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The Sphere-Cal Process: Fabrication of Fuel Pellets From Gel Microspheres

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THE SPHERE-CAL PROCESS: FABRICATION OF FUEL PELLETS FROM GEL MICROSPHERES

S. M. Tiegs, P. A. Haas,* and R. D. Spence*

ABSTRACT

The sphere-cal process uses gel-derived microspheres as feed material for fuel pellet fabrication. Microspheres, because of their free-flowing and dust-free nature, are improved pellet press feed over conventional powder-derived material. The basic sphere-cal process consists of microsphere gelation, drying, and calcining followed by pellet pressing and sintering. We studied each of these process steps to try to determine the important parameters for the production of high quality UO_2, ThO_2, and $(Th,U)O_2$ fuel pellets.

We conducted a statistical experiment to study various microsphere calcining temperatures, forming pressures, and pellet sintering rates. The results were used to select parameters for a standard pellet fabrication screening test, which was a modified ASTM sinterability test procedure. Pellets were fabricated from batches of microspheres produced by using various gelation and drying conditions. Urania microspheres were formed by internal gelation, and thoria and mixed thoria-urania spheres were produced by either internal or external gelation.

From results of the statistical experiment, we determined that UO_2 sintered pellet densities increase both with decreasing calcination temperature (1000—600°C) and with decreasing forming pressure (414—138 MPa). Thermogravimetric analysis results indicate that a minimum calcination temperature of 600°C is necessary for complete reduction of the UO_3 gel microspheres to UO_2. Batch screening test results suggest that use of minimum gel aging, fine-sized microspheres (50—400 μm), and fast drying (warm air or oven) will produce the highest quality UO_2 pellets. Thoria and thoria-urania microspheres produced by internal gelation or by external gelation (KFA method) were hard and compacted poorly, resulting in pellets with a remnant sphere structure. However, thoria-urania microspheres produced by the SNAM external gelation process were softer, resulting in more homogeneous pellets.

Development work to date has shown that the sphere-cal process is a promising alternative to conventional fuel pellet fabrication. Excellent pellets with homogeneous microstructures and high densities have been produced from urania microspheres. Thoria-urania microspheres produced by the SNAM external gelation process are also promising pellet press feed material. Future work will be directed toward optimization of the sphere-cal process parameters.

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*Chemical Technology Division.

INTRODUCTION

An alternative process for fabrication of nuclear fuel pellets is the sphere-cal process. This process uses microspheres rather than powder-derived granules as feed material for pellet pressing. The sphere-cal process has several advantages over conventional pellet fabrication methods.

The sphere-cal process is simpler, requiring fewer steps for pellet fabrication than powder processes. The gel microspheres are inherently free flowing. Therefore, preslugging and granulation, which are necessary for powder to produce free-flowing feed material for automatic pellet presses, may be eliminated. Powder milling, which may cause impurities to be introduced into the fuel material, is unnecessary in the sphere-cal process. Furthermore, powder blending would not be necessary to produce mixed-oxide or diversion resistant fuel pellets. Homogeneous heavy metal loadings and uniform spikant dispersion would be more easily attained by the sphere-cal process since mixed nitrate solutions are used for gel microsphere formation. Pellet centerless grinding may also be eliminated as a result of the more uniform die loading and sintering characteristics of the gel-derived microspheres, which may permit sintering to size.

The sphere-cal process is readily adaptable to remote processing while producing the conventional pellet fuel form. It is especially suited for fuel refabrication since gel microspheres are produced from nitrate solutions. Because the microspheres are free flowing, they are suitable for pneumatic transport. Material holdup problems would be reduced by the use of microspheres rather than powder. Therefore, material accountability and safeguards operations would be improved. Since the gel microspheres are relatively dust free, the spread and buildup of contamination would be minimized. This would reduce both personnel radiation exposure and equipment decontamination times.

Our development work is ongoing to produce urania, thoria, and mixed thoria-urania fuel pellets by the sphere-cal process. The basic sphere-cal process is shown in Fig. 1. First, microspheres are produced

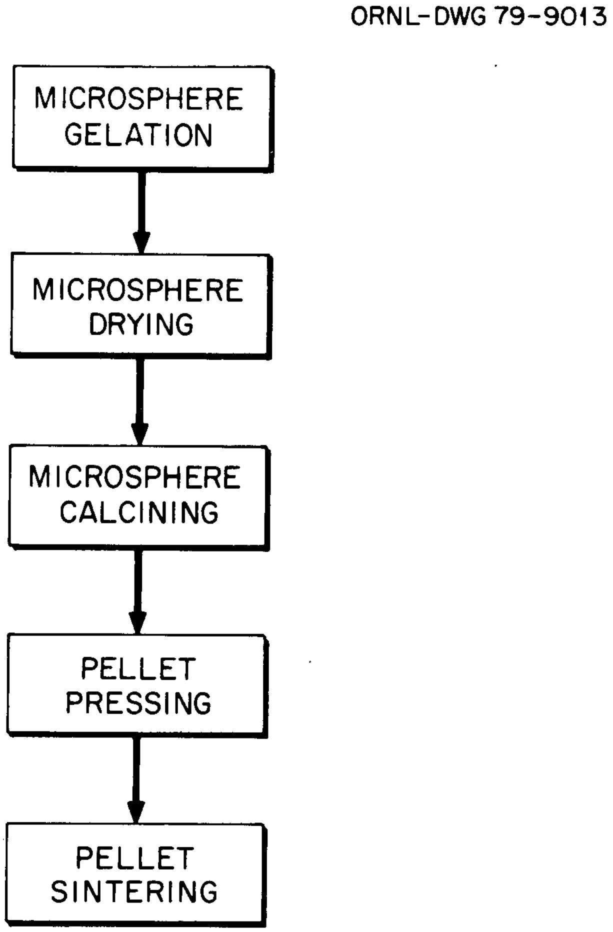

Fig. 1. Sphere-Cal Process.

by chemical gelation — internal gelation for urania microspheres and either internal or external gelation for thoria and mixed thoria-urania microspheres. The microspheres are dried and then calcined to remove water and organics remaining after gelation. During calcination the uranium oxide, which is in the form of UO_3, is reduced by use of mixed argon-hydrogen. The calcined microspheres are then cold pressed to form pellets. The pellets are sintered in a reducing atmosphere to produce the sphere-cal products — UO_2, ThO_2, or mixed $(Th,U)O_2$ fuel pellets. The sphere-cal fuel forms (dried microspheres, calcined microspheres, as-pressed pellets, and sintered pellets) are shown in Fig. 2. Each of the sphere-cal processes will be described in detail in the following sections together with results of our development work to date.

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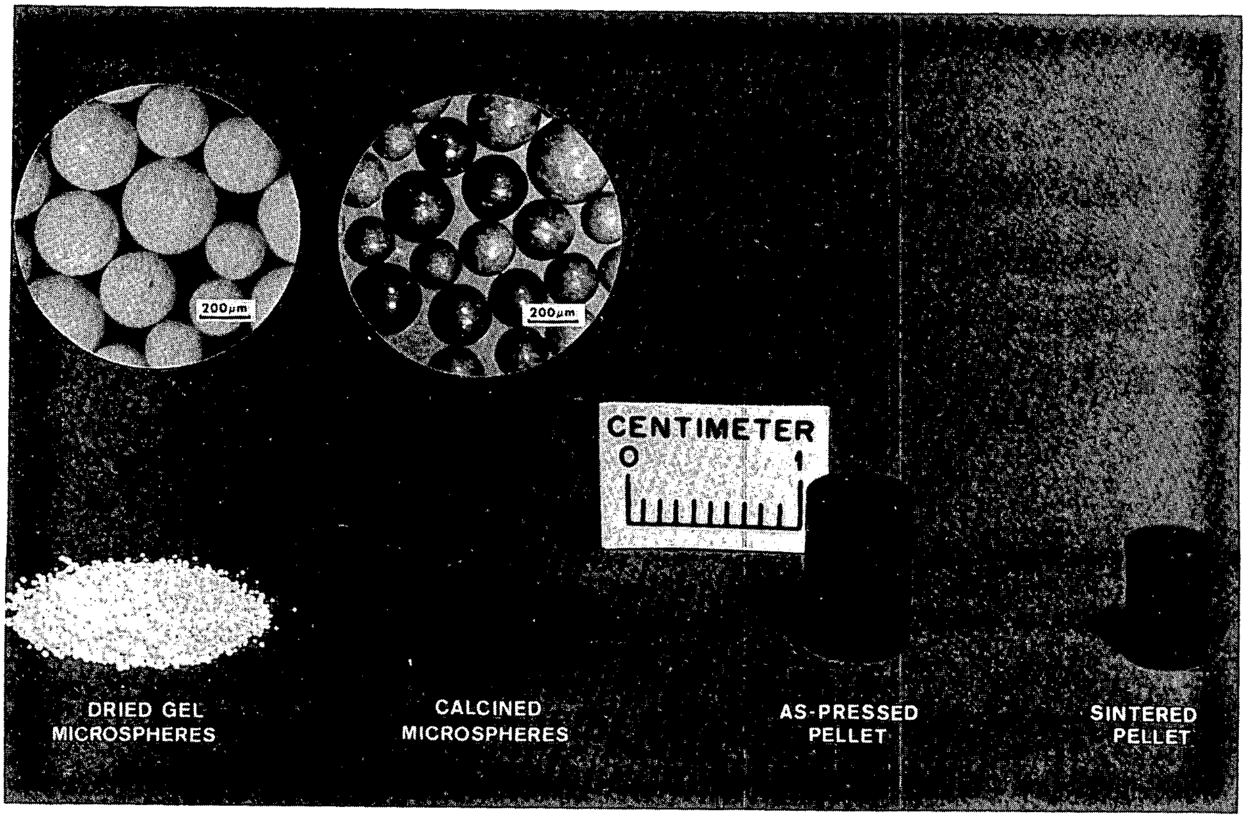

Fig. 2. Fuel Forms During the Sphere-Cal Process.

Previous development work in this area has been mainly concentrated on the use of sol-gel derived powders or shards for pellet fabrication.[1–4] However, a brief development program was conducted on fabrication of $(U,Pu)O_2$ pellets from microspheres formed by water extraction.[5] Relatively low-density pellets with a remnant microsphere structure were produced during this program. Presently, the Italians at CNEN*[6] are developing a process to utilize microspheres formed by the SNAM† external gelation method for the fabrication of $(U,Pu)O_2$ fuel pellets.

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*Comitato Nazionale per L'energia Nucleare, Casaccia, Roma, Italy.

†SNAM Progetti S.p.A., Italy.

MICROSPHERE GELATION

Microspheres that were evaluated for use as sphere-cal process feed material were produced by several gelation methods. Urania microspheres were formed by internal gelation, thoria spheres were produced by external gelation, and mixed thoria-urania spheres were fabricated by either internal or external gelation.

Initially, flowsheets and procedures developed for production of microspheres for the sphere-pac[7–9] process were applied to prepare gel spheres for the sphere-cal process. Based on results from sphere-cal batch screening tests, the gel sphere preparation conditions have been modified to improve the gel sphere properties as they relate to pellet fabrication. The basic gelation flowsheets used for the preparation of microspheres for the sphere-cal process will be described in the following sections.

Urania Microspheres

The microspheres used for the production of UO_2 fuel pellets were formed by internal gelation (modified KEMA* process).[10,11] A water-soluble chemical that releases ammonia when heated is used to precipitate the heavy metal to gel spheres internally. Since the ammonia donor and the heavy metal ions are dissolved in the same solution, the gelation occurs rapidly and uniformly throughout the drop.

The flowsheet for internal gelation is shown in Fig. 3. First, a broth is prepared, which contains an acid-deficient solution of the heavy metal (in this case uranium) with urea added and an ammonia donor solution of hexamethylenetetramine [HMTA, $(CH_2)_6N_4$]. The broth is pumped through a dispersion device that forms drops, which are then gelled in a hot organic medium. The gelation reaction is

$$2UO_2(NO_3)_2 + (CH_2)_6N_4 + (8 + 2x)H_2O \overset{\Delta}{\rightarrow} 4NH_4NO_3 + 6CH_2O + 2UO_3(H_2O)_x \, .$$

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*Keuring van Elecrotechnische Materialen, Arnhem, Netherlands.

