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A NEW PROCESS FOR THE REMOTE PREPARATION AND FABRICATION OF  
FUEL ELEMENTS CONTAINING URANIUM-233 OXIDE-THORIUM OXIDE

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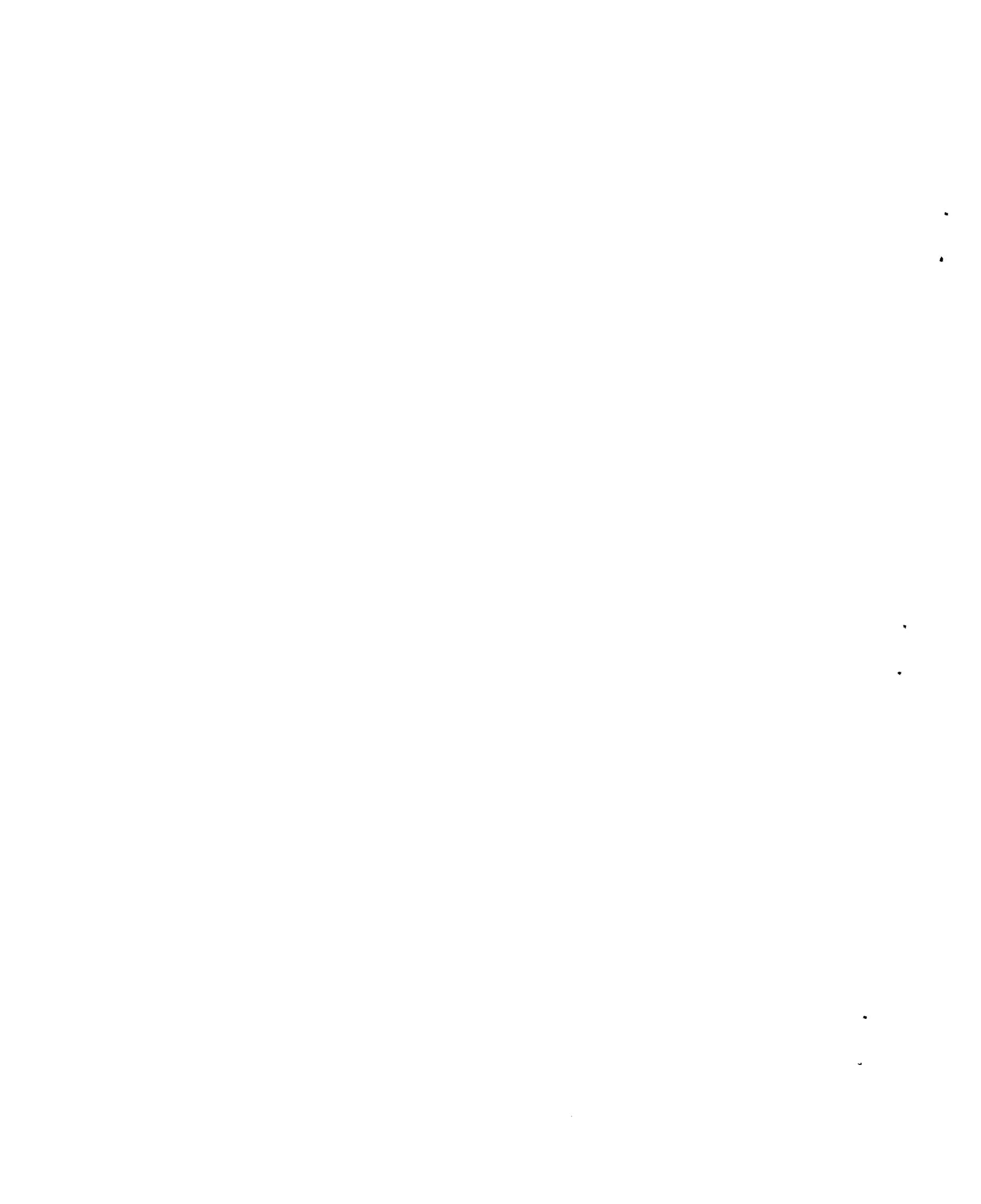
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## A NEW PROCESS FOR THE REMOTE PREPARATION AND FABRICATION OF FUEL ELEMENTS CONTAINING URANIUM-233 OXIDE-THORIUM OXIDE

### ABSTRACT

A remotely operated pilot plant for the engineering development of the sol-gel--vibratory-compaction procedure for preparing reactor fuel has been constructed at Oak Ridge National Laboratory. This plant is called the Kilorod Facility. The facility is being used to prepare about a thousand Zircaloy-2-clad fuel elements for a zero-power criticality experiment at Brookhaven National Laboratory. The rod-like fuel elements are about 1/2 in. in diameter and 46 in. long. Each will contain 890 g of oxides in solid solution ( $U^{233}$  to Th wt ratio, 3/97). During this work, the feasibility, safety, and economy of remote recovery, preparation, fabrication, and inspection of  $U^{233}O_2$ - $ThO_2$  fuels are being evaluated on an engineering scale. Upon completion of this project, the facility may be used to prepare  $UC_2$ - $ThC_2$  fuels by the sol-gel process.

The procedure includes solvent extraction recovery of  $U^{233}$  by means of di-sec-butyl phenylphosphonate in diethylbenzene; the sol-gel process, a new procedure for preparing dense oxide fuels; oxide particle sizing; vibratory compaction loading of fuel tubes, followed by end-closure welding, cleaning, and inspecting. Gamma-ray scanning will be used to determine the uniformity of the fuel density. All steps in the procedure, and the equipment for conducting it, were designed for critically safe, remote operation. Instruments are provided for remote control of the process and for monitoring the radioactivity and evaluating the hazards to workers at each step of the operation.

Twelve pilot-plant runs involving uranium decontamination, sol-gel preparation of 50 kg of oxide, and fuel sizing and classification have been completed, with only minor difficulties. Previously, all steps had been successfully operated outside of the cell at full scale, using  $U^{238}$  as a stand-in, to confirm the equipment



design and operational procedures. The adaptability of the process and equipment, however, can be proved only by operation of the integrated facility with  $U^{233}$ .

The results of examination after irradiation of 17 test capsules at burnups to 17,000 Mwd/metric ton of fuel showed the sol-gel-prepared oxide to perform satisfactorily with respect to stability and fission gas release.

Much of this procedure is new, including the sol-gel process. While early results are encouraging, it is too early to report a complete evaluation.

In laboratory experiments, uranium-thorium dicarbide fragments and microspheres were prepared by the sol-gel process at a maximum temperature of 1600°C.

## INTRODUCTION

The purpose of this paper is to present the objectives, design, development, and operational performance of the Kilorod Facility, a pilot plant for preparing  $U^{233}$  oxide-thorium oxide fuel and fabricating it into fuel rods by the sol-gel-vibratory-compaction process behind shielding.

Processing and handling of  $U^{233}$  and recycled thorium fuels need to be conducted behind shielding because of the high-energy gamma radiation emitted by the decay products of  $U^{232}$  that is associated with  $U^{233}$  (refs 1 and 2).

Extensive process development for each step was carried out outside of shielding to optimize equipment and procedures for remote or semi-remote operation. Some well-established procedures were modified, and some new processes were introduced, in order to provide a safe, low-cost  $U^{233}$ -thorium fuel cycle suitable for remote operation. The facility was designed and built primarily to carry out the Kilorod program, in which approximately 1000 fuel rods, containing  $U^{233}$  oxide-Th oxide ( $U^{233}$  to Th wt ratio of 3/97), are being prepared for zero-power criticality experiments at Brookhaven National Laboratory. In addition to the production of the rods, the program affords an excellent opportunity to extend thorium fuel cycle technology. Much valuable processing and fabrication experience is being obtained. Data on radiation exposure to workers for each operation will be provided to determine what

operations, if any, can be carried out outside of shielding. Much-needed cost data will be obtained for thorium-U<sup>233</sup> fuel cycles. Although designed to produce a specified fuel rod, all the equipment with the exception of that used for rod fabrication and inspection is of a sufficiently general design to afford considerable functional flexibility. For example, when the Kilorod program is completed, the facility may be used for scaled-up development of elements containing uranium and thorium dicarbides.

#### ACKNOWLEDGMENT

The development, design, and operation of the Kilorod fuel cycle pilot plant is the culmination of the efforts of many people at ORNL. The authors are specially indebted to D. E. Ferguson, J. C. Bresee, J. L. Matherne, P. A. Haas, C. C. Haws, J. W. Snider, S. D. Clinton, K. H. McCorkle, A. T. Kleinsteuber, M. G. Baillie\*, E. C. Moncrief, F. W. Davis\*\*, A. R. Irvine, and B. B. Klima of the Chemical Technology Division, and D. A. Douglas, S. A. Rabin, W. S. Ernst, Jr., J. D. Sease, J. Van Cleve, and B. E. Foster of the Metals and Ceramics Division for contributions which made this paper possible.

