the ammonium nitrate waste.

Increasing feed rate while maintaining a narrow sphere size distribution is needed for the medium (200–350-μm-diam) spheres. An improved method for forming fines having higher product yield in the 20–50-μm-diam range is desired. The use of spiked fuel may require modification of the process flowsheets. Remotely operable and maintainable equipment is needed for fissile spheres, and prototype contact equipment for fertile fines is still required.

5.3 DRYING OF GEL SPHERES

5.3.1 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 batchwise and also continuously on wire mesh belts.

5.3.2 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.

5.4 CALCINING AND SINTERING

5.4.1 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 at 1450°C after calcination at 450°C to remove volatiles remaining after drying. Sphere sintering, however, has not been demonstrated for all proposed fuel compositions being considered. Most experience has been with batch operations. Plutonia experience has been limited to batch sizes of several hundred grams.

5.4.2 Future Work

Detailed processes for calcining and sintering spheres of the required composition(s) must be developed for the specific gel process(es) selected. Variables that must be considered are heating rate, temperature, 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 more reliable heating elements could be used. However, the extent to which sintering temperatures can be lowered could be limited by the grain size adequate for fission gas retention rather than density considerations. While sintering furnace development can draw from previous pellet work, special requirements may exist 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 the earlier work the product was always handled in inert-atmosphere glove boxes after sintering. 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.

5.5 CHARACTERIZATION OF SPHERES

5.5.1 Status

Contact or glove-box laboratory-scale techniques have been used to thoroughly characterize spheres of several compositions. With 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.

5.5.2 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. Grain size specifications must be established relatively soon, as these requirements could have a significant impact on sintering furnace design.

5.6 SPHERE-PAC LOADING AND ROD INSPECTION

5.6.1 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 alternate loading procedures are currently being investigated. In one method all three sphere size fractions are either preblended or simultaneously fed into the fuel rod. In the second process the two larger size fractions are simultaneously loaded into the rod and the smallest spheres are subsequently infiltrated through this initial bed. This process is understood at the laboratory scale but poorly 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.

5.6.2 Future Work

Extensive development is required to optimize the required blend of spheres of various sizes, to specify allowable size range limits, and to develop the optimum loading scheme (preblending vs fines infiltration). The loading process must be optimized to yield not only high smear density and uniformity, but practical loading time as well. 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 arrangements may need to be devised.

Existing pneumatic transfer techniques must be modified to accomodate 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 all three size fractions. Equipment for blending two or three sizes of spheres and transferring the blend without size segregation must be more fully developed.

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 rod during loading and to subsequently verfity axial 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.

5.7 IRRADIATION PERFORMANCE

5.7.1 Status

Although over 200 sphere-pac fuel rods have been irradiated, additional work must be conducted to confirm the good irradiation performance observed to date. In particular, sphere-pac fuel rods must be irradiated under representative LWR operating conditions in sufficient number to obtain Nuclear Regulatory Commission licensing of sphere-pac fuel for use in commerical LWRs.

5.7.2 Future Work

The following additional work on the thermal and irradiation performance of sphere-pac fuels is required.

1. Determine the thermal conductivity and gap conductance of sphere-pac LWR-size fuel rods.

2. Determine the quantitative steady-state irradiation performance of sphere-pac fuels at burnups of about 30 MWd/Mg heavy metal and at linear powers of 16 to 39 kW/m (5–12 kW/ft). Pellet fuel rods must be irradiated side by side with the sphere-pac fuel rods.

3. Conduct power increase studies of sphere-pac fuel rods after various levels of burnup. Pellet fuel rods should be exposed to the same power increases.

4. Determine the probability of fuel washout in sphere-pac fuel rods during operation under steady state and under power increase conditions; companion fuel rods of pellet fuel must accompany the sphere-pac fuel rods to assess both the relative and absolute probabilities of fuel washout.

5.8 SCRAP RECYCLE

5.8.1 Status

Work in this area is just beginning 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-catalyzed dissolution in nitric acid, and cleanup by solvent extraction and/or ion exchange. This operation was performed remotely but directly maintained after facility cleanout.

5.8.2 Future Work

An engineering analysis of the type and quantity of scrap 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.

5.9 IN-PLANT WASTE TREATMENT

5.9.1 Status

The present status is similar to scrap recycle: it has not been considered to any depth under the gel-sphere-pac work, but has been treated under the HTGR Fuel Recycle Program. Many wastes are generic; for example small side streams of organic solvents, discarded equipment and tools, decontamination solutions, and various off-gases. These generic wastes are being considered by other programs. However, some wastes are specific to gel sphere procedures, such as large quantities of ammonium nitrate and some of the organics, such as urea, used during gel sphere formation.

5.9.2 Future Work

The major areas requiring attention are ammonium nitrate and organic handling. At least two choices are available for the ammonium nitrate: catalyzed decomposition to water and nitrous oxide, and regeneration of NH_3 and HNO_3 via a calcium oxide process. For organics such as urea and hexamethylenetetramine, the preferred treatment is internal recycle, but suitable processes still need to be developed.

5.10 COMMERCIAL FACILITY

5.10.1 Status

Very little effort to date 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.

5.10.2 Future Work

An engineering study of a commerical-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 need to be estimated. Schemes for sampling, inspection, accountability, safeguards, maintenance, scrap recycle, and waste handling must be generated. An economic analysis for such a commerical plant should be performed.

5.11 REFERENCE

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