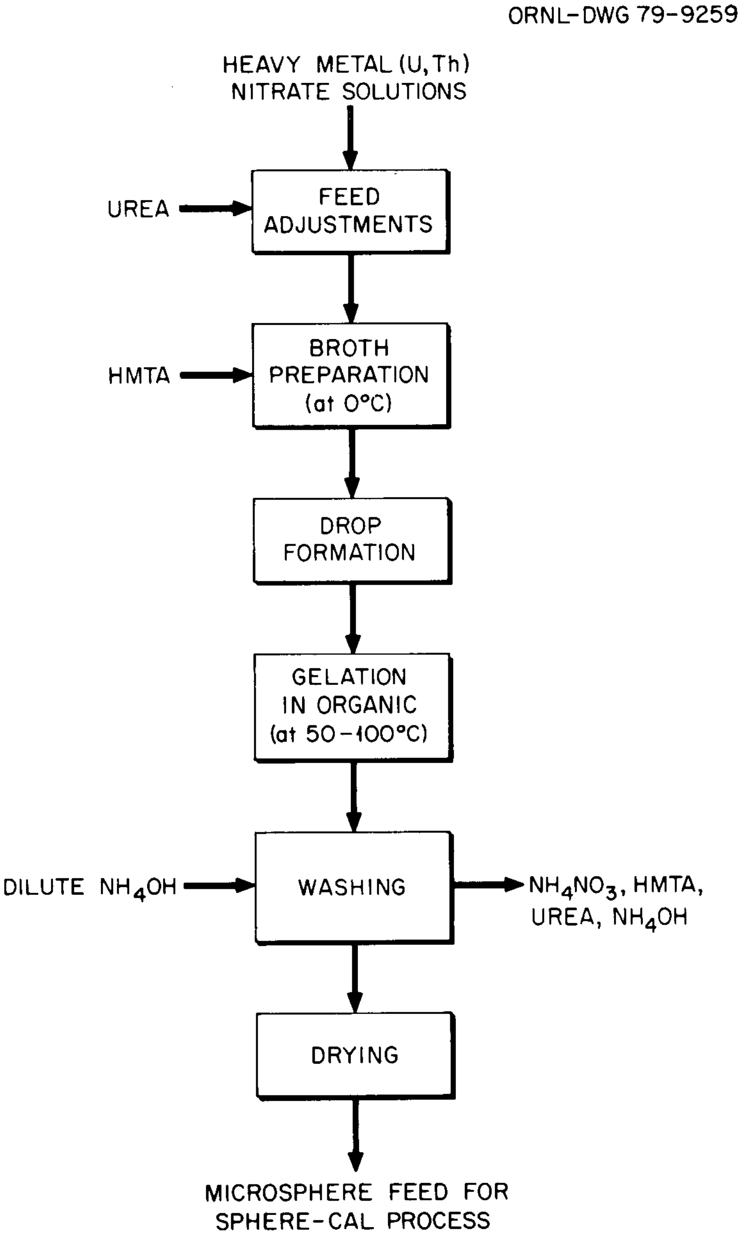

Fig. 3. Microsphere Preparation by Internal Gelation.

The organic medium is then removed by an air purge or with a suitable solvent (e.g., isopropyl alcohol), and the spheres are washed with dilute aqueous ammonia (NH_4OH) to remove HMTA, urea, and ammonium nitrate (NH_4NO_3). With proper gelation conditons the spheres are opaque and have a large enough crystallite size so that the urea, HMTA, and NH_4NO_3 can be easily washed out.

Standard broth preparation includes the following mole ratios of the components: 1.5–1.7 NO_3^-/U, 1.1–1.3 HMTA/U, and 1.25 urea/U. The broth is held at –5 to 0°C to reduce the decompositon rate of HMTA and thus prevent premature gelation. Also, urea is added to complex the uranyl ions (UO_2^{2+}) to help prevent them from reacting with the slowly decomposing HMTA.

The chilled broth is then pumped to a disperser, which forms drops of the required size in the hot immiscible organic liquid. Microspheres were formed by two different methods for use as sphere-cal feed material. Coarse spheres, about 600 μm when dried, were formed by using a vibrated nozzle, which produces a narrow range of sphere sizes. Fine spheres, about 100 μm when dried, were formed in a turbulent shear nozzle to increase the sphere production rate. This produces spheres with a much wider range of sizes. From preliminary results it appears that a dried gel sphere of about 200 μm is optimum, and microspheres in this size range may be produced in either the coarse or fines forming equipment.

In the hot liquid the rate of HMTA decomposition overcomes the urea-uranyl ion complex and causes precipitation of ammonium diuranate, resulting in gelation of the drops. Two different organic liquids, 2-ethyl-1-hexanol (2-EH) and trichloroethylene (TCE), were used during the production of urania spheres for sphere-cal feed. Organic temperatures between 45 and 88°C were used for gelation.

Several urania batches were produced by a modified internal gelation process — the "H" process. The broth was prepared with the following mole ratios of the components: 2.2 NO_3^-/U, 0.5 NH_4^+/U, 2.0 HMTA/U, 2.0 urea/U. Higher dried sphere bulk densities, which are desirable for improved compaction ratios, were obtained by this process. However, the microspheres were much harder and compacted poorly. Results of sphere-cal tests that used material formed by the "H" process will be discussed in a later section of this report.

Urania microspheres used as sphere-cal feed were produced in both lab scale equipment (with batch preparation of broth and typically 0.1 to 0.6 kg product per test) and engineering scale equipment (with continuous preparation of broth and a capacity to produce larger quantities of material per test).

Thoria and Thoria-Urania Microspheres

Thoria-urania microspheres (about 12–25% U) used as sphere-cal feed material were produced by either internal or external gelation. One batch of pure thoria spheres produced by external gelation was also tested to determine its suitability as feed for the sphere-cal process.

The internally gelled thoria-urania spheres were formed according to the same flowsheet (see Fig. 3) as the internally gelled urania spheres. Best results were obtained when the broth was prepared from a solution of thorium nitrate mixed with powdered UO_3. The thorium-uranium feed was prepared with the following ratios: $HMTA/NO_3^- = 0.7$, $urea/U = 2.0$, $NO_3^-/(Th + U) = 3.0$. Microspheres (about 300 μm when dried) containing approximately 25% uranium were produced by this method for use in sphere-cal testing.

Mixed thoria-urania microspheres were formed according to two different external gelation flowsheets — the Italian-SNAM process[12] and the German KFA*-Jülich process.[13] Thoria microspheres were also produced by the KFA external gelation process.

The original external gelation method was the Italian-SNAM process, which is a gel-supported precipitation process. The flowsheet for this process is shown in Fig. 4. To form microspheres by the SNAM process, a water-soluble organic polymer is added to the heavy metal solution. This polymer supports the particle spherical shape during gelation. Besides the polymer a modifier is added to protect the polymer from acid attack and to adjust the viscosity.

The spheres are formed by dripping the broth from a capillary or by flowing the broth through a vibrating nozzle into air. Spherical drops form from the effect of surface tension before exposure to the precipitation chemical. Deformation may occur as the spheres impinge upon the precipitating chemical medium. To prevent this the droplet is exposed to ammonia gas to strengthen the surface of the sphere. The droplet is then completely gelled in a solution of ammonium hydroxide (NH_4OH).

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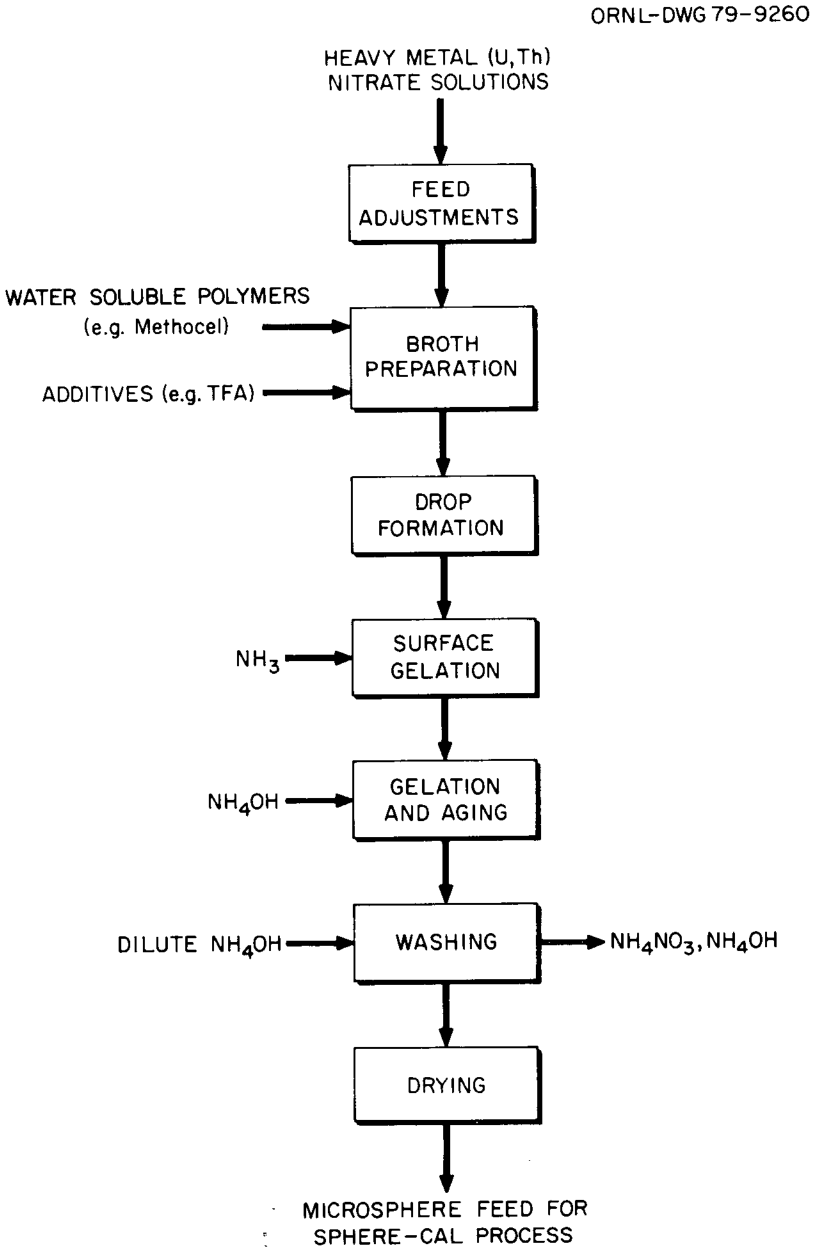

Fig. 4. Microsphere Preparation by External Gelation.

The spheres are aged in the ammonium hydroxide until gelation has been completed through to their centers. They are then washed with dilute ammonium hydroxide. Salts such as ammonium nitrate, which may cause sphere cracking during drying, are removed during the washing process.

To produce mixed thoria-urania microspheres by the SNAM process for sphere-cal testing, a thorium-containing sol and a uranium-bearing solution were mixed. The thorium-containing sol was prepared from a thorium nitrate [$Th(NO_3)_4$] solution preneutralized approximately 75% to $Th(OH)_4$ by NH_4OH addition. The resulting sol was then mixed with a hydroxypropyl methylcellulose (Methocel) polymer (about 7 kg/m^3). The sol had a final heavy metal concentration of 0.7 *M* Th. The uranium-bearing solution was prepared from a uranyl nitrate solution with no pretreatment necessary. A Methocel polymer and a tetrahydrofurfuryl alcohol (TFA) modifier were mixed with the uranyl nitrate. The final uranium solution was 0.7 *M* U, 20% TFA, and 7 kg/m^3 Methocel. Spheres containing about 20% U with a dried size about 700 μm in diameter were produced from a mixture of these two solutions. The spheres were formed with a vibrating nozzle, although the broth was fairly viscous. These spheres were promising sphere-cal material because of their soft gel structure, as will be discussed in a later section of this report.

Thoria-urania microspheres produced by the KFA-Jülich external gelation process were formed from a mixture of thorium nitrate and uranyl nitrate. This heavy metal solution was neutralized with ammonia gas to a pH end point of about 4.0. Attempts to produce a sol with greater than 15% U were unsuccessful. No polymer or other additives were used in the KFA process.

The spheres were formed from the resulting sol by a method similar to the SNAM process. The sol was pumped through a vibrating nozzle to form spheres in air. The spheres were surface hardened with ammonia gas and gelled in a mixture of ammonium hydroxide and ammonium nitrate. Mixed thoria-urania microspheres containing about 12% U (about 700 μm in diameter when dried) were produced by the KFA process. Thoria microspheres (about 700 μm in diameter when dried) for sphere-cal pelletizing tests were also produced by the KFA external gelation process with use of a thorium nitrate sol produced with ammonia gas neutralization.

Thoria and thoria-urania microspheres produced by internal gelation or by KFA-Jülich external gelation processes proved too hard to easily compact into pellets and therefore were not as promising as spheres produced by the SNAM external gelation process for use as sphere-cal feed material. These results will be discussed in more detail in a later section of this report.

MICROSPHERE DRYING

The microspheres were dried following gelation and washing to remove residual water and low-boiling organics. Drying must be properly controlled so that cracks or other microsphere defects are not produced. The rate of drying must be limited to allow the water time to escape from the spheres without producing cracks. Dried spheres with a high bulk density are desirable for pellet pressing to minimize the compaction ratio.

We have tested several drying techniques: drying by using a vacuum to pull room temperature (RT) air through the wet gel beads and drying in an oven at 220°C. In the latter case the wet gel beads were placed in a container with a restricted opening and were therefore dried in a humid or steam atmosphere. To increase the dried sphere densities, we developed a warm air drying technique. Air was heated to 60°C before being passed through the bed of gel spheres. By this method internally gelled urania sphere densities were increased about 25% over spheres dried by conventional procedures.

MICROSPHERE CALCINING

Calcincation of the gel microspheres is necessary for controlled release of water and residual organics that remain following microsphere gelation and drying. It is also necessary, in the case of uranium-containing material, for reduction of the oxygen-to-metal ratio (O/M) before pelletizing. Therefore, an inert gas-hydrogen mixture is used during calcination.

During preliminary experiments to determine a satisfactory calcination temperature, urania microspheres (batch GT-371) were calcined at 400, 600, and 800°C in Ar—4% H_2. We used a heating schedule of 100°C/h with a 4-h hold time at temperature. Pellets were cold pressed at 138 to 414 MPa (20,000–60,000 psi) and sintered at 1450°C in Ar–4% H_2.