#### THE KILOROD PROGRAM

Figure 1 shows the product of the Kilorod Facility, the Bookhaven National Laboratory fuel rod for the zero-power critical experiment assembly. The program requires the production of about 1000 of these elements. Each of the Zircaloy-2 tubes contains 890 g of U<sup>233</sup>-thorium as oxides (U<sup>233</sup> to Th wt ratio, 3/97). The U<sup>233</sup> contains nominally 40 ppm of U<sup>232</sup>. The cone-shaped bottom fitting serves to locate the rods in the lattice, and the top fitting

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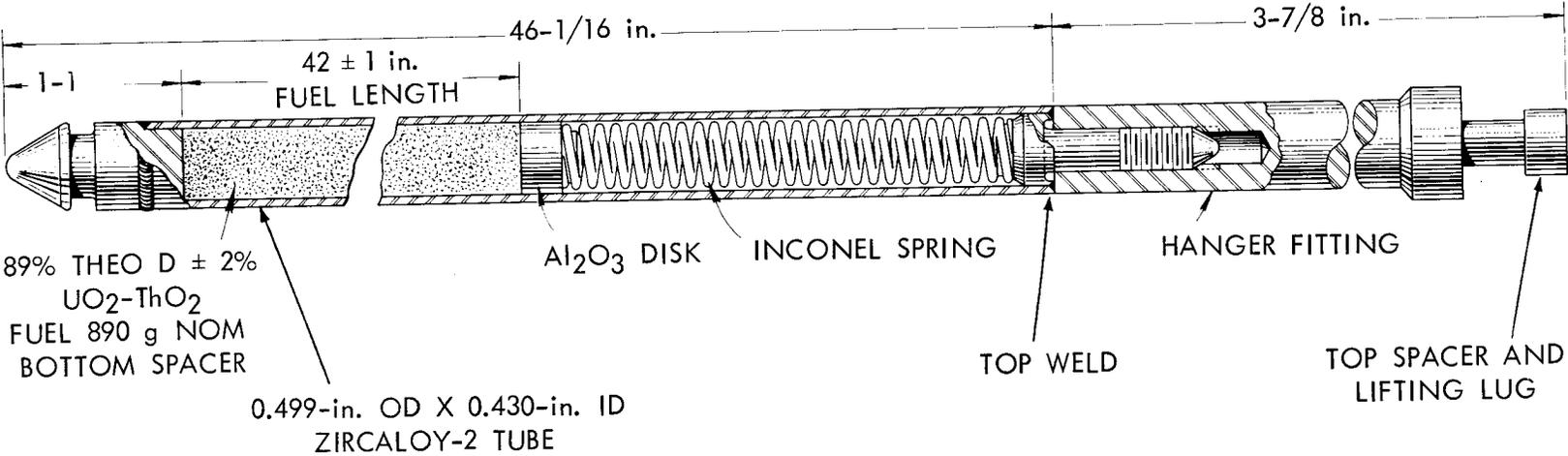


Fig. 1. Design Features of the BNL Fuel Rod.

supports the rods in the lattice and provides a lifting plug for handling. The compression spring and alundum spacer prevent fuel movement if the rods are inverted. In addition to the 46-in.-long by 0.43-in.-ID rods shown, about two-hundred rods, 18 in. long and each containing 310 g of oxide, will be prepared. By specification, the bulk density of the fuel must be 89% of the theoretical crystal density (10.035 g/cc), with a variability of not greater than  $\pm 2\%$  over a segment of the rod equal to a standard pellet or from rod to rod. In addition, the variation in concentration of  $U^{233}$  over the length of the rod and from rod to rod must conform to the same specification.

### THE KILOROD FACILITY

The plant, though integrated, will be discussed as three processing sections for the sake of convenience (see Fig. 2). In section I impure  $U^{233}$  as metal or as uranyl nitrate solution is purified by solvent extraction, removing decay products of  $U^{232}$  and ionic impurities. In section II dense, homogeneous particles containing  $U^{233}$  oxide-thorium oxide, suitable for vibratory compaction loading of fuel tubes, are prepared by the sol-gel process. The production capacity is 10 to 15 kg of  $U^{233}$  oxide-thorium oxide per day. In section III the Zircaloy-2 rods are loaded by vibratory compaction, sealed, cleaned, and inspected. This section is designed to prepare 10 to 15 finished fuel rods per day.

#### Uranium-233 Purification Facility

Fuel dissolution, feed preparation, and solvent extraction are carried on remotely in a processing cell apart from the oxide preparation and rod fabrication facilities. The cell shielding is 5 ft of barytes concrete. Provisions are made for complete containment of solids and solutions and for criticality safety described in a later section.

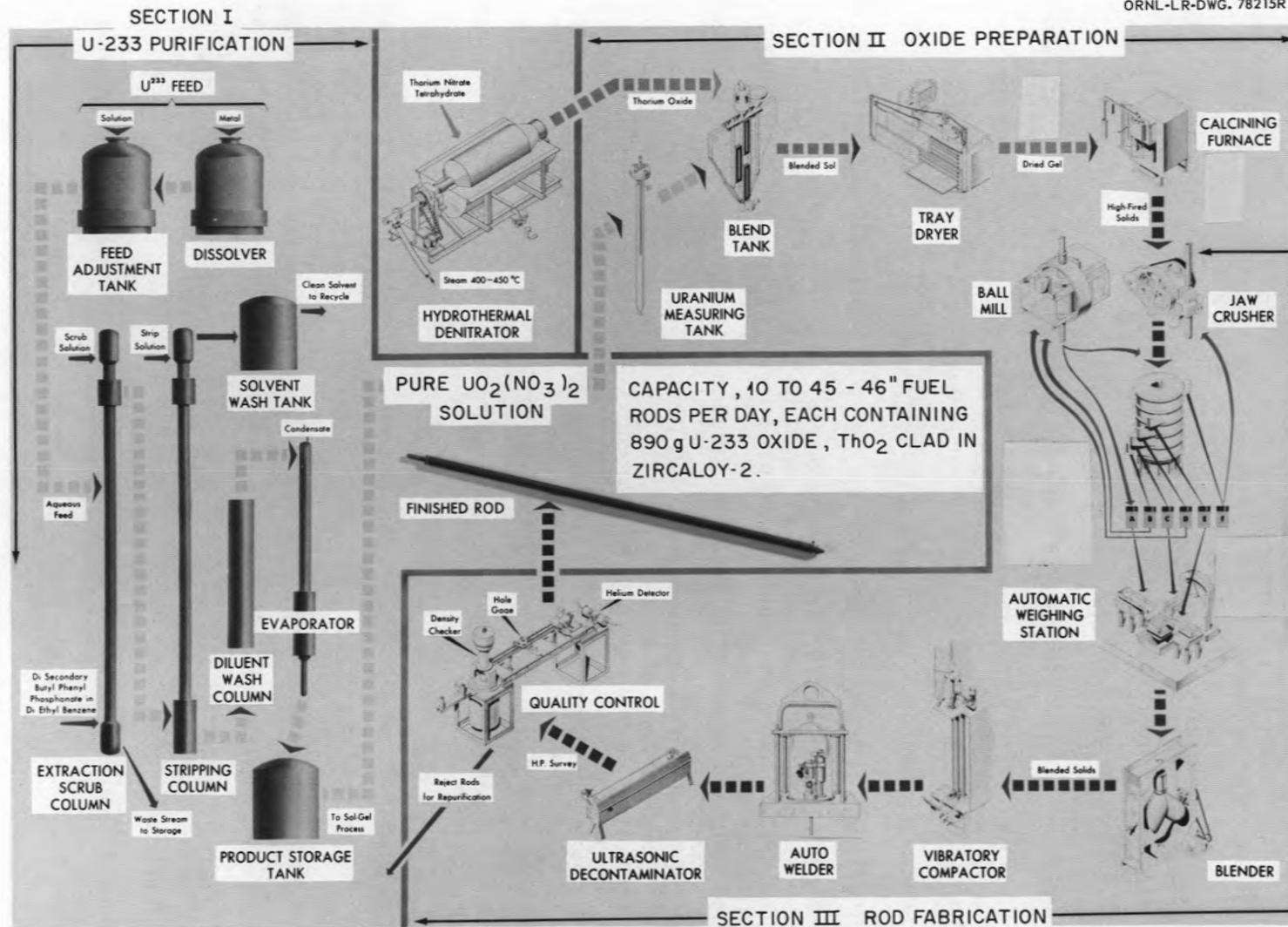


Fig. 2. The ORNL Kilorod Facility Flowsheet.

### Oxide Preparation and Rod Fabrication Facilities

The sol-gel oxide preparation and rod-fabrication process equipment (Fig. 3) is located within a 20 x 19 x 27-ft cell, separate from the purification facility. This cell is being used for secondary containment of radioactivity that might escape from the cubicles. There are three operating levels provided with an enclosure of 4.5-in. armor plate or 8-in. barytes concrete for gamma-ray shielding and an all-welded steel liner for primary alpha-particle containment which completely surrounds and seals all operation space. Areas outside the shielding are personnel access areas from which operations can be conducted semiremotely or remotely. Operation of the third-level cubicle (the sol-gel process) will be conducted by gloved access or by remote solution transfer. The rod-fabrication operations in the cubicles on the first and second levels will be accomplished by Castle manipulators or gloved access. Located on one corner of the first level and extending to the top of the second level is the 4- x 7-ft powder-conditioning shaft. Directly adjacent to this shaft on the first level are three fabrication cubicles that extend along two walls. The first of these cubicles is used for vibratory compaction and welding, the second for decontamination, and the third for inspection. A gloved repair box is located on the second level adjacent to the powder preparation shaft and directly above the vibratory compaction-welding cubicle and the decontamination cubicle. The box is equipped with a large bag-out port and a monorail crane that runs the length of the glove box and will be used to lift and convey equipment. Access to the powder preparation shaft is through a door in the side of the shaft, while access to the fabrication cubicles is through ports in the floor of the box.