Excellent pellets with homogeneous microstructures were fabricated from the microspheres calcined at 600°C. Pellet densities, measured by mercury pycnometry, were as high as 95.2% of theoretical density (T.D.). All the pellets formed from microspheres that were calcined at 400°C cracked apart during sintering, and the pellets pressed from the 800°C calcined spheres were lower in density.

Thermogravimetric analysis (TGA) of a batch of urania microspheres revealed that 600°C was a good calcination temperature. A sample of dried microspheres was heated to 900°C in Ar–4% H_2, while weight loss and water evolution were continuously monitored. Reduction of the material appeared to be complete with stabilized weight loss and water evolution by 550°C, as shown in Fig. 5.

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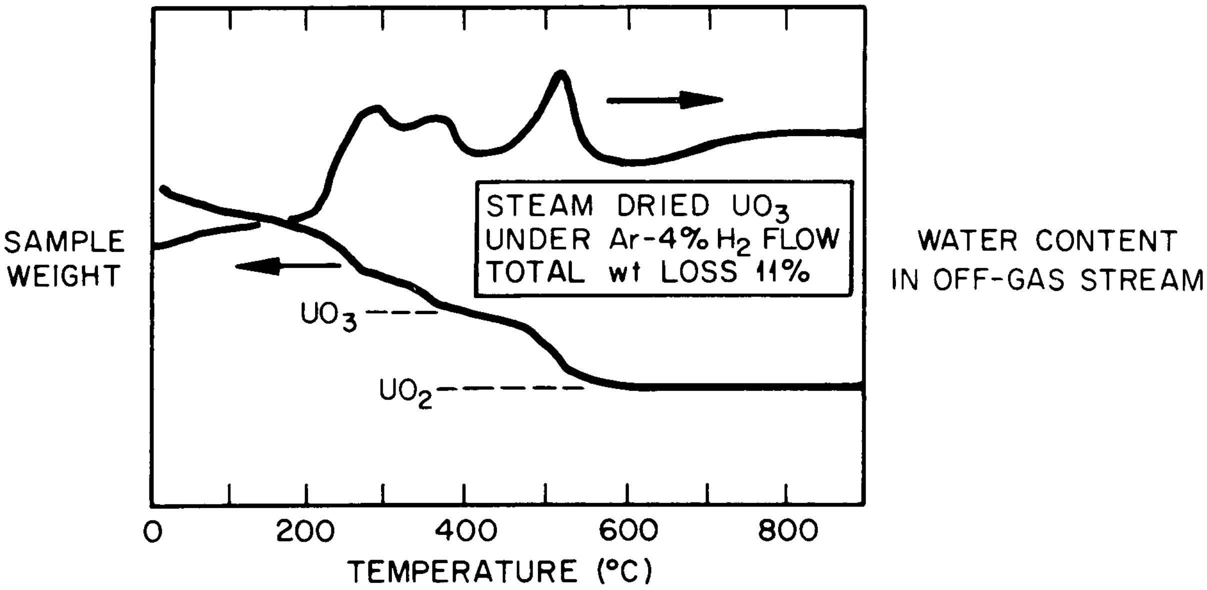

Fig. 5. Weight Loss and Water Evolution During Thermogravimetric Analysis of Urania Gel Microspheres.

The O/M ratios of two batches of urania microspheres (GT-371 and IGT-60) were measured following calcination runs made at various temperatures (400–1000°C). Our results, that is, O/M ratio values from 2.2 to 2.7, were unexpected. Therefore, we concluded that the microspheres had oxidized upon exposure to room air following calcination. A sample of urania microspheres (IGT-61B) calcined at 620°C was removed under inert atmosphere protection. An O/M ratio of 2.0 was measured for this sample, showing that the reduction reaction was complete at this calcination temperature. This sample was then exposed to room air, and it reoxidized. The O/M ratio was 2.40 after 10 min in air and 2.48 after 1 h.

As shown in Fig. 6 the O/M ratio decreases with increasing calcination temperature. It appears that increased calcination temperature reduces the potential for microsphere reoxidation. This finding is consistent with results showing that the sinterability of the microspheres is reduced as calcination temperature increases. These results will be discussed in the pellet sintering section of this report.

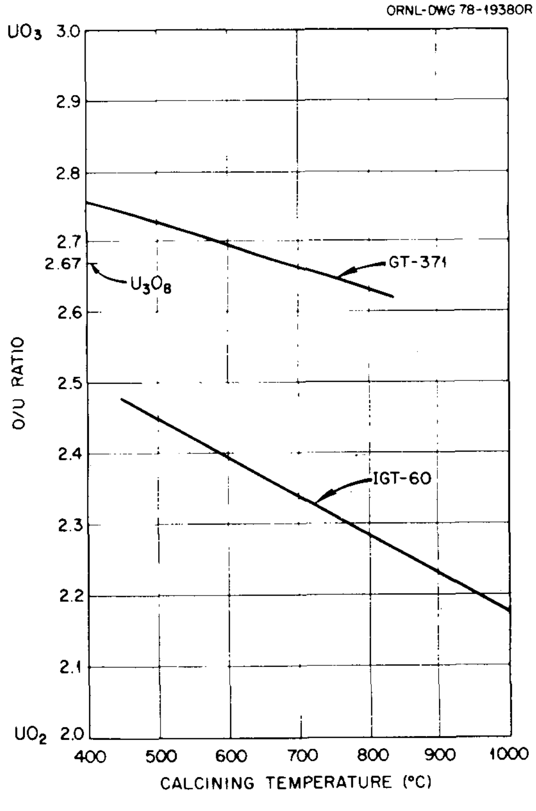

Fig. 6. The O/M Ratio of Calcined Urania Microspheres Following Room Air Exposure for Several Days (Batches GT-371, About 250-μm spheres and IGT-60, About 800-μm spheres).

We have initiated development work to determine a method to increase the oxidation resistance of the microspheres following calcination without appreciably reducing sphere sinterability. Doubling the hold time at temperature from 4 to 8 h during calcination at 600°C did not appear to stabilize the microspheres. Microspheres calcined at 600°C in pure hydrogen appeared to be especially reactive and oxidized completely to U_3O_8 (O/M = 2.67) upon exposure to room air.

Thoria and mixed thoria-urania microspheres were not calcined before pressing since calcining at even low temperatures caused several microsphere batches to become very hard to compact. However, thoria-urania microspheres formed by the SNAM external gelation process have a soft gel structure, and our development work is ongoing to optimize the calcination conditions for this material to be used as pellet press feed.

PELLET PRESSING

Microspheres were cold pressed into cylindrical pellets with a manual hydraulic press and forming pressures from 138 to 414 MPa (20,000–60,000 psi). Dies with two movable punches and diameters from 6.35 to 12.7 mm (1/4–1/2 in.) were used. Pellet length to diameter ratios (L/D) were usually between 1 and 2. A solution of stearic acid in acetone was used as a die lubricant. Other pellet lubricants and binders such as Sterotex* and Carbowax† did not appear to be necessary for successful pelletizing.

Calcined urania microspheres deformed readily under pressure to form good compacts. The crushing strength of these microspheres could not be measured since they readily deformed, and a break point could not be easily distinguished. Figure 7 shows a fracture surface of an as-pressed (unsintered) pellet. A polished surface view is shown in Fig. 8. This pellet was fabricated from microspheres (IGT-60) calcined at 1000°C, which should have greater crushing strength than microspheres calcined

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*Product of Capitol City Products Company, Division of Stokely-Van Camp, Inc., Columbus, Ohio.

†Product of Carbide and Carbon Chemicals Company, Division of Union Carbide Corporation, South Charleston, West Virginia.

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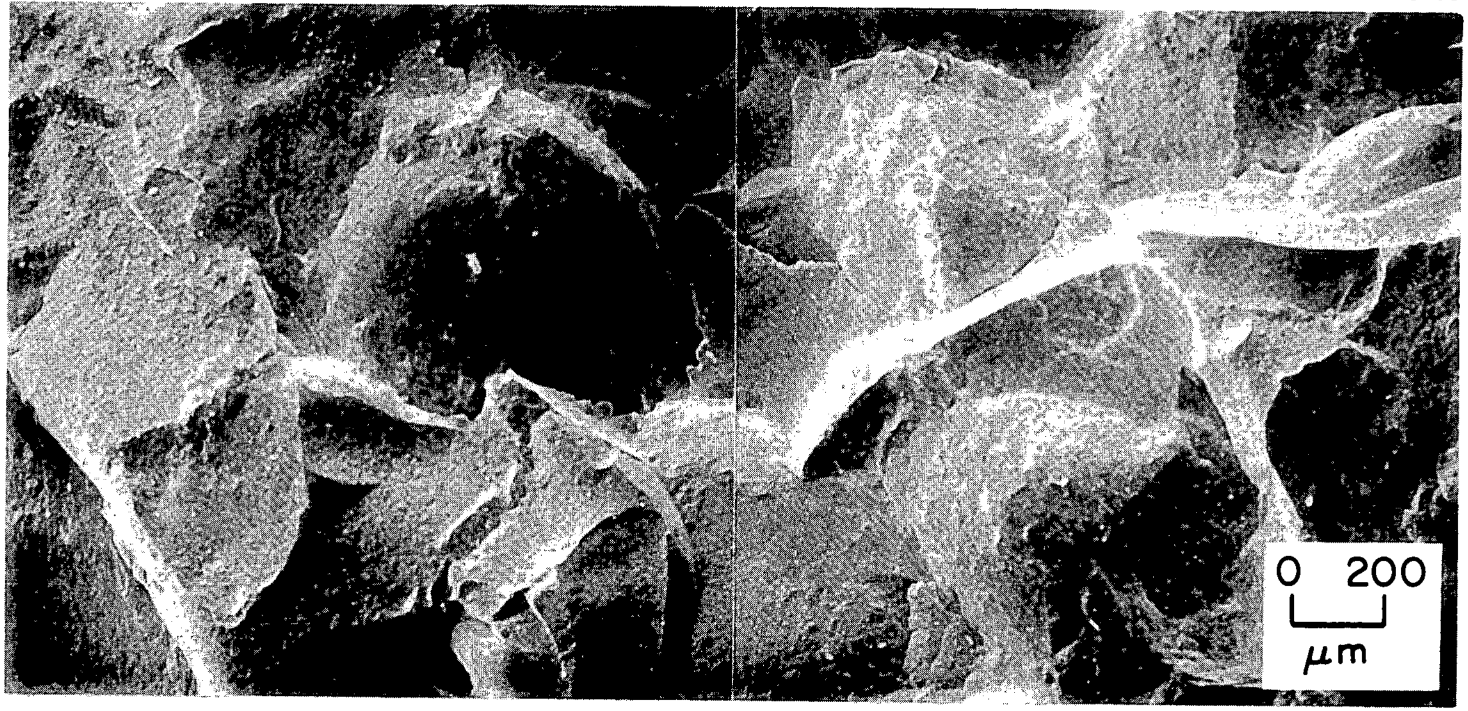

Fig. 7. Fracture Surface of As-Pressed Urania Pellet (Batch IGT-60, About 800-μm Spheres, 1000° Calcine).

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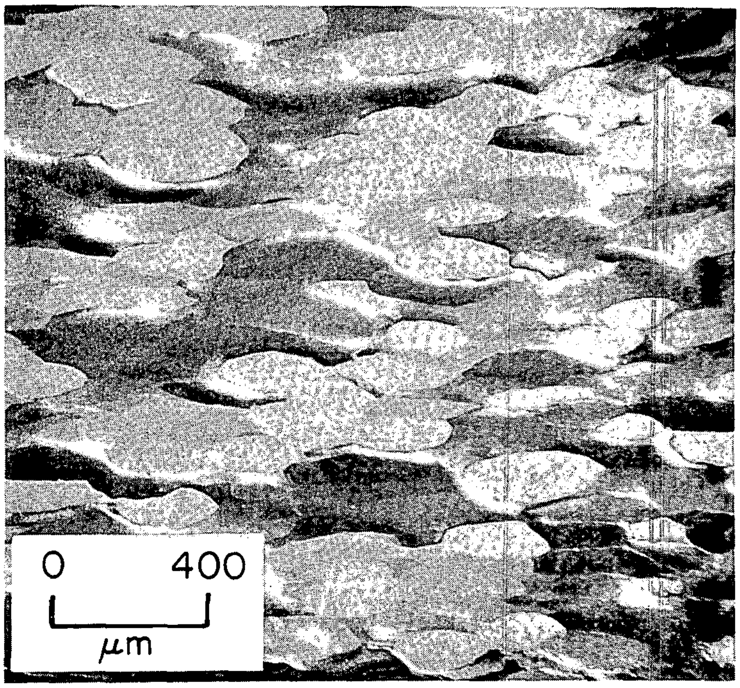

Fig. 8. Polished Section of As-Pressed Urania Pellet (Batch IGT-60, About 800-μm Spheres, 1000° Calcine).

at 600°C. The forming pressure was 138 MPa (20,000 psi), and the microspheres deformed readily to fill in the voids between spheres.

However, most batches of thoria and mixed thoria-urania microspheres were very hard to compact and fractured rather than deforming under pressure. A typical microstructure of a sintered mixed thoria-urania pellet is shown in Fig. 9. Remnants of the original microspheres are clearly visible together with shards from fractured spheres. The mixed thoria-urania spheres were not calcined before pressing since calcining at even low temperatures caused the microspheres to become harder to press. Pellets with this appearance were produced from thoria and mixed thoria-urania microspheres formed by either internal or external gelation (KFA method). Pellets pressed from urania microspheres formed by the "H" process (internal gelation) also had a similar type microstructure. This process appears to produce spheres too hard to be suitable as sphere-cal feed material.

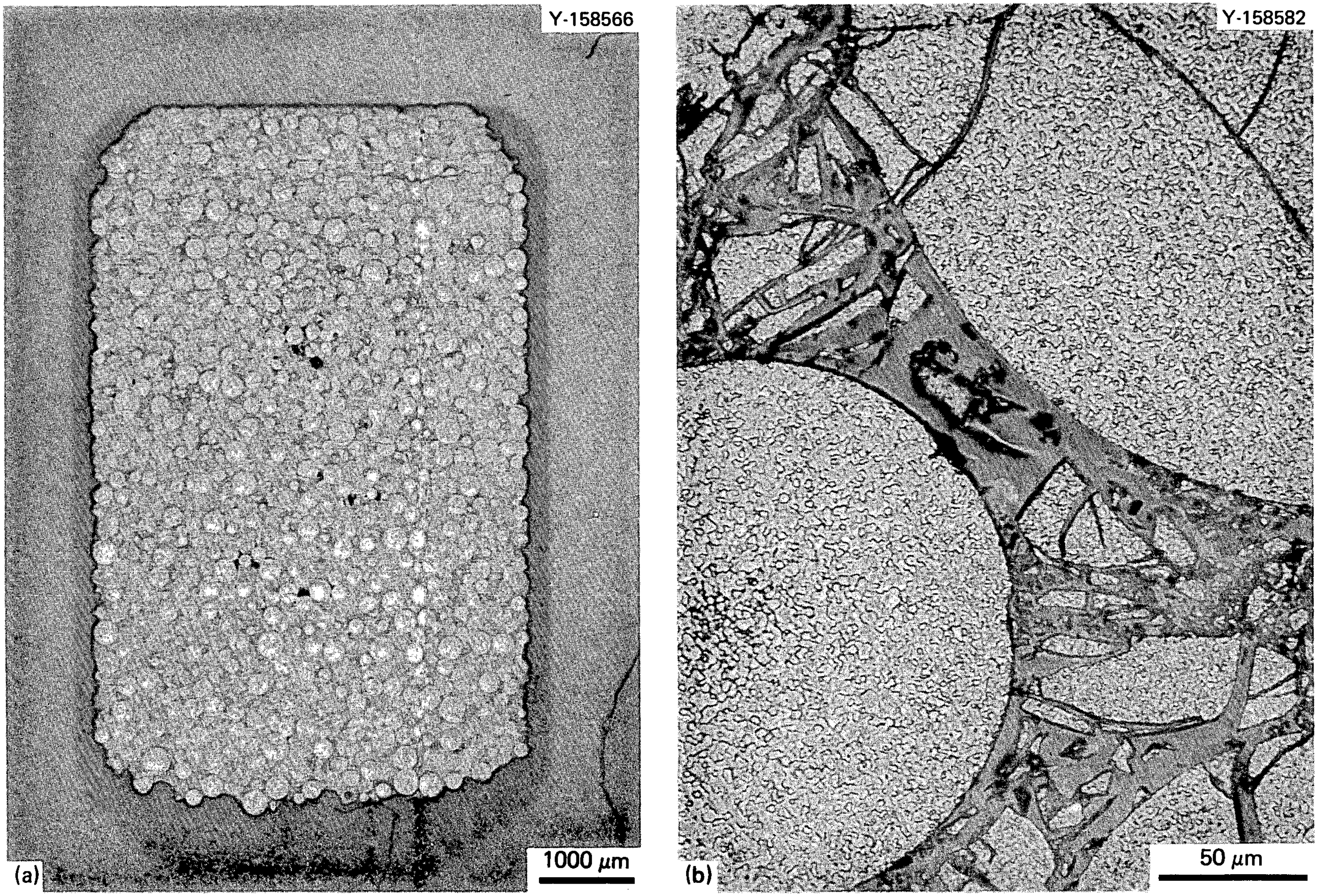

Fig. 9. A $(Th,U)O_2$ Pellet with Remnant Microsphere Structure (Batch GT-484, About 300-μm Spheres, Internal Gelation, Th/U = 3). (a) As polished. (b) Etched (30 H_3PO_4:1 HF).

Thoria-urania microspheres formed by the SNAM external gelation process gave promising results since they have a much softer gel structure. Pellets pressed from SNAM-type microspheres were more homogeneous, and individual sphere remnants were not as visible since the microspheres sintered together better. Our development work is ongoing to optimize the calcination conditions for SNAM-type microspheres to be used as sphere-cal feed material.

We performed a statistical experiment to study various urania microsphere calcining temperatures, forming pressures, and sintering rates. The levels of the variables are shown in Table 1. Results showed that green pellet densities increase with increasing forming pressure, as shown in Fig. 10, and that sintered pellet densities decrease with increasing forming pressure, as shown in Fig. 11. The latter result was unexpected but may possibly be explained by the fact that many pellets in this experiment contained cracks. Pellet feed material had oxidized upon exposure to air following calcining, and therefore, the pellets underwent reduction during sintering. Pellets with higher green density may have been more prone to cracking as a result of the release of trapped water vapor during pellet reduction.[14]

Table 1. Statistical Experiment $3^2 \times 2$ Design

Process Variables	Levels
Calcining temperature (°C)	600, 800, 1000
Forming pressure (MPa)	138, 276, 414
Sintering schedule	(1) 100°C/h to 1450°C (2) 100°C/h to 450°C and 300°C/h to 1450°C

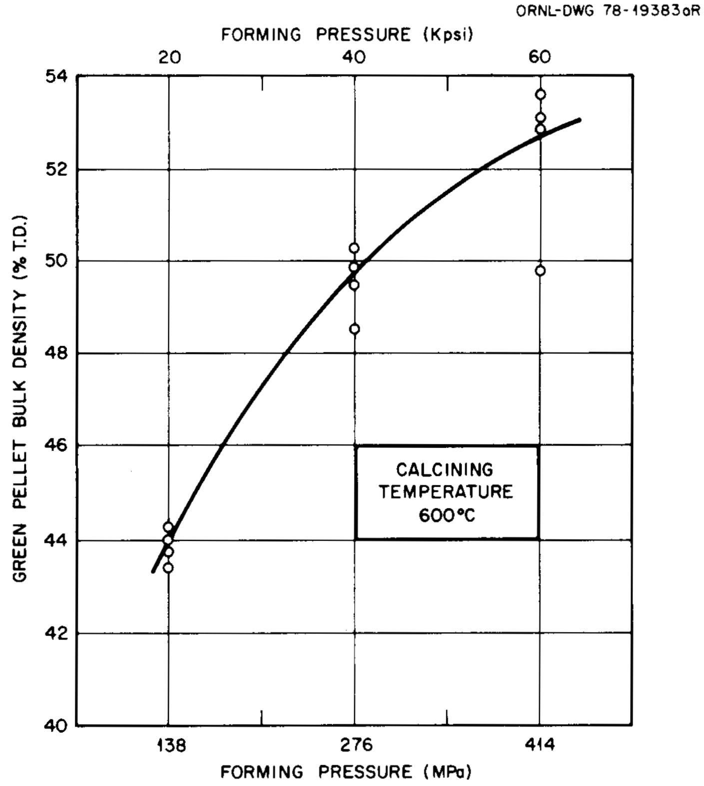

Fig. 10. Green Pellet Densities Increased with Increasing Pressure.

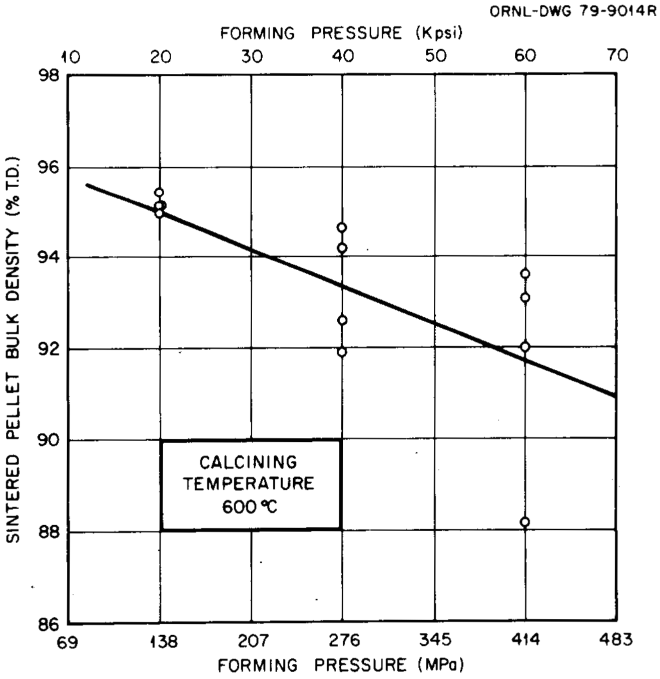

Fig. 11. Sintered Pellet Densities Decreased with Increasing Pressure.

PELLET SINTERING

For ease of comparison of the sinterability and quality of various gel microsphere batches, we selected a single sintering schedule. This schedule had been shown[15] to be satisfactory for sintering individual urania, thoria, and thoria-urania microspheres to greater than 99% T.D. Our schedule (Fig. 12) was a heating rate of 100°C/h to 450°C followed by a heating rate of 300°C/h to 1450°C. The pellets were allowed to soak during a 4-h hold at 1450°C. Then they were cooled slowly as the furnace cooled to room temperature at a rate of approximately 100°C/h. A reducing atmosphere, Ar—4% H_2, was used during the heatup and soak periods, and argon was used during furnace cool-down.

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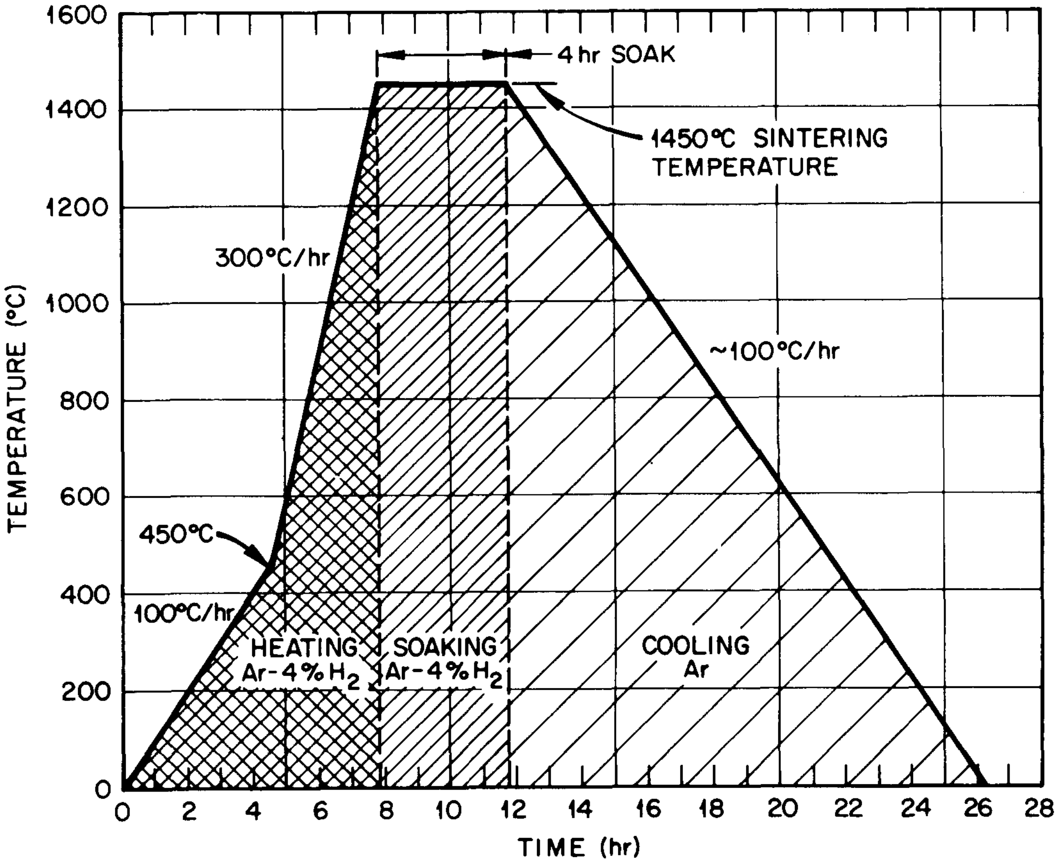

Fig. 12. Sphere-Cal Pellet Sintering Schedule.

To confirm that this sintering schedule was satisfactory, a slower heating rate was tested in a statistical experiment (see Table 1). Half of the urania pellets in the experiment were sintered by using the standard schedule described above, and half were fired with a heating rate of 100°C/h to the sintering temperature of 1450°C. Results from this experiment were inconclusive since many of the pellets cracked, but little difference was detected between the two sintering schedules.