The fabrication cubicles have 20 windows; 31 ports are provided to allow outfitting with either gloves or manipulator tongs and allow interchange of gloves and tongs without loss of containment. The rod fabrication process is operated with nine manipulators and two glove ports. The remaining 20 glove ports are used for maintenance.

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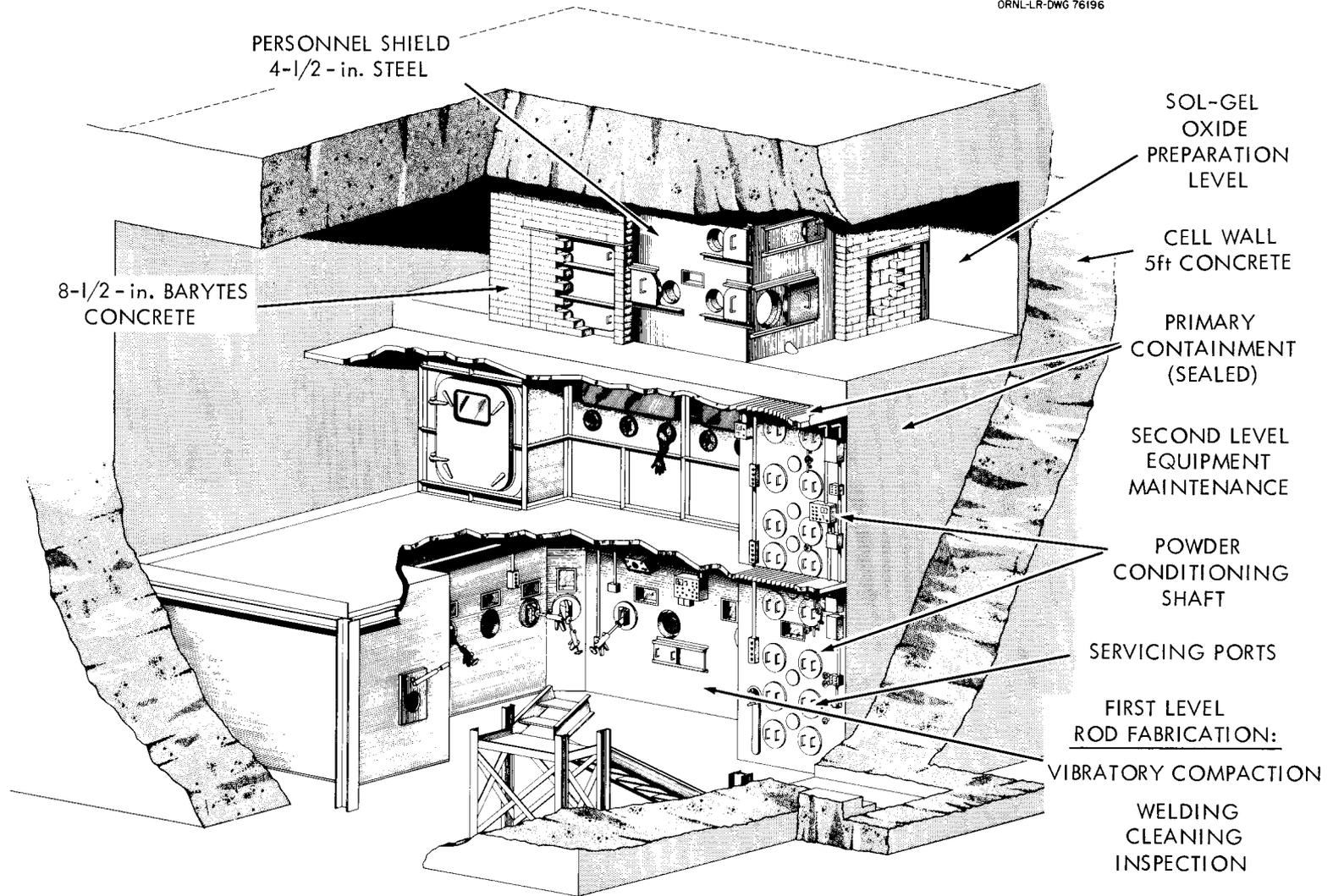


Fig. 3. Kilorod Solids Preparation and Rod Fabrication Facility.

### Uranium-233 Purification

Solvent Extraction Feed Preparation.—The sources of  $U^{233}$  for the Kilorod Program are massive, 4-kg pieces of metal and uranyl nitrate solutions containing 60 to 150 g/liter of  $U^{233}$ . The  $U^{232}$  content of the  $U^{233}$  is 38 ppm. The radioactivity of the metal, at its surface, is 40 r/hr.

The massive metal is broken then dissolved in 1.4 *M* thorium nitrate—4 *M* nitric acid in a 5-ft-diam, 2000-liter vessel (Fig. 4). The adjusted solvent extraction column feed contains 5 g/liter of  $U^{233}$  (half that of the recommended safe maximum concentration), 200 g/liter of thorium, and 2.4 *M*  $HNO_3$ . One complete dissolution of 4 kg of broken  $U^{233}$  metal required 40 hr.

Solvent Extraction.—The solution feed for the extraction column is pumped into the midpoint of the pulsed contactor where the uranium is removed from the downward-moving aqueous phase by two volumes of organic extractant per volume of feed solution (Fig. 5). The thorium in the feed serves two major functions in this operation: It provides salting strength and it acts as a soluble neutron poison for criticality control. The uranium-bearing organic stream is then scrubbed as it moves upward through 0.8 *M*  $Al(NO_3)_3$  which is 0.4 *M* acid deficient in order to remove ionic contamination and entrained thorium, and it is then delivered to the stripping column. The aqueous waste stream contains less than 0.01% of the uranium fed to the system. The uranium is removed from the organic phase with demineralized water in the stripping column. In the aqueous product, the concentration of uranium is 10 g/liter. This dilute product solution from stripping is passed through a static diluent wash column to remove traces of extractant which tends to hydrolyze to products troublesome to the sol-gel process while concentrating the dilute uranium product to 100 to 150 g/liter.

Results of Runs to Test the Flowsheet and Equipment.—Feed solutions that contained tracer concentrations of  $U^{233}$  and others that contained 0.5 g/liter of  $U^{233}$  in addition to the other components specified by the  $U^{233}$  purification flowsheet were subjected to solvent extraction in the Kilorod equipment. Results are

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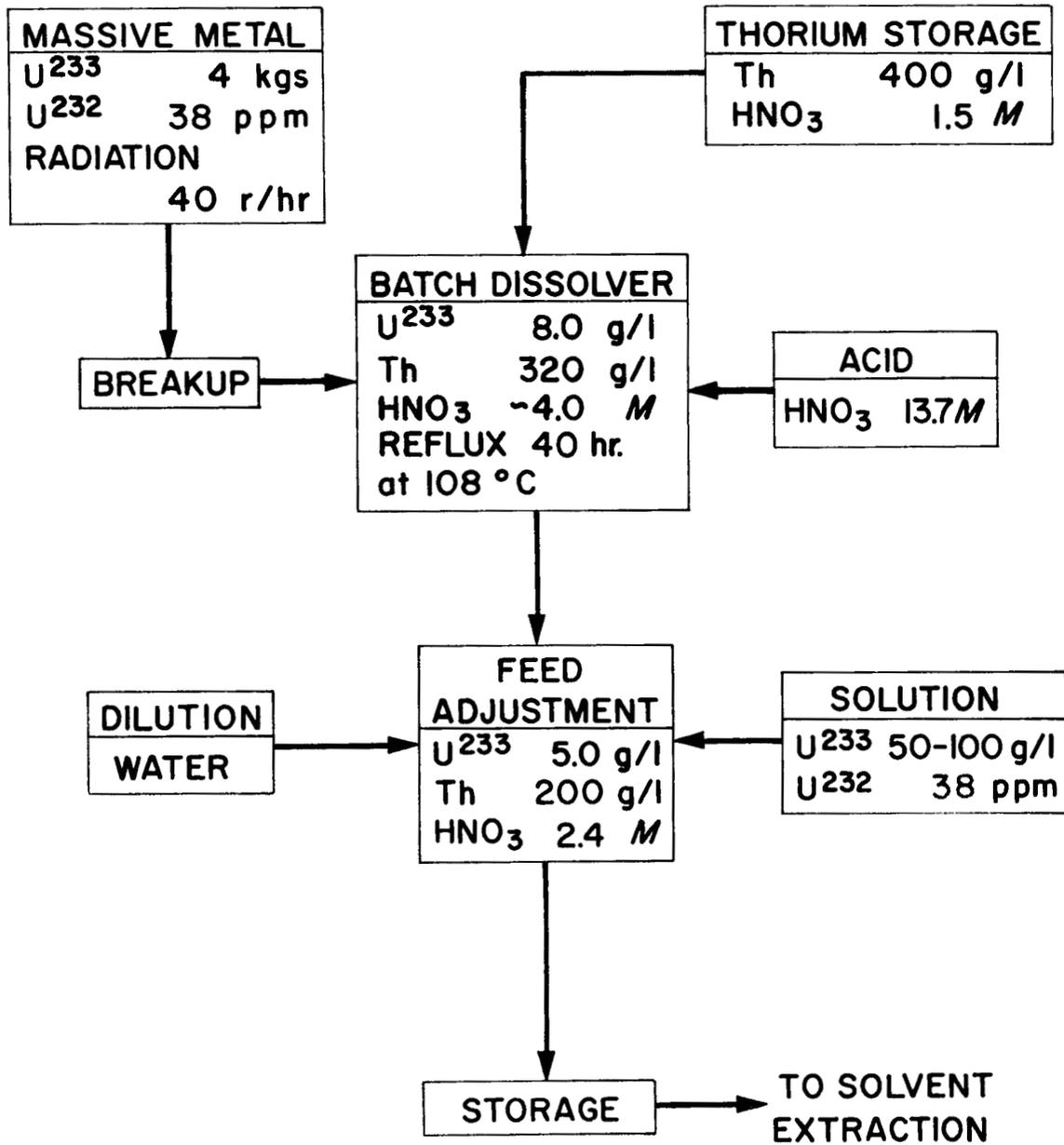