In the same statistical experiment (to study calcining temperature, forming pressure, and sintering schedule) we determined that the sinterability of urania microspheres was reduced as the calcination temperature increased. Sintered pellet densities decreased with increasing calcination temperature, especially above 800°C, as shown in Fig. 13. Scanning electron microscope (SEM) micrographs of the fractured surface of a pellet from this experiment, which contained spheres calcined at 1000°C, are shown in Fig. 14. Individual spheres did not sinter together well, and cracks between spheres were still present.

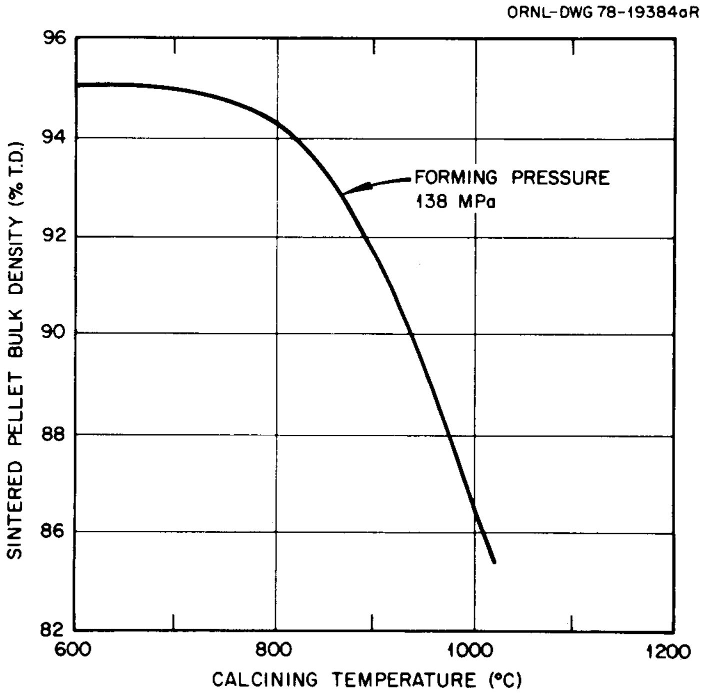

Fig. 13. Sintered Pellet Densities Decreased with Increasing Calcination Temperature.

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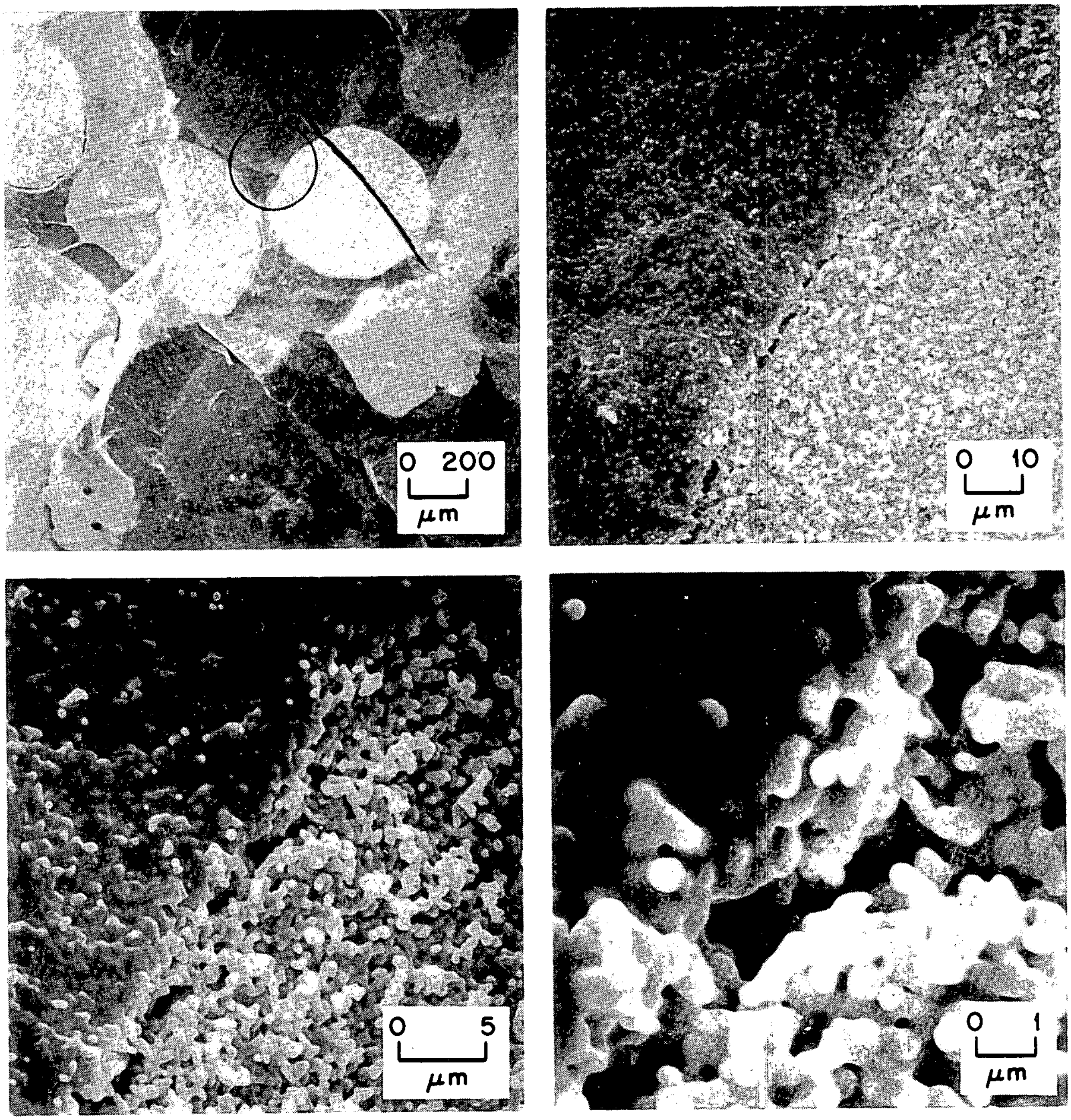

Fig. 14. Incomplete Sintering Between Microspheres Comprising a UO_2 Pellet (Batch IGT-60, About 800-μm Spheres, 1000°C Calcine).

Many of the thoria and thoria-urania microsphere batches sintered poorly, even when the pellets were formed from uncalcined spheres. The thoria and thoria-urania microspheres, produced by either internal or external gelation (KFA method), sintered individually rather than between spheres (see Fig. 9). However, thoria-urania microspheres produced by the SNAM external gelation process sintered together better and are promising sphere-cal feed material.

SPHERE-CAL BATCH SCREENING TESTS

Twenty-one urania, one thoria, and five thoria-urania gel microsphere batches were tested for sphere-cal performance with a standard screening test, which was a modified ASTM sinterability test procedure (ASTM specification C-753-73, Sect. A2.2). The batches differed from each other in that various sphere forming and drying conditions were used during their production. A sample of microspheres from each of the urania batches was calcined at 600°C in Ar—4% H_2. The thoria and thoria-urania spheres were not calcined. The microspheres were then pressed with forming pressures between 138 and 414 MPa (20,000 and 60,000 psi). We used as high a pressure as possible, until end capping was observed, to obtain maximum green pellet densities. The pellets were then sintered at 1450°C in Ar—4% H_2 by using the standard schedule (see Fig. 12): 100°C/h heating rate to 450°C, then 300°C/h heating rate to 1450°C.

Green and calcined microsphere size, green and calcined sphere tap density, calcined sphere O/M ratio, green and sintered pellet geometric density, sintered pellet density (measured by mercury pycnometry), sphere weight loss during calcining, pellet weight loss during sintering, and pellet diametrical shrinkage were measured. Also, the gel microspheres themselves were characterized as to sinterability. Unpressed microspheres from each batch were measured for sintered sphere size, density, and weight loss during sintering. The heavy metal ratio (Th/U) was determined for the mixed thoria-urania batches. Also polished cross sections of representative pellets from each gel microsphere batch were examined for porosity distribution, grain size, and internal cracking or other defects. These measurements for all of the gel microsphere batches that were tested are tabulated in the Appendix.

We compared results of the sphere-cal pellet fabrication screening tests with the gel microsphere forming and drying conditions for each batch. Microstructures from the UO_2 pellets could be categorized into one of three general groups: pellets with high density matrices (Fig. 15), pellets with porosity located mainly around remnant sphere boundaries (Fig. 16), and pellets with internal cracks (Fig. 17).

Our preliminary conclusions are discussed below. Pellets having dense matrices were often produced from batches of calcined spheres having O/M ratios approaching 2.67, which corresponds to U_3O_8. However, most of these pellets crack apart during sintering as a result of water vapor release during reduction, phase changes, or excessive shrinkage. Pellets with a structure containing porosity around remnant sphere boundaries were often produced from microsphere batches dried slowly with room temperature air.

The aging changes in wet gel appear to cause sphere distortions and reduced dried gel densities. Aging also appears to contribute to gross cracking and other defects in pellets. Drying with room temperature air seems to contribute to pellet cracking, but this may be an effect of wet aging during the slow drying process. In addition, pellets pressed from spheres with diameters larger than 400 μm usually contained more internal cracks.

Pellet inhomogeneity was a problem when several batches of gel microspheres were mixed, as shown in Fig. 18. Even within a batch grain size and porosity distribution sometimes varied between individual spheres comprising a pellet. This was more often the case for microspheres calcined at temperatures approaching 1000°C.

Results to date suggest that the sphere-cal conditions that will produce the highest quality UO_2 pellets are: minimum gel aging, fine microspheres (50—400 μm), fast drying (warm air or oven), a calcination temperature of 600°C, and a low O/M ratio. The best urania pellets were produced from microspheres (batch GT-371) having minimum gel aging (about 5 h), with a diameter of about 250 μm when dried, dried at 220°C in an oven with a steam atmosphere, and calcined at 600°C in Ar—4% H_2. Excellent pellets with homogeneous microstructures and high densities (95.2% T.D.) were fabricated from these microspheres, as shown in Fig. 19. However,

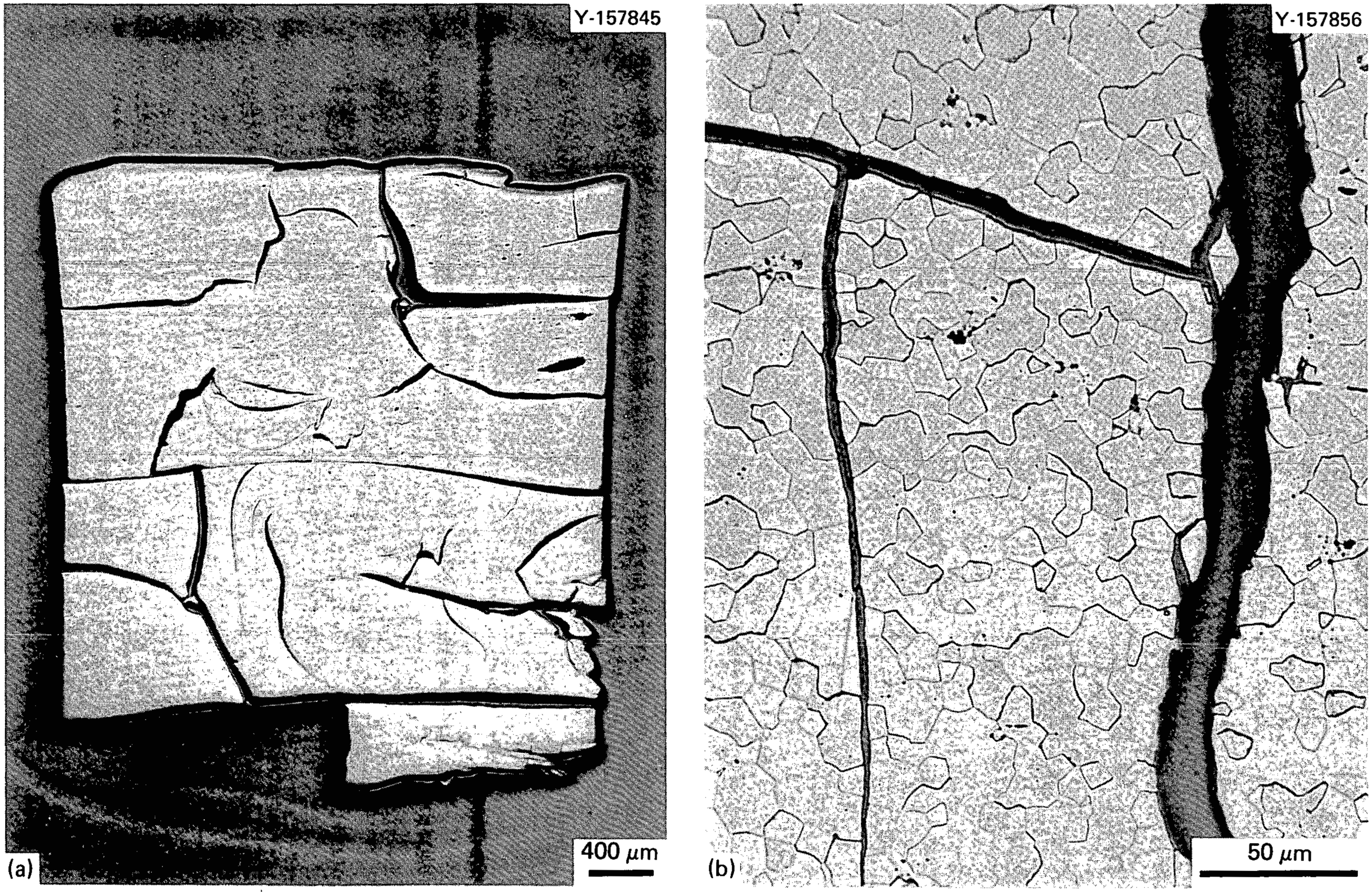

Fig. 15. Representative Microstructure of a UO_2 Pellet with High Density Matrix (Batch FGT-8, About 50-µm Spheres, 450°C Calcine). (a) Polished section. (b) Etched ($H_2SO_4:2H_2O_2:7H_2O$).