Fig. 4. Purification of Uranium-233: Feed Preparation.

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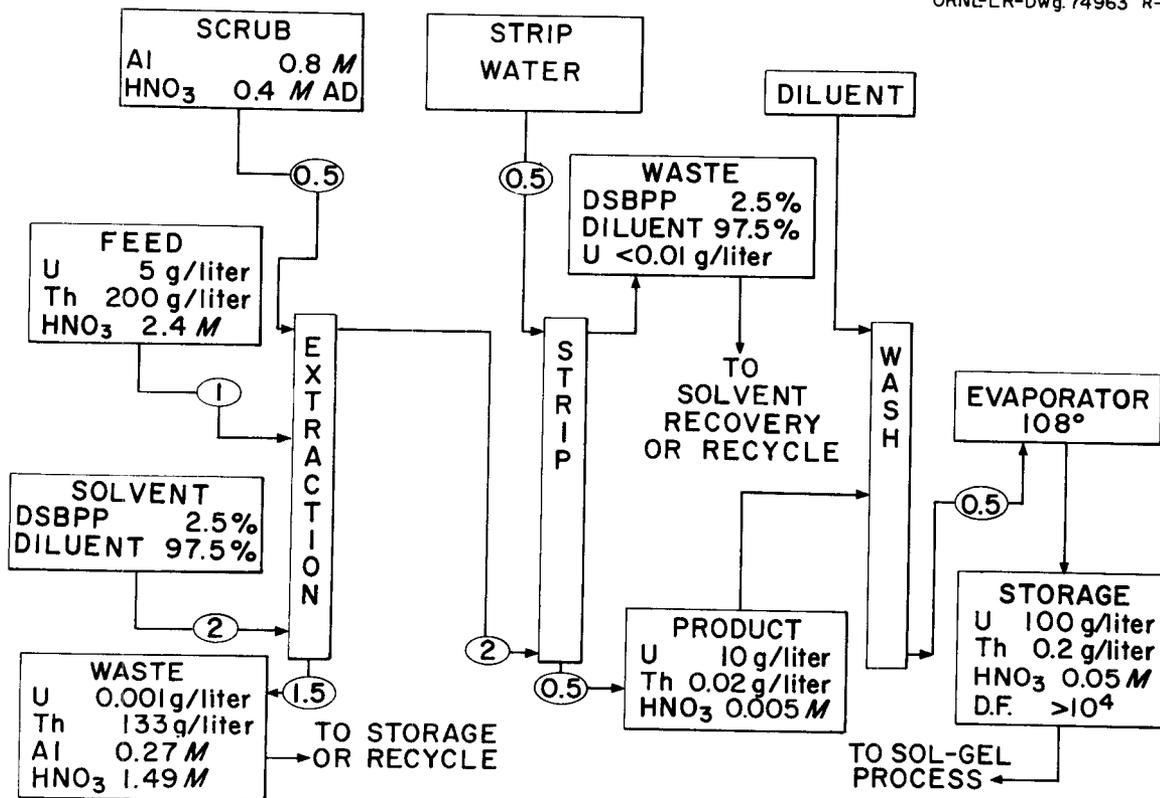


Fig. 5. Purification of Uranium-233: Solvent Extraction.

summarized in Table 1. The decontamination factors for gross gamma and for thorium easily met the specifications of 100 for gross gamma and 1000 for thorium.

Table 1. Uranium-233 Purification: Results of Solvent Extraction Test Runs

Activity Level	Over-all D.F.		Uranium Losses, %		
	Gross $\gamma$	Thorium	Extraction Raffinate	Stripped Solvent	Evaporator Overhead
Trace	100-130	$1 \times 10^3$ to $2.5 \times 10^4$	-	-	-
Intermediate	500	$2 \times 10^3$	0.06	<0.005	0.35

### Section II - Oxide Preparation: The Sol-Gel Process<sup>3,4</sup>

Thorium Oxide Preparation.—Thorium oxide that is readily dispersible to stable sol particles of about 70-Å diam is prepared outside the facility by means of a rotary steam denitrator. Crystalline thorium nitrate containing 15 kg of  $\text{ThO}_2$  or thorium nitrate solution is charged batchwise to the denitrator. The denitrator which is surrounded by electric heaters is rotated in a horizontal position while the temperature is increased over a 1-hr period to 180°C with flowing heated air. About half of the water of hydration is removed by this treatment. The air is displaced by superheated steam which is passed over the rotating charge as the wall temperature is raised to 475°C and held for 1 hr (6 hr total run time). The thorium oxide powder product contains a highly reproducible 0.025 to 0.030 moles of nitrate residue per mole of  $\text{ThO}_2$  (see Fig. 6). Over 700 kg of thorium oxide have been prepared for the Kilorod program by this method. Uranium feed for the process will be received into a 3-in.-diam (critically safe geometry) steel and glass vessel (Fig. 7). The normal batch size will be 3 liters of solution (100 g of uranium per liter) which will

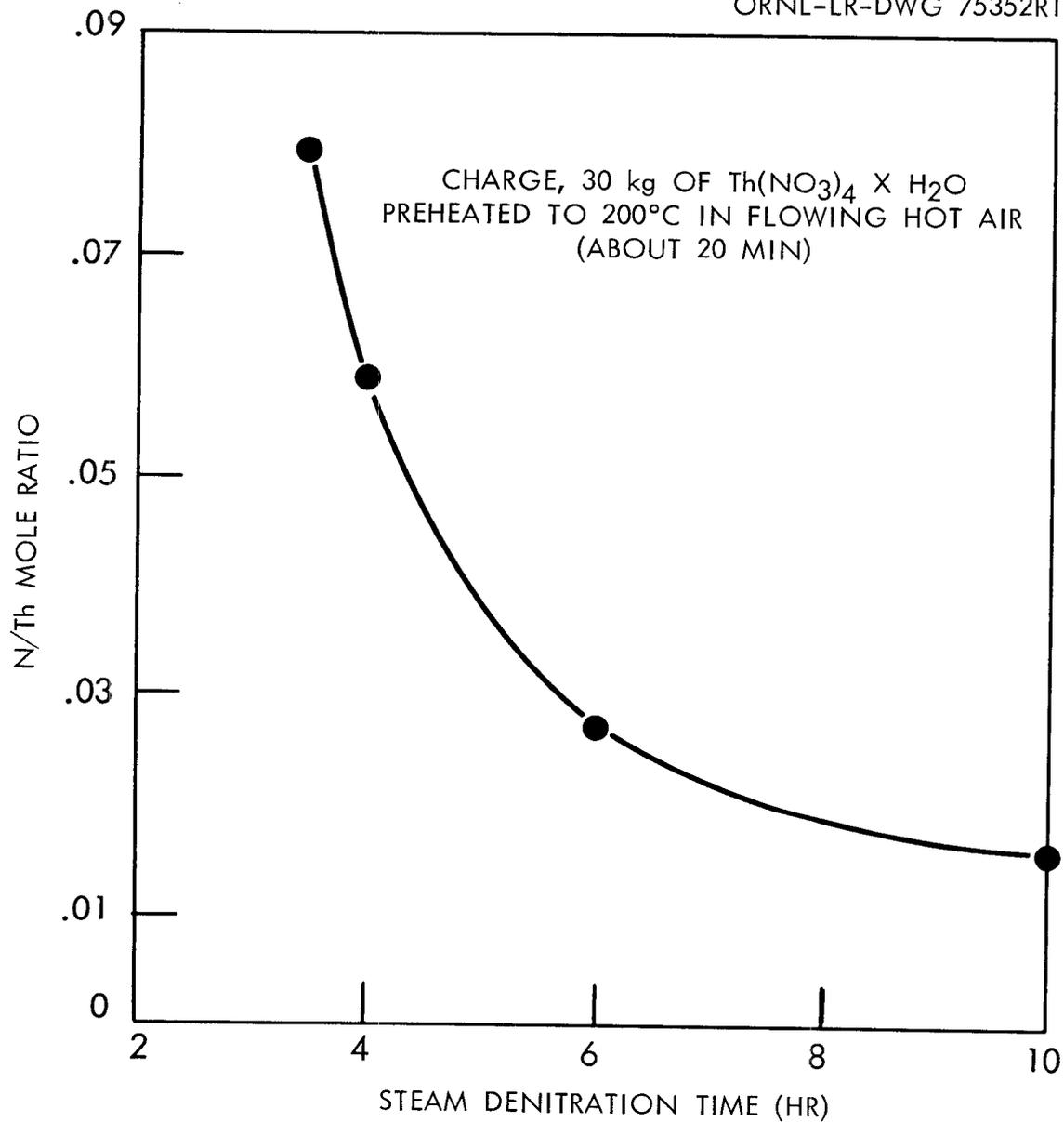
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Fig. 6. The Effect of Steam Denitration Time on Residual  $\text{NO}_3^-/\text{ThO}_2$  Mole Ratio of Product of Denitration.