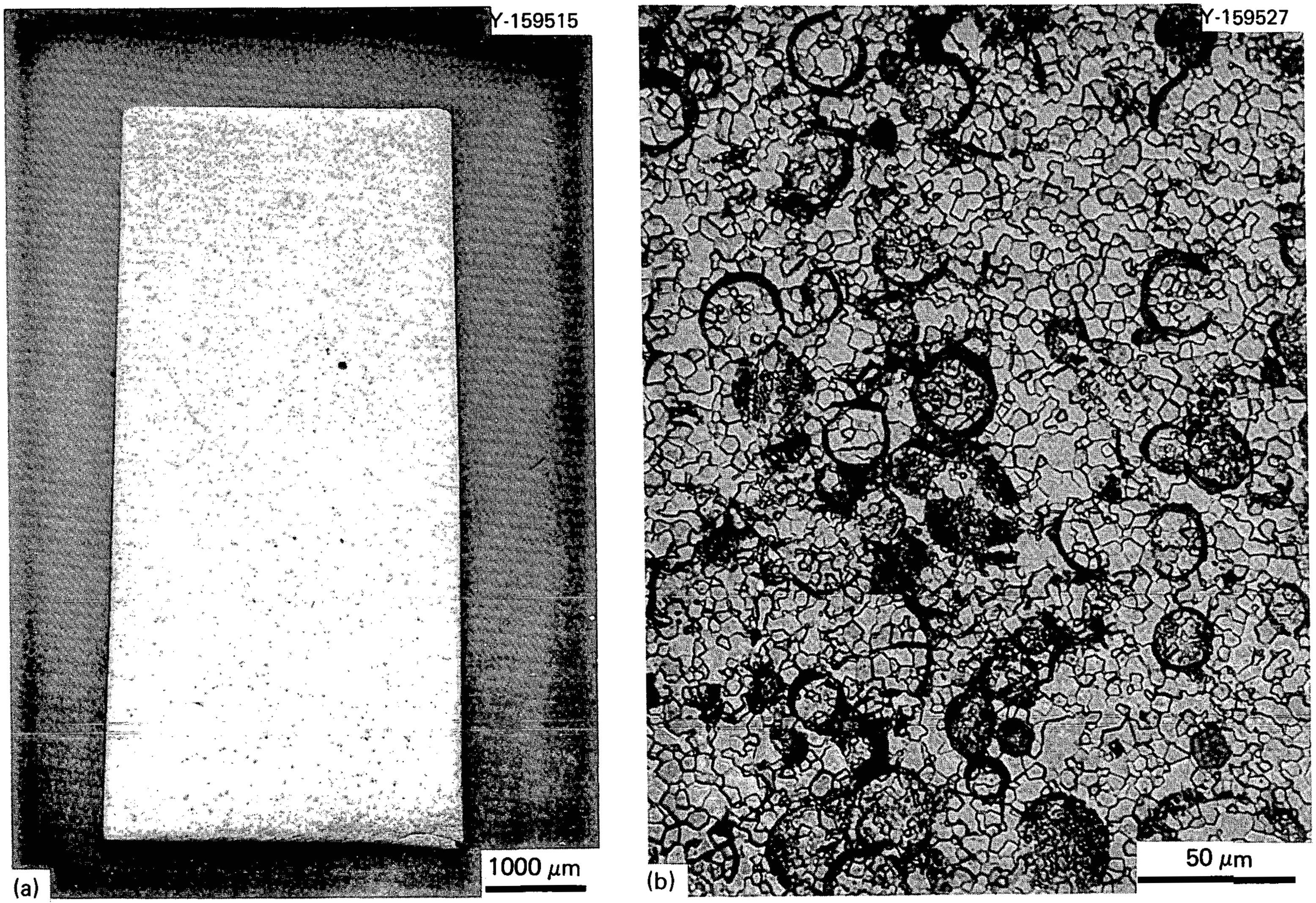

Fig. 16. Representative Microstructure of a UO_2 Pellet with Porosity Around Remnant Sphere Boundaries (Batch FGT-23A, About 50-μm Spheres, 600°C Calcine). (a) Polished Section. (b) Etched ($H_2SO_4:2H_2O_2:7H_2O$).

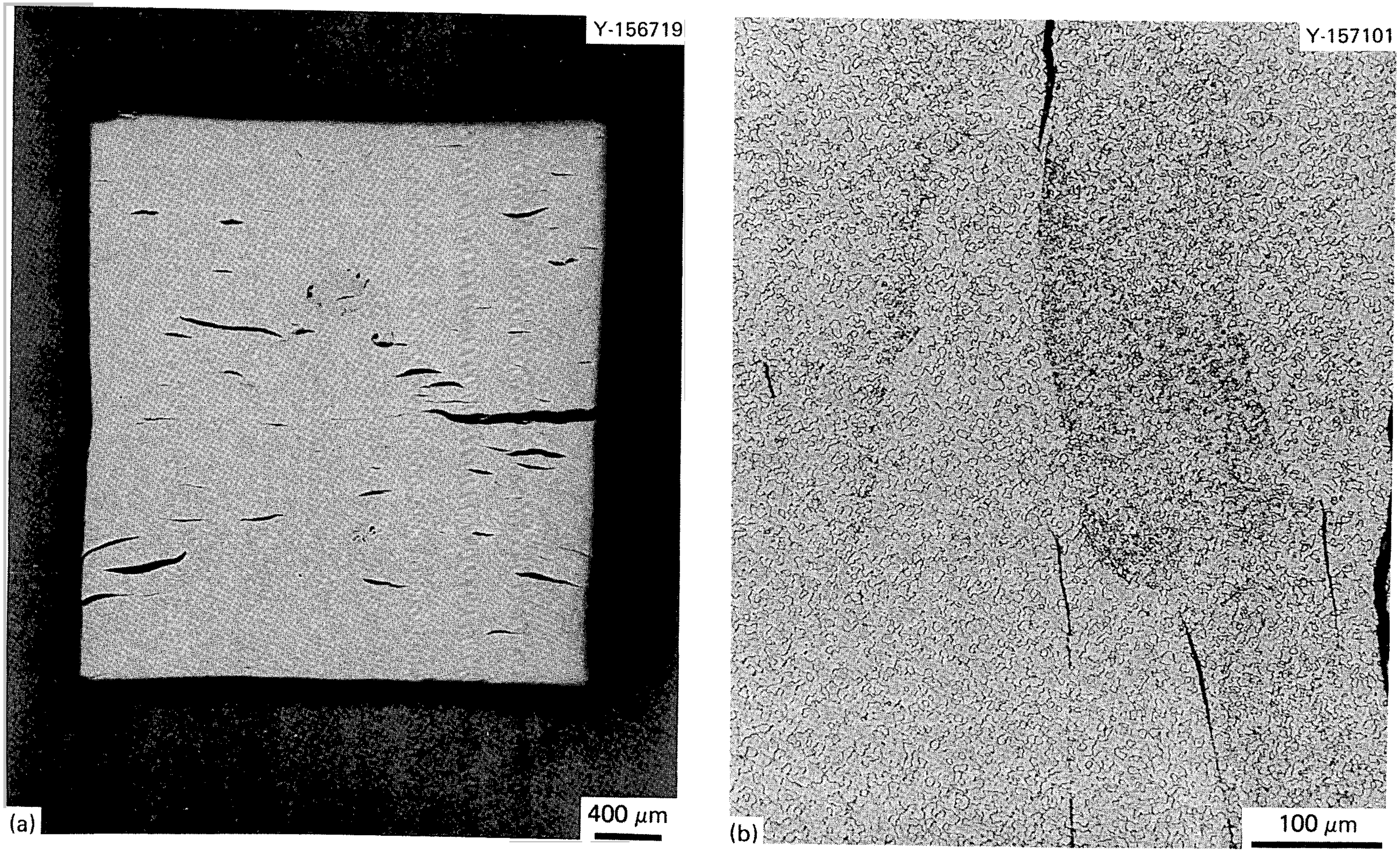

Fig. 17. Representative Microstructure of a UO_2 Pellet with Internal Cracks (Batch IGT-60, About 800-μm Spheres, 600°C Calcine). (a) Polished section. (b) Etched ($H_2SO_4:2H_2O_2:7H_2O$).

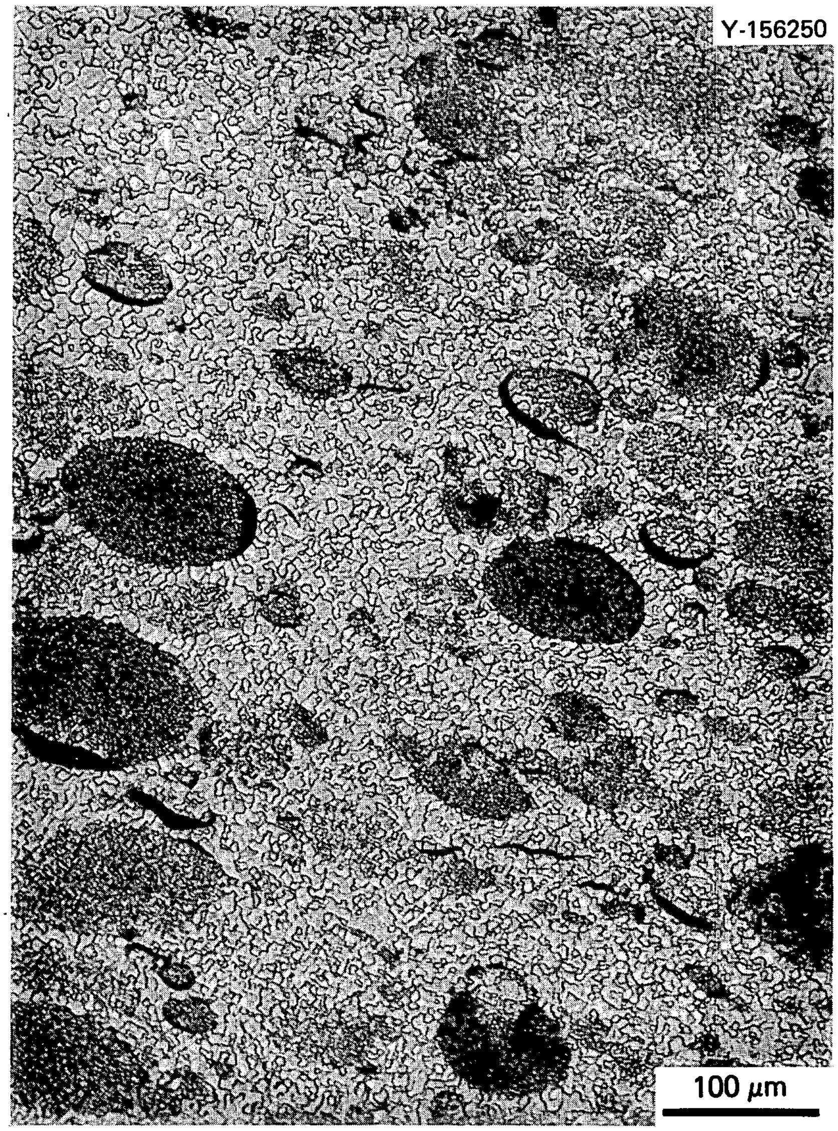

Fig. 18. Pellet Inhomogeneity (Mixed Batch, About 100-μm Spheres, 600°C Calcine). Etched ($H_2SO_4:2H_2O_2:7H_2O$).

these microspheres oxidized during handling in air following calcination, and development work is necessary to determine a method to stabilize calcined microspheres. Our attempts to reproduce the excellent results from this microsphere batch have been only partially successful with other batches of gel microspheres.