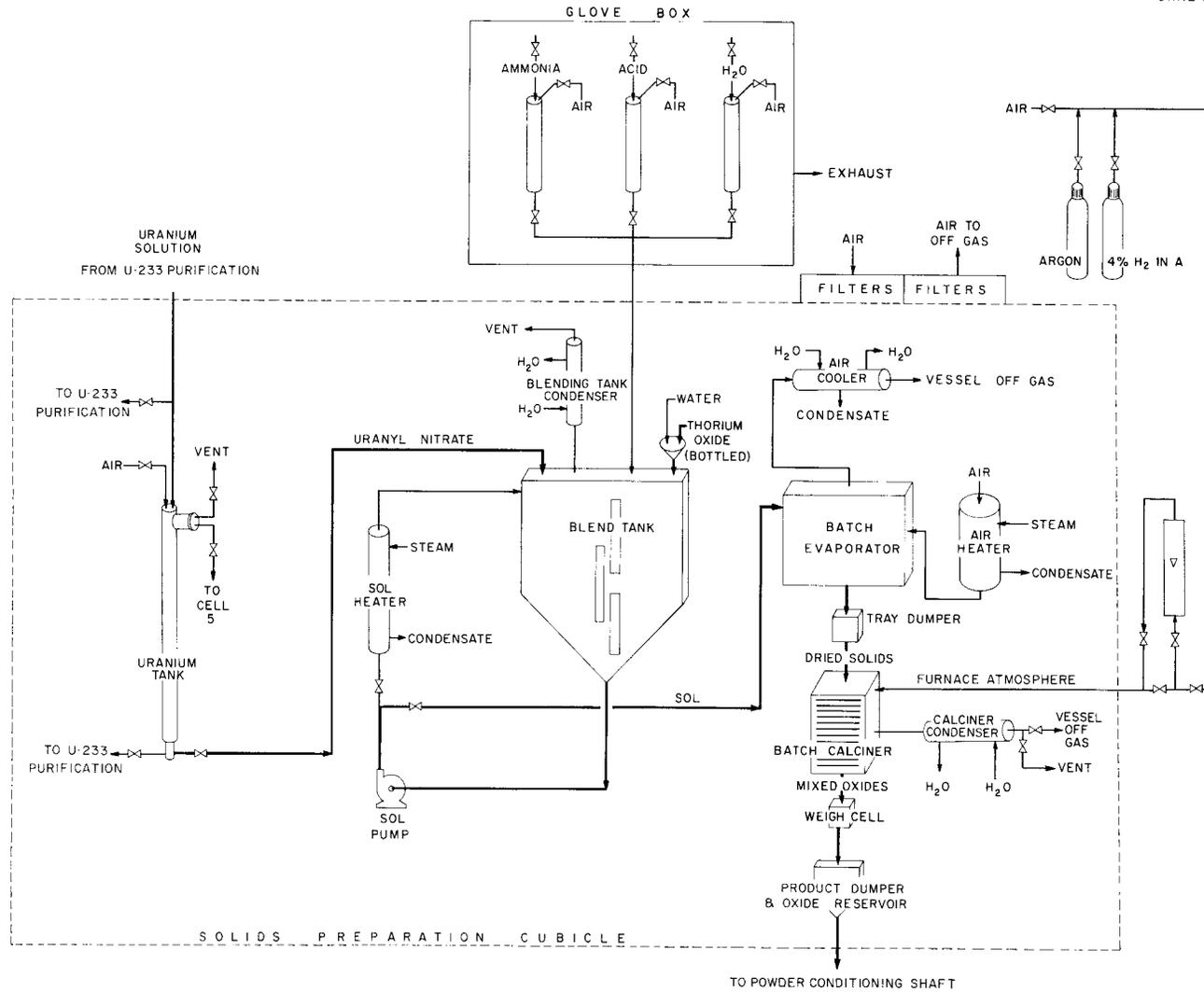


Fig. 7. Thorium-Uranium-233 Oxide-Solids Preparation Cubicle Flowsheet.

be delivered from the solvent extraction system (located in the  $U^{233}$  purification cell). Measurement of the volume of uranium solution in this vessel must be precise, therefore, a cathetometer is used. Also, the solution is sampled and analyzed for its uranium and nitrate content.

The equipment to be used for demonstration and engineering evaluation of the sol-gel process is housed within the cubicle on the third level (see Fig. 3).

Sol Preparation.— Following volume and concentration measurement, the uranyl nitrate solution is transferred to a critically safe slab-tank blender. The mockup used in development of sol preparation is shown in Fig. 8. While recirculating the solution and heating it to  $80^{\circ}\text{C}$ , preweighed  $\text{ThO}_2$  powder is flushed with the correct amount of water through a funnel into the uranyl nitrate solution adjusted to a  $\text{NO}_3^-/\text{Th}$  mole ratio of 0.077, then mixed and digested for about 1 hr to ensure its dispersion to a stable uranium thorium-oxide sol. The hydrogen ion concentration of the sol is then adjusted to  $10^{-3}$  to  $10^{-4}$  M (pH of 3.8 to 4) by the addition of 0.017 mole of  $\text{NH}_4\text{OH}$  per mole of  $\text{ThO}_2$ . The preparation of a stable sol, leading to a homogeneous oxide product, requires that the uranyl nitrate contain nitrate ion equivalent to an  $\text{NO}_3^-/\text{ThO}_2$  mole ratio of 0.077 and that the adjusted sol contain 0.017 mole of  $\text{NH}_4\text{OH}$  per mole of  $\text{ThO}_2$ . Table 2 shows that excessive nitrate produces low-density, poorly compactible oxide particles having poor uranium distribution (e.g., the uranium tends to concentrate in the fine particles). The use of ammonia overcomes these defects if the  $\text{NO}_3^-/\text{Th}$  mole ratio is not greater than 0.1. If the  $\text{NO}_3^-/\text{Th}$  mole ratio is below optimum, the uranium will also become maldistributed, and if extremely low, the oxide particles will lack density.

Drying of Sol to Gel.— After dispersion the sol is pumped to the tray dryer (Fig. 7). A constant level overflow in the center of each of the trays distributes 5 kg of oxide as sol to each tray. Each of the two compartments within the dryer contains three trays, one to collect spillage. The batches of sol are then dried with sufficient preheated air to maintain a drying temperature of  $80^{\circ}\text{C}$ . The drying

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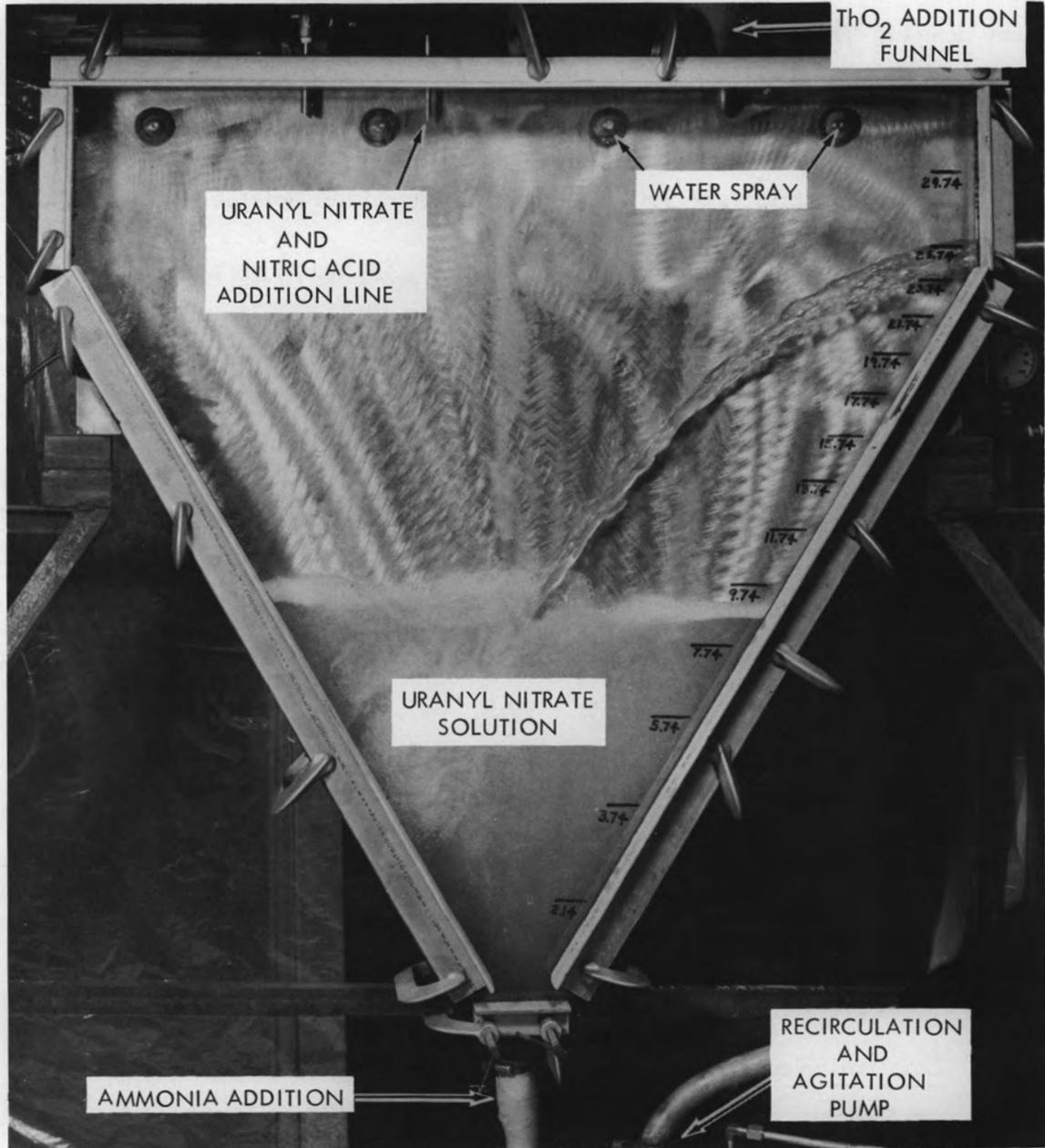


Fig. 8. Critically Safe Sol Blending Tank (Development Model).

is complete in about 24 hr for a 10-kg batch of gel, which breaks away from the walls and sides of the trays and forms fragments from 1 cm in size down to 150  $\mu$ . The two trays are then removed with specially designed tools and placed into the tray dumper. This unit was designed to eliminate the dusting problems involved in transferring dried gel to the alundum crucibles for subsequent operations.

Table 2. Effects of Sol Adjustment on Quality of Sol-Gel Product

Results from typical development runs, producing 7-kg batches of 3% uranium-thorium oxides

Conditions in Sol		Properties of Product				
Moles $\text{NO}_3^-$ Added per Mole $\text{ThO}_2$	Moles $\text{NH}_3$ Added per Mole $\text{ThO}_2$	pH	Density, % of Theoretical		U Distribution in Product, % deviation from mean U/Th mole ratio	
			Particles <sup>a</sup>	Vibratorily Compacted Solid	Coarse Particles	Fine Particles
0.077	0.017	3.92	99.5	91.0	+0.03	-0.03
0.093	0	2.90	96.5	86.0	-4.37	+6.58
0.080	0.020	3.80	98.6	87.8	-0.40	+1.56
0.067	0	3.31	99.3	90.6	-1.62	+1.75

<sup>a</sup>Pycnometric method, using toluene.

Calcination of the Dried Gel to Oxide.— The crucibles are placed in a calcining furnace. The temperature is increased from 200 to 500°C at the relatively slow rate of 100°C/hr to eliminate nitrogenous gases,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$  without shattering the gel, and then at 300°C/hr to 1150°C, at which temperature it is calcined in air for 1 hr to densify the gel. The air is then swept from the furnace retort with argon, and the calcination is continued for 4 hr in noncombustible 4%

H<sub>2</sub>--argon to reduce higher uranium oxides to UO<sub>2</sub>. It is then cooled to 200°C under argon and removed from the furnace. After further cooling to room temperature, it is discharged through a 1/2-in. screen to the rod-fabrication system.

During calcination only minor degradation of particles occurs. Process development now in progress shows that the drying and calcination steps can be simplified and made continuous, and that particle-size control adequate for vibratory compaction is feasible without grinding and sizing. With good furnace atmosphere control, satisfactorily low O/U ratios (2.05) are achievable with purified argon containing no hydrogen.

Results of the Operation.—A total of about 100 kg of 3% uranium (depleted)-thorium oxides has been processed through the sol-gel cubicle in a series of twelve test runs. The runs were made to test equipment, to train operators, and to determine whether product specifications could be met in existing equipment. After difficulties with high residual gas content and high O/U ratios in products of early test runs, minor modifications to the equipment were made, and in the last two test runs product specifications were met.

### Section III - Rod Fabrication

Rod Fabrication Process.—The procedures employed to fabricate the fuel rods have already been outlined (Fig. 2), and the location and arrangement of the apparatus with respect to the facility has been presented (Fig. 3).

The size distribution required to achieve maximum density by vibratory compaction, using the sol-gel product, now appears to be a mixture of three size fractions: a coarse, a fine, and an intermediate fraction. As seen in the flow diagram for the complete Kilorod facility (Fig. 2), these fractions are produced by crushing, classifying, and ball milling the product of the sol-gel process. Following comminution and classification of the bulk fuel into the three working fractions, appropriate quantities of each fraction for loading one fuel rod are blended.

In the vibratory-compaction operation, the blended fuel is loaded into a fuel tube, to which has been attached one end plug, and vibrated to the specified

density. This loaded fuel tube is transferred to a welding fixture where the final end-closure weld is made and visually inspected.

Following the visual inspection, the loaded and sealed fuel rod is decontaminated by ultrasonic cleaning in water and then a "smear" or "wipe" sample is taken in order to determine the level of surface contamination. The integrity of the end-closure weld is evaluated by helium leak testing, and the density of the fuel is determined with a gamma-absorption scanning device. Finally, the hanger fitting is attached prior to loading into a shipping cask.

### Rod Fabrication Equipment

Because of the experimental nature of the equipment, several pieces were tested and evaluated under simulated conditions outside of the cell. The powder preparation equipment, due to its complexity, was tested in a mockup using depleted-U oxide-Th oxide (U to Th wt ratio of 3/97) produced by the sol-gel process. The other pieces of equipment were evaluated under similar test conditions, but without the use of the oxide. A number of flaws in the equipment were detected by the mockup experiments. These were corrected before the equipment was installed in the facility.

Powder Preparation.— The powder-preparation equipment was designed to afford maximum dust confinement and to use gravity feed for transporting the fuel through pipes from one equipment unit to the next. All the equipment in the powder-preparation shaft (Fig. 9) is remotely controlled either electrically or by flexible shafts. Minor repairs to the equipment can be made in place through glove access ports. To facilitate making major repairs, the equipment is mounted on movable racks in the front half of the shaft. The defective piece of equipment can be removed by pushing the equipment rack to the rear and lifting the piece with a hoist to the glove maintenance area on the second floor.

Located on the top rack of the shaft is the jaw crusher and ball mill. The jaw crusher is a standard laboratory-size unit, modified for dust containment. Directly above the jaw crusher is a valve used to control the rate of feed. The ball mill uses