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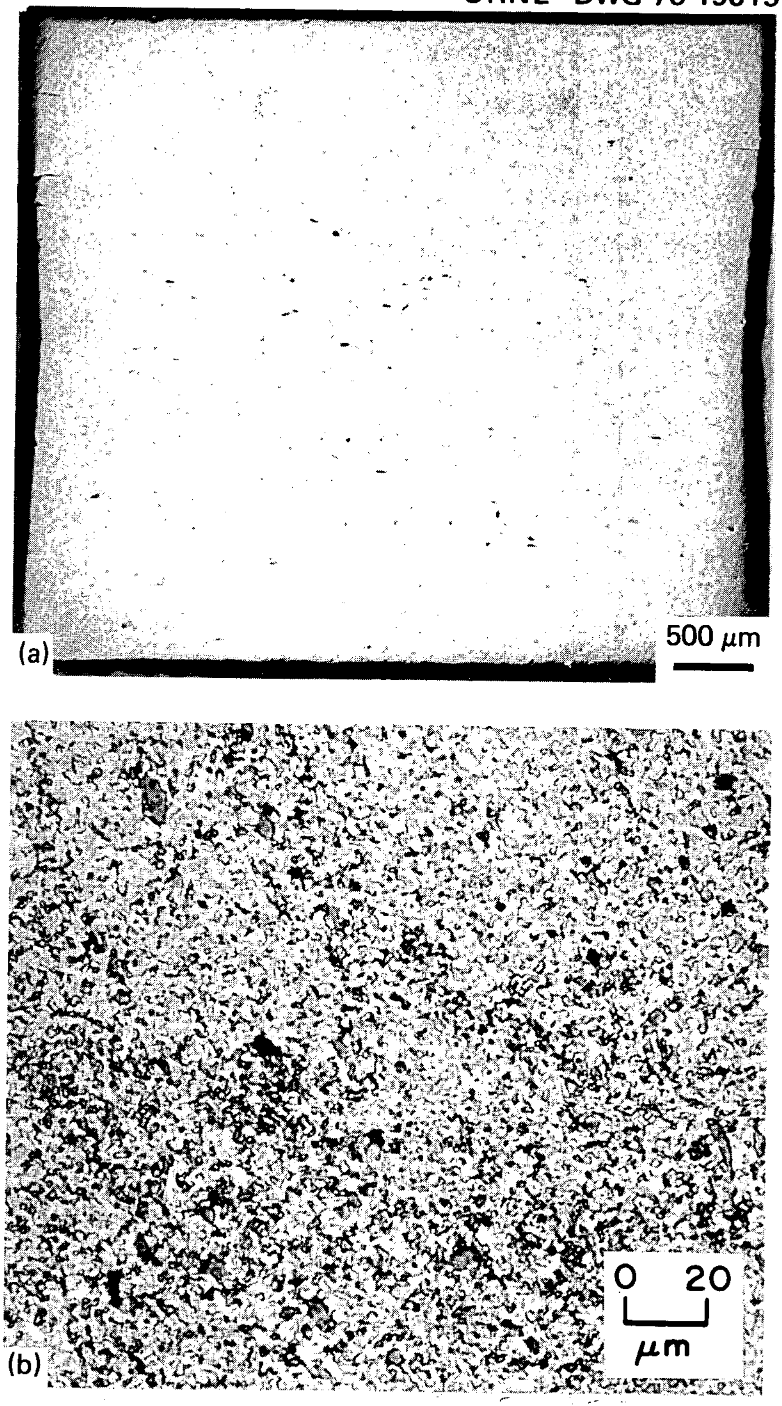

Fig. 19. A UO_2 Fuel Pellet Fabricated from Gel Microspheres (Batch GT-371, About 250-μm Spheres, 600°C Calcine). (a) Polished section. (b) Etched ($H_2SO_4:2H_2O_2:7H_2O$).

The best thoria-urania pellets were produced from microspheres (batch MGT-104) formed by the SNAM external gelation process, which have a soft gel structure. These microspheres, which contained about 20% U, had a diameter of about 700 µm when dried and were dried at 200°C in an oven with a steam atmosphere. The SNAM-type microspheres compacted easily and sintered together to produce a fairly homogeneous structure (90.2% T.D.), as shown in Fig. 20. Since these microspheres were not calcined before pressing, holes in the pellet structure were probably caused by the decomposition and release of the gel support polymer and other organics during sintering. Our development work is ongoing to optimize the calcination conditions of SNAM-type microspheres to be used as sphere-cal feed material.

SUMMARY

We studied each sphere-cal process step (microsphere gelation, drying, calcining, pellet pressing, and sintering) to try to determine the important parameters for the production of high quality UO_2, ThO_2, and $(Th,U)O_2$ fuel pellets. Urania microspheres used as pellet press feed material were formed by internal gelation, while thoria and mixed thoria-urania microspheres were produced by either internal or external gelation.

Excellent uranium oxide (UO_2) fuel pellets with homogeneous microstructures and densities (greater than 95% T.D.) were produced from gel-derived microspheres. Results to date suggest that the sphere-cal process conditions that will produce the highest quality UO_2 pellets are: minimum gel aging, fine microspheres (50–400 µm), fast drying (warm air or oven), a calcination temperature of 600°C, and a low O/M ratio. From a statistical experiment we determined that UO_2 sintered pellet densities increase both with decreasing calcination temperature (1000–600°C) and with decreasing forming pressure (414–138 MPa). Thermogravimetric analyses revealed that a minimum calcination temperature of 600°C was necessary to ensure complete reduction of the UO_3 microspheres to UO_2. However, upon exposure to room air following calcination, the microspheres partially reoxidized.

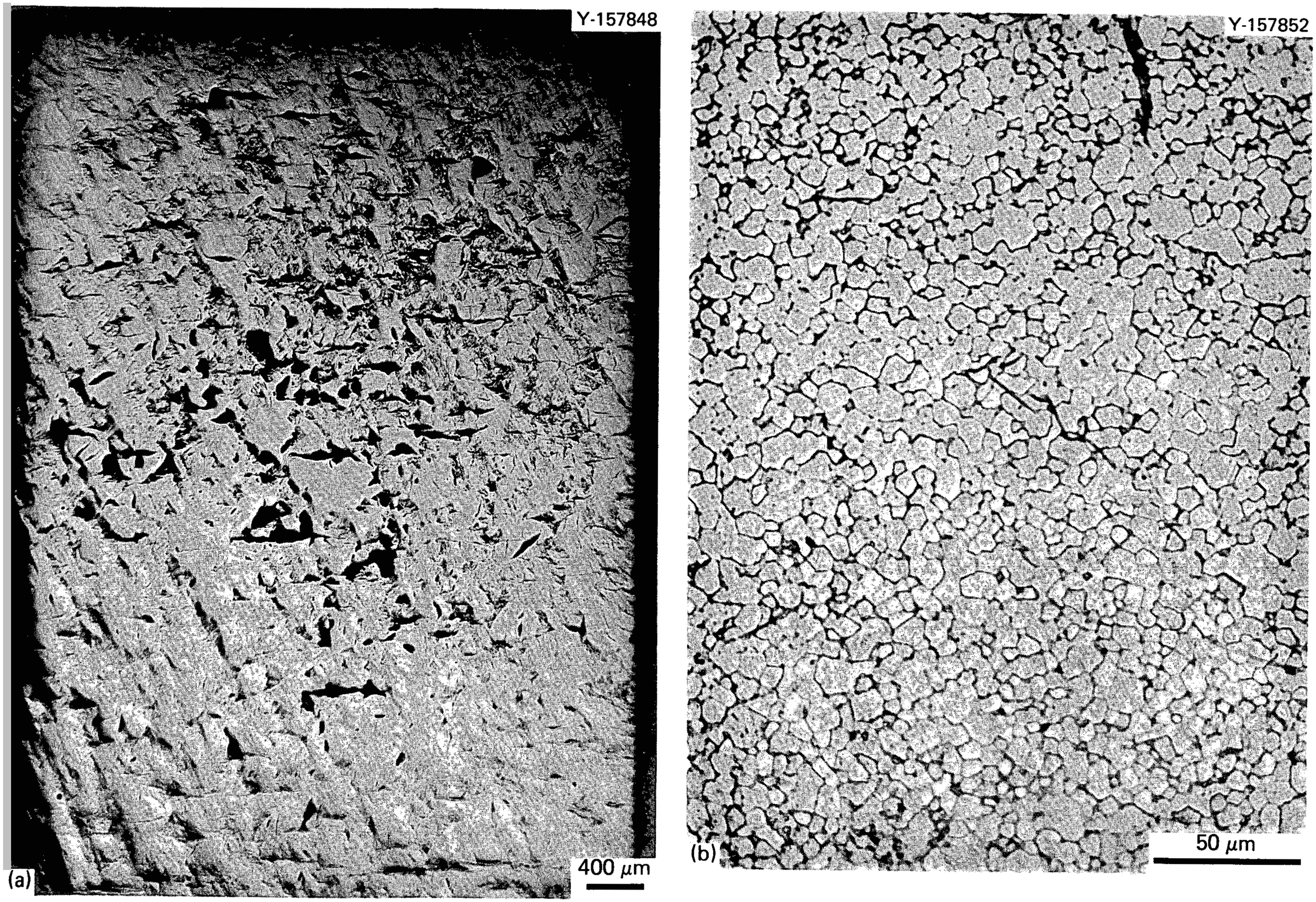

Fig. 20. A $(Th,U)O_2$ Pellet Fabricated from SNAM-Type Microspheres (Batch MGT-104, About 700-µm Spheres, External Gelation-SNAM Process, Th/U = 4). (a) As polished. (b) Etched ($30H_3PO_4$:1HF).

Thoria and mixed thoria-urania microspheres produced according to internal or external (KFA process) gelation flowsheets were hard and compacted poorly, even as dried. Pellet microstructures containing remnant microspheres and shards were obtained, and microspheres sintered individually rather than sintering between spheres. Urania microspheres produced by the "H" process gave similar results. However, thoria-urania microspheres produced by the SNAM external gelation process were softer, compacted easily, and sintered together to produce a more homogeneous pellet structure.

Our future development work will be directed toward optimization of sphere-cal process parameters. In particular, calcination schedules will be studied to stabilize the O/M ratio of urania-bearing microspheres without appreciably decreasing their sinterability. Optimum microsphere size, gelation medium, and drying conditions must also be determined for urania sphere-cal feed material. Our development work will continue toward defining a $(Th,U)O_2$ sphere-cal flowsheet with emphasis on gelation and calcination conditions.

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APPENDIX

Table Al. Urania Sphere-Cal Feed Material

Batch	Gelation Flowsheet[a]	Gelation Equipment[b]	Gelation Organic[c]	Gelation Temperature (°C)	Wet Aging[d] (h)	Drying Conditions[e]	Calcination Temperature (°C)	Sphere Size, μm			Tap Density, g/cm^3		O/U Ratio Calcined	Sphere Weight Loss, %		Sphere Mercury Density (% T.D.)
								Dried	Calcined	Sintered	Dried	Calcined		During Calcining	During Sintering	
GT-371	Standard	Lab, F.	TCE	65	5	Steam 220°C	400	250	271	85	0.79		2.690	10.9	13.8	93.0
GT-371	Standard	Lab, F.	TCE	65	5	Steam 220°C	600	250	226	85	0.79	1.02	2.735	11.5	13.8	93.0
GT-371	Standard	Lab, F.	TCE	65	5	Steam 220°C	800	250	222	85	0.79		2.632	10.4	13.8	93.0
GT-412	Standard	Lab, F.	TCE	58	10	Air R.T.	600	68.5	60.5	37.5	1.32	2.28	2.426	18.8	18.8	100
GT-357	Standard	Lab, S.C.	TCE	72	5	Steam 220°C	600	601	535	262	0.78	0.99	2.352	17.2 12.4	18.3	98.3
IGT-60	Standard	Interim, S.C.	TCE	70	140	Steam ∿220°C	500	786		397	0.65		2.440	7.0	11.5	96.3
IGT-60	Standard	Interim, S.C.	TCE	70	140	Steam ∿220°C	600	786	557	397	0.65	0.88	2.398	9.6 9.8	11.5	96.3
IGT-60	Standard	Interim, S.C.	TCE	70	140	Steam ∿220°C	800	786		397	0.65		2.262	9.9	11.5	96.3
IGT-60	Standard	Interim, S.C.	TCE	70	140	Steam ∿220°C	1000	786		397	0.65		2.203	10.0	11.5	96.3
J-819 (Mixed)	Standard	Lab, F.	TCE (Most)	65 (Most)		Air R.T. (Most)	600		280	39.6		1.58	2.450		6.9	98.5
IGT-68-69B	Standard	Interim, S.C.	TCE	70	300	Steam 200°C	450				0.76	0.99	2.59	10.5	12.5	96.6
GT-469	Standard	Lab, F.	TCE	50	5	Steam 220°C	450	271		105	0.88	1.28	2.56	15.4	15.2 15.4	93.3 97.9
IGT-61B	Standard	Interim, S.C.	TCE	70	800	Steam 200°C	450			323.5	0.75	0.99	2.63	7.7	10.2 10.1	69.2 96.9
J-829 (Mixed)	Standard	Lab, S.C.	TCE (Most)	70 (Most)		Steam 220°C (Most)	450	488	390		0.81	1.09		11.25		
J-829 (Mixed)	Standard	Lab, S.C.	TCE (Most)	70 (Most)		Steam 220°C (Most)	600	488	370		0.81	1.11		13.1		
FGT-8	Standard	Interim, F.	2EH	53	20	Steam 200°C	450		39			0.773		9.5		
FGT-8	Standard	Interim, F.	2EH	53	20	Steam 200°C	600					1.04	2.46			
IGT-76	Standard	Interim, S.C.	TCE	53	10	Steam 210°C	600	567	486		1.00	1.42		9.2		
FGT-1	Standard	Interim, F.	2EH	45	120	Air R.T. then Oven 200°C	600	82	113		0.70	0.88	2.511	9.4 10.0	12.2	91.1
FGT-20A-I	Standard	Interim, F.	2EH	50	10	Air 80°C then Oven 220°C	600	161	109		1.52		2.453	5.6		
FGT-10	Standard	Interim, F.	2EH	50	60	Air R.T. then Oven 200°C	600	212	137		0.97	1.29	2.506	4.5		
GT-468	Standard	Lab, F.	TCE	50	10	Air R.T.	600	215	180		1.44	2.03	2.328	16.8		
IGT-61A	Standard	Interim, S.C.	TCE	70	800	Air R.T.	600	626	502		1.06	1.47	2.270	16.1		
FGT-23B	Standard	Interim, F.	2EH	50	40	Air R.T. then Oven 225°C	600	36	33		1.46	1.98	2.457	7.1		
FGT-23A	Standard	Interim, F.	2EH	50	40	Air R.T. then Oven 225°C	600	32	34		1.52	2.19	2.274	7.6		
H06	"H" Process	Lab	2EH	88	5	Air 60°C then Oven 225°C	600	181	151		2.17	3.67	2.28	9.1		
FGT-21	Standard	Interim, F.	2EH	50	60	Air R.T. then Oven 225°C	600	38	26		1.02	1.62	2.372	7.4		
FGT-20	Standard	Interim, F.	2EH	50	80	Air R.T. then Oven 225°C	600	155	274		1.23	1.65	2.34	7.3		

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[a] Standard indicates mole ratios of broth components as follows: 1.1–1.3 HMTA/U, 1.25 urea/U, 1.5–1.7 NO_3^-/U. "H" Process indicates mole ratios of broth components as follows: 2.0 HMTA/U, 2.0 urea/U, 2.2 NO_3^-/U, 0.5 NH_4^+/U.