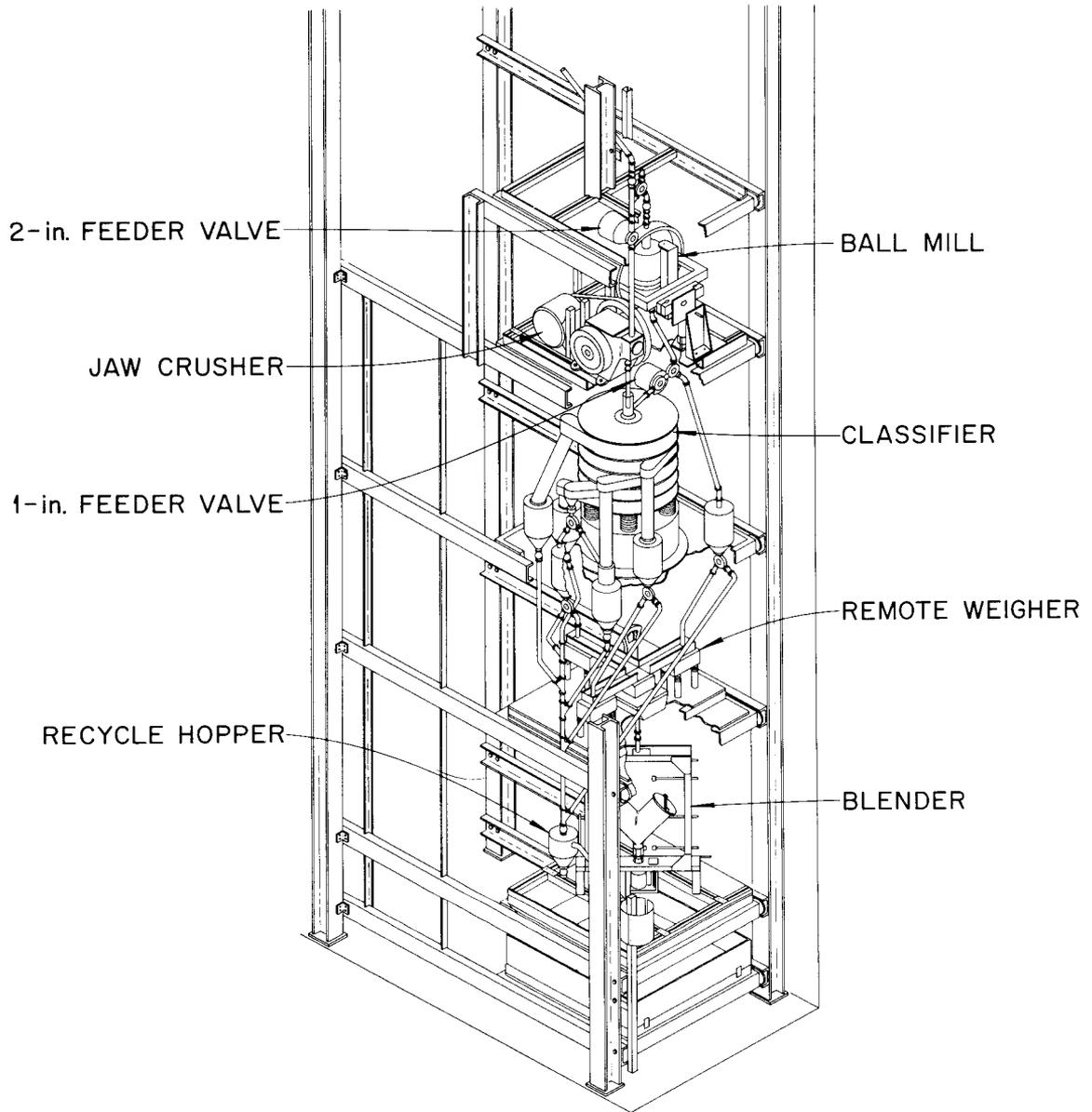


Fig. 9. Kilorod Facility Powder Preparation Shaft.

an alumina grinding jar and a single-roll mill incorporated in a device that allows filling, grinding, and discharge while maintaining a seal from the cubicle atmosphere. The classifier, located directly below the jaw crusher and ball mill, continuously classifies the feed material into dispensing hoppers. The rate of feed to the classifier is controlled either by the feeder valve controlling the feed to the jaw crusher or by a feeder valve controlling the feed rate from the ball mill. Six transparent glass storage hoppers, three for the working fractions and three for the recycle fractions are located around the base of the classifier. The three recycle hoppers are connected directly to a recycle manifold. The recycle manifold empties into a recycle hopper used to convey material to the jaw crusher or the ball mill for recycling.

Directly below the classifier is a remote weigher by means of which exact quantities of each of the working fractions are obtained. As each fraction is weighed, it is dumped directly into the blender located below the weigher. The blender is a V-type blender modified to facilitate loading and discharging.

#### Vibratory-Compaction Apparatus

The uniformity with which a fuel tube is loaded and the rigidity with which the tube is held during vibration are the two important considerations in the design of vibratory-compaction apparatus. The vibratory-compaction equipment (Fig. 10) consists of two main components, the tube-filling assembly and the chuck assembly. The tube-filling assembly is located in the power-preparation shaft at the upper right corner of the vibratory-compaction welder cubicle, but it is separated from it by a Nylon iris valve. The fuel tube is inserted through the iris into the filler mechanism.

The tube-filling assembly consists essentially of a hopper into which blended fuel is received and a vibratory feeder which enables close control of the fuel feeding. Also included in this assembly is a funnel for directing the fuel into the tube without spreading dust, and a mechanism for applying a static load to the fuel column during vibration. The static load mechanism consists of a rack gear connected directly to a load and a disengageable pinion gear that enables the lowering of the

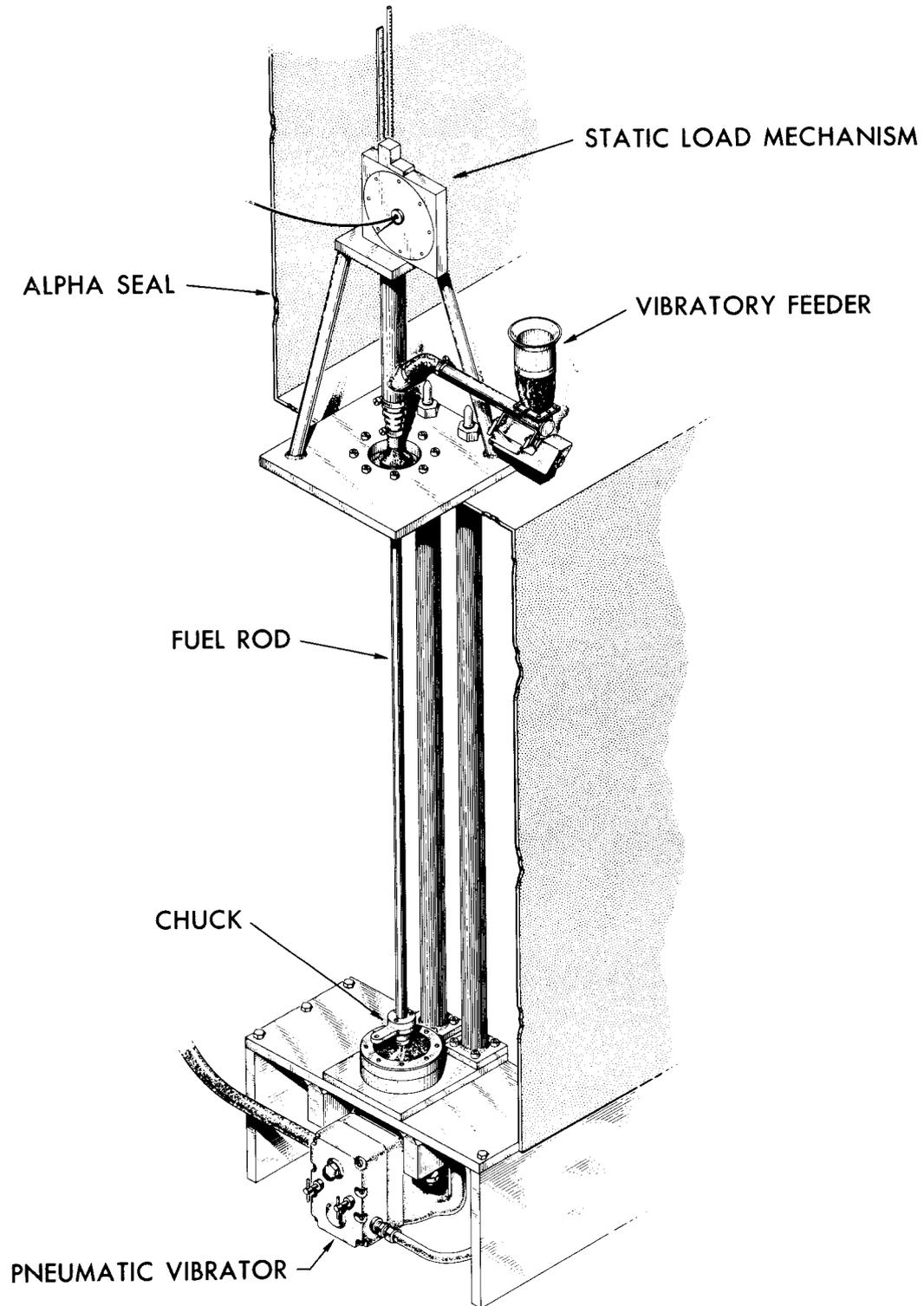


Fig. 10. Vibratory Compaction Assembly.

static load onto the fuel column. The rack gear also serves as a direct means of measuring the height of the fuel column in the tube.

The vibrator-chuck assembly consists of an anvil, to which the chuck is attached and through which the vibrational energy is transmitted, and a "Branford" variable-impact vibrator. The chuck employs cam-actuated sliding tapered jaws. When the chuck is closed on the fuel rod, the tapered jaws engage the matching end plug of the rod, making a rigid connection. The chuck and anvil are placed inside the cubicle. To allow convenient servicing, the vibrator is located outside the cubicle. The vibrator is sealed from the cubicle by a Neoprene diaphragm.

### End-Cap Welding Machine

The vertical end-cap welding machine (Fig. 11) was specifically designed to weld the top end plug onto the fuel rod by a fusion lip weld. The unit is also equipped with a press for seating the top end plug on the fuel rod immediately after the rod has been evacuated and backfilled with helium. The welding machine is comprised of two main components, an elevation mechanism and the welding chamber.