[b] F. is abbreviation for fines; S.C. is abbreviation for small coarse. Lab indicates small scale with batch preparation of broth and typically 0.1 to 0.6 kg product per test. Interim indicates engineering scale with continuous preparation of broth and more than 0.6 kg product per test.

[c] TCE is abbreviation for trichloroethylene; 2EH is abbreviation for 2-ethyl-1-hexanol.

[d] Wet aging indicates elapsed time between gelation and final drying as 5, 10, 20, 40, 60, etc. h.

[e] Steam indicates drying in an oven in a partially closed container to provide a humid drying atmosphere.

Table A2. UO_2 Sphere-Cal Pellets

Batch	Pellet	Calcination Temperature (°C)	Forming Pressure (MPa)	Green Bulk Density[a] (% T.D.)	Sintered Bulk Density (% T.D.)	Mercury Density (% T.D.)	Weight Loss (%)	Diametrical Shrinkage (%)	Pellet Integrity	Microstructure
GT-371	SP-1-1	400	138	31.8			3.4	26.5	Cracked	
GT-371	SP-1-2	400	138	31.7	78.3		6.4	24.5	Cracked	Homogeneous.
GT-371	SP-7-4	400	207	38.0			10.2	23.3	Cracked	
GT-371	SP-2-9	400	276	39.5			7.8	22.4	Cracked	
GT-371	SP-3-1	600	138	36.1	87.9	93.4	3.8	23.9	Good	Excellent homogeneity.
GT-371	SP-4-4	600	207	34.0	89.6	95.2	2.8	22.5	Good	Excellent homogeneity.
GT-371	SP-5-7	600	276	42.9	87.2		3.1	19.8	Cracked	
GT-371	SP-6-9	600	276	44.2			3.8	19.4	Cracked	
GT-371	SP-10-1	800	138	38.8	86.9	90.5	3.8	22.3	Good	
GT-371	SP-11-4	800	207	42.1	87.5		3.4	20.7	Cracked	
GT-371	SP-12-7	800	276	44.1	88.6	90.6	3.4	19.5	Good	Very homogeneous, stress crack.
GT-412	SP-13-1	600	138	41.1	92.2	93.1	1.9	23.6	Good	
GT-412	SP-14-4	600	207	45.7	96.5	96.3	1.9	21.8	Good	Some porosity around remnant spheres.
GT-412	SP-15-7	600	276	49.1	95.1	97.4	2.2	20.2	Good	
GT-357	SP-16-1[b]	600	138	44.7	95.1	98.4	2.7	25.1	Good	Internal cracks, few bad spheres.
GT-357	SP-16-4[b]	600	207	47.2	94.5	98.9	2.4	20.3	Good	Internal cracks, few bad spheres.
GT-357	SP-16-7[b]	600	276	49.8	93.3	99.1	2.8	18.9	Good	Internal cracks, few bad spheres.
IGT-60	SP-17-1	600	138	44.6	93.7		2.3	21.4	Cracked	
IGT-60	SP-17-4	600	207	47.2	94.2	97.5	2.2	19.9	Good	Internal cracks, few bad spheres.
IGT-60	SP-17-7	600	276	50.7	94.5	96.2	2.7	18.5	Good	Internal cracks, few bad spheres.
IGT-60	SP-19-1A	600	138	42.9	84.6		4.8	20.9	Cracked	Internal cracks.
IGT-60	SP-19-4	600	207	45.5	85.9		4.0	19.4	Good	
IGT-60	SP-19-7	600	276	47.5	80.4		7.5	17.7	Cracked	Internal cracks.
J-819	SP-19-1B	600	138	43.0	86.9	97.3	2.7	21.4	Good	
J-819	SP-19-2	600	207	46.0			3.0		Broke	Sphere-to-sphere variability, some porosity around remnant spheres.
J-819	SP-19-3	600	276	49.1	88.9	99.7	3.1	18.7	Good	
IGT-68-69B	SP-25-1	450	172	41.4	92.2		2.0	22.9	Slightly cracked	Few cracks and bad spheres.
GT-469	SP-25-2	450	172	40.9	91.3		4.0	23.7	Slightly cracked	Some porosity around remnant spheres, few bad spheres.
IGT-61B	SP-27-1	450	172	42.1	88.0		5.5	21.9	Good	Few cracks and bad spheres.
IGT-61B	SP-27-2	450	172	42.9	92.0		3.9	22.3	Good	Some varability between spheres, small amount of porosity around remnant spheres.
J-829	SP-31-1	450	207	46.6	93.4		4.7	21.0	Cracked	
J-829	SP-31-2	600	207	47.9	94.8		4.6	20.7	Cracked	
FGT-8	SP-34-1	450	207	39.8			8.1		Broke	Very dense, homogeneous matrix.
FGT-8	SP-34-2	450	207	38.7			8.1		Broke	Very dense, homogeneous matrix.
FGT-8	SP-38-1[c]	450	138	34.9			9.0	21.2	Broke	Poor, internal cracks, voids.
FGT-8	SP-38-2[c]	450	207	34.4			10.9	22.4	Broke	Poor, internal cracks, voids.
FGT-8	SP-38-3[c]	450	276	39.5			8.3	21.1	Broke	Poor, internal cracks, voids.
FGT-8	SP-39-1[c]	450	138	35.6			8.8	25.2	Broke	Poor, internal cracks, voids.
FGT-8	SP-39-2[d]	450	207	40.2			10.9	23.3	Broke	Few internal voids.
IGT-76	SP-34-3	600	207	45.4			3.4		Broke	Few internal voids, dense matrix.

Table A2. (Continued)

Batch	Pellet	Calcination Temperature (°C)	Forming Pressure (MPa)	Green Bulk Density[a] (% T.D.)	Sintered Bulk Density (% T.D.)	Mercury Density (% T.D.)	Weight Loss (%)	Diametrical Shrinkage (%)	Pellet Integrity	Microstructure
FGT-1	SP-31-3	600	207	45.8			3.7		Broke	Very dense matrix, few remnant spheres.
FGT-1	SP-37-1[c]	600	138	41.0	82.4	94.5	5.4	20.6	Good	Some internal cracks, voids, and porosity around remnant spheres.
FGT-1	SP-37-2[c]	600	207	45.9	86.1	96.2	4.4	18.3	Good	Some internal cracks and voids near edge.
FGT-1	SP-37-3[c]	600	276	48.9	89.3		5.1	18.2	Good	Internal cracks, edge discoloration.
FGT-20AI	SP-42-1	600	345	49.9	95.2		2.6	20.4	Cracked	End capping, some porosity around remnant spheres.
FGT-20AI	SP-42-2	600	276	46.4	92.0		3.1	21.1	Good	Some porosity around remnant spheres.
FGT-10	SP-44-1	600	207	46.6	86.6		4.6	19.9	Cracked	Internal cracks.
FGT-10	SP-44-2	600	276	49.7	86.9		5.2	18.8	Cracked	Internal cracks.
FGT-10	SP-44-3	600	345	50.7	86.4		6.2	17.9	Cracked	Internal cracks.
GT-468	SP-45-1	600	207	46.4	88.0		2.8	19.9	Cracked	Internal cracks and voids.
GT-468	SP-45-2	600	276	49.3	90.6		2.7	19.4	Cracked	Internal cracks and voids.
GT-468	SP-45-3	600	345	51.2	81.1		12.8	18.4	Cracked	Internal cracks and voids.
IGT-61A	SP-46-1	600	207	40.4	88.7		2.6	22.5	Good	Few internal cracks.
IGT-61A	SP-46-2	600	276	46.4	88.9		2.0	18.9	Flaked	Few internal cracks.
FGT-23B	SP-47-1	600	207	41.0			3.1		Broke	Some porosity around remnant spheres, end capping, pressing lamination.
FGT-23B	SP-47-2	600	276	43.9			3.4		Broke	Some porosity around remnant spheres.
FGT-23A	SP-48-1	600	207	42.9	86.0		2.1	20.6	Broke	Some porosity around remnant spheres.
FGT-23A	SP-48-2	600	276	44.4	87.2		2.1	20.2	Broke	Some porosity around remnant spheres.
H06	SP-49-2	600	207	49.7	76.3		2.8	14.5	Crumbly	Internal cracks, remnant sphere structure with little sintering between spheres.
H06	SP-49-3	600	276	51.2	78.7		3.4	14.7	Crumbly	Internal cracks, remnant sphere structure with little sintering between spheres.
FGT-21	SP-50-1	600	207	39.7			2.8	23.3	Broke	Some porosity around remnant spheres, pressing lamination.
FGT-21	SP-50-2	600	276	39.6	85.2		3.0	22.3	Good	Few large cracks, some porosity around remnant spheres.
FGT-20	SP-51-1	600	138	36.8	82.8		3.1	23.7	Good	Porosity around remnant spheres.
FGT-20	SP-51-2	600	207	39.6	87.3		2.6	23.4	Good	

[a] Green bulk density is expressed in terms of percent of theoretical UO_2 density.

[b] Sintering furnace blew fuse at 1000°C; pellets were refired to 1450°C and held at temperature for 2 h.

[c] Sterotex was added to the pellet press feed.

[d] Carbowax was added to the pellet press feed.

Table A3. Thoria and Thoria-Urania Sphere-Cal Feed Material[a]

Batch	Gelation Flowsheet	Th/U Ratio	Gelation Conditions	Drying Conditions[b]	Sphere Size, µm		Tap Density Dried (g/cm^3)	Sphere Weight Loss During Sintering (%)	Sphere Mercury Density (% T.D.)
					Dried	Sintered			
MGT-103	Internal gelation	3.60	Perc[c] mineral oil, 95°C	Steam-220°C	2463		1.72	16.9	89.5
MGT-104	External, SNAM	3.97	NH_3 gas, then NH_4OH	Steam-200°C	724	573	2.23		
Th-U-3.84	External, KFA-Jülich	7.27	NH_3 gas, then $NH_4OH + NH_4NO_3$	Steam-220°C			2.20	3.4	100
MGT-111	External, KFA-Jülich	100% ThO_2	NH_3 gas, then $NH_4OH + NH_4NO_3$	Steam-224°C			2.65	3.3	100
MGT-127	External, KFA-Jülich	5.93	NH_3 gas, then $NH_4OH + NH_4NO_3$	Steam-220°C			2.11	4.0	100
GT-484	Internal gelation	2.86	TCE,[c] 69°C	Steam-250°C			2.09		

[a] *Note:* The thoria and mixed thoria-urania batches were not calcined before pressing.

[b] Steam indicates drying in an oven in a partially closed container to provide a humid drying environment.

[c] Perc is abbreviation for perchloroethylene, TCE is abbreviation for trichloroethylene.

Table A4. Thoria and Thoria-Urania Sphere-Cal Pellets[a]

Batch	Pellet	Composition		Forming Pressure (MPa)	Green Bulk Density (% T.D.)	Sintered Bulk Density (% T.D.)	Mercury Density (% T.D.)	Weight Loss (%)	Diametrical Shrinkage (%)	Pellet Integrity	Microstructure
		UO_2 (%)	ThO_2 (%)								
MGT-103	SP-18-1	21.74	78.26	345	34.3	76.9		17.8	30.4	Cracked	Remnant spheres and shards, internal cracks.
MGT-104	SP-22-1	20.12	79.88	345	40.1	90.2	97.1	8.0	26.9	Good	Internal cracks, voids.
Th-U-3.84	SP-28-1	12.09	87.91	345	41.5			9.9	24.8	Cracked	Remnant spheres and shards, internal cracks.
MGT-111	SP-41-1	0	100	345	39.9	73.7		10.4	22.3	Cracked	Remnant spheres and shards, internal cracks.
MGT-127	SP-41-2	14.43	85.57	276	40.6	89.1		8.4	26.2	Good	Remnant spheres and shards, internal cracks.
GT-484	SP-41-4	25.91	74.09	345	44.3	75.3		5.5	18.2	Crumbly	Remnant spheres and shards, internal cracks.
GT-484	SP-42-3	25.91	74.09	276	42.2	70.9		6.9	18.3	Crumbly	Remnant spheres and shards, internal cracks.

[a] Note: The thoria and mixed thoria-urania batches were not calcined before pressing.

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