The elevation mechanism employs a synchronous drive motor and a lead screw arrangement for inserting the fuel rod into the welding chamber. The elevator also actuates a vacuum seal around the fuel rod as it is seated in the welding chamber.

In the welding chamber is located the helium-arc torch and the end-plug press. The press uses a lead screw and a synchronous motor drive arrangement for inserting the end plugs. The torch is positioned by two high-ratio, lead-screw motor arrangements. During welding the rod is rotated by a constant-speed motor.

### Decontamination Equipment

A 1-kw ultrasonic cleaner is used to decontaminate the completed fuel rods one at a time. The cleaner is equipped with a cover that embodies a mechanism

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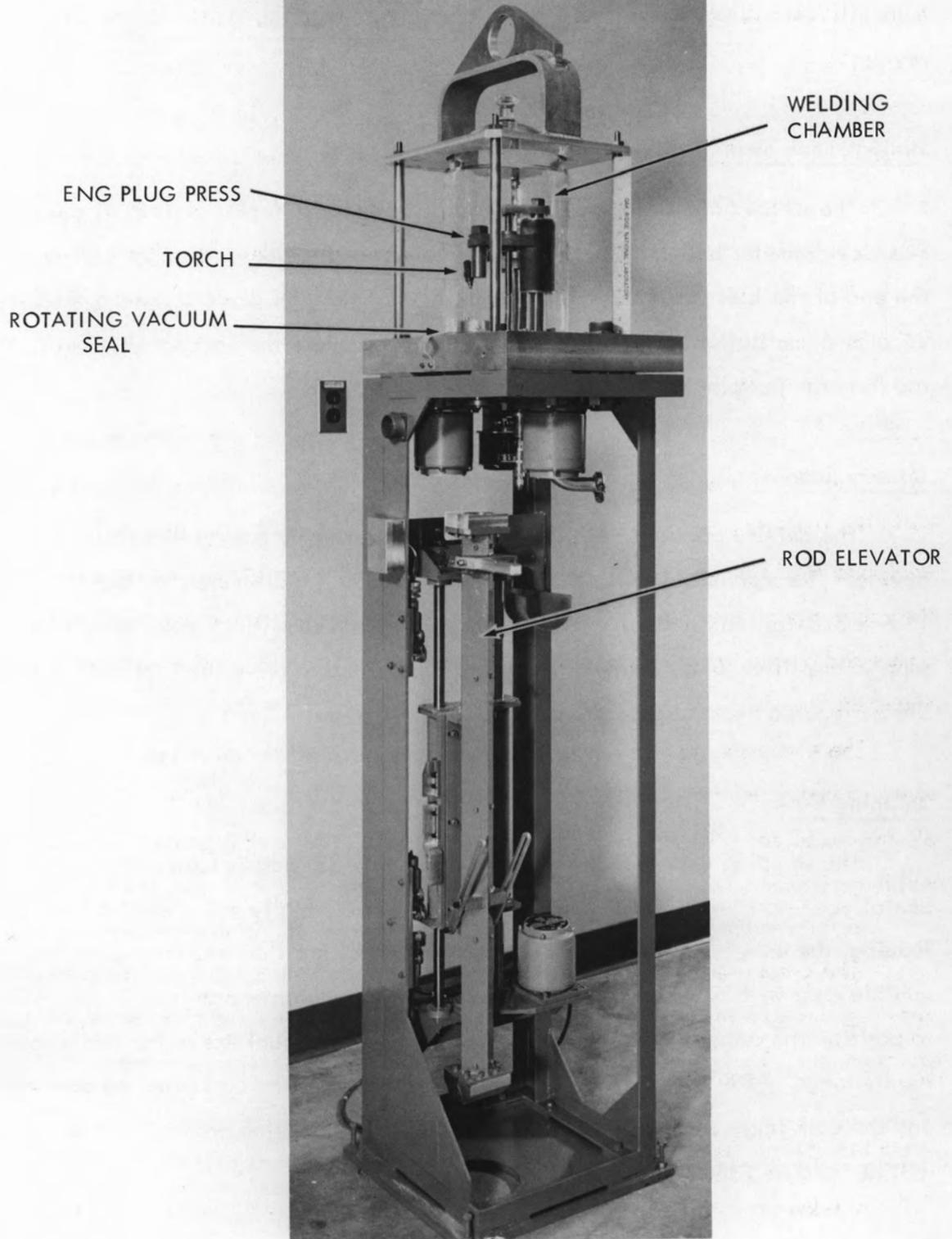


Fig. 11. End-Cap Welding Machine.

for holding and rotating the rods during cleaning. The cleaning, which is manually controlled, consists of filling, cleaning, emptying, spray-rinsing, and drying.

#### Helium-Leak Detection System

The welded and decontaminated rod is checked for leak tightness with a mass spectrometer helium-leak detector. The system includes a chamber in which the end of the fuel rod is sealed, a standard leak, the leak detector, and a roughing vacuum-pump station. Particle filters are used to isolate the vacuum chamber for the rod from the pumping and detection station.

#### Density Scanner

The density of each rod is determined by means of a gamma-absorption scanning device. The scanner consists of a 1-curie  $\text{Co}^{60}$  source, collimated through a 1/8- x 3/8-in. longitudinal slot, and a detecting crystal with its associated power supply, amplifier, and recorder. A trolley is provided to drive the fuel rod through the collimated beam at a constant rate.

#### Shipping Cask

The shipping cask, which is designed to hold 132 rods, is loaded in the horizontal position in the facility and then discharged vertically at its destination. For loading, the cask is held on a dolly in the horizontal position and secured to the cubicle door with turnbuckles. The lattice structure which is provided in the cask to position the rods is partially inserted into the loading cubicles to facilitate loading by tongs. After loading, the lattice is retracted into the cask, the top secured, and the cask removed by means of an overhead crane. During production two casks will be used in a shuttle system.

### Safety in the Kilorod Facility

Criticality.— The major criticality hazard in the Facility is one of accidental criticality excursions in the solvent extraction system. To minimize this hazard, several criticality safeguards have been included by equipment design and process control. In the other sections where  $\text{ThO}_2$  is mixed with the uranium in the U/Th ratio of 3/97, the critical mass of fuel is greatly increased by neutron poisoning due to the high thermal neutron absorption cross section of thorium. The two pieces of equipment in the oxide preparation section (the metering tank and sol preparation tank) where  $\text{U}^{233}$  solutions exist unpoisoned by thorium in sufficient concentration to offer a criticality hazard are geometrically safe. The capacity of the oxide preparation and rod fabrication facilities for the mixed oxide fuel is not great enough to generate a criticality hazard.

The total mass of  $\text{U}^{233}$  allowed in the solvent extraction system is limited. Concentration control of process solutions is limited to a maximum of 10 g/liter of uranium except in the geometrically safe evaporator (100 to 150 g/liter). The concentrated product is stored in a vessel containing 4% boron pyrex raschig rings. The uranium concentration limitation is controlled by a series of flow-rate controls and alarm devices. The uranium concentration in the organic streams is controlled by limiting the concentration of the extractant [2.5% di-sec-butyl phenylphosphonate (DSBPP)] in the diethylbenzene (DEB) diluent. Saturation of the extractant by uranium is only 10 g/liter.

As a final safety feature, 4%-boron pyrex raschig rings were placed in process vessels not having critically safe geometry, expanded pulsed-column sections, and process cell sumps.

### Radiation Safety of the Facility

One of the major objectives of the Kilorod program is to determine radiation doses sustained by the workers in performing each task. Estimates have been made of gross gamma dose rates expected from the steps in oxide preparation and rod

fabrication in the Kilorod process. The data obtained from the actual operations will be compared with the estimates to facilitate reliable scaleup for higher  $U^{232}$  levels.<sup>5</sup> The level expected for  $U^{233}$  products from pressurized water reactors such as the Consolidated Edison is about 400 ppm of  $U^{232}$  for the first fuel cycle to 4000 ppm for many cycles.

The solvent extraction system is remotely operated, therefore exposure levels are minimal and have not been considered. The estimated exposures take into account the probable increase in contamination associated with each new batch, the buildup of gamma-emitting decay products from the  $U^{232}$ , the estimated average distance of hands and arms from the radioactive material, and the probable time of exposure for each operation.

The cell facility ventilation system was designed so that cubicles will be maintained at pressures below atmospheric, through the use of existing ventilation systems in the vicinity of the cell. The cell is maintained at -0.3 in. pressure (water gage) with respect to atmospheric, and the cubicles are maintained, in turn, at a pressure of -0.3 in. (water gage) with respect to pressure within the cell. All air entering or leaving the cell and cubicles is filtered with high efficiency filters. Cubicle and cell pressures are controlled by manually operated dampers and safeguarded with backflow preventers and differential pressure alarms and indicators.

#### PROPERTIES OF SOL-GEL OXIDES

Some chemical and physical properties that are typical of satisfactory uranium-thorium oxides are presented (Table 3) for a large batch especially prepared by vibratory compaction of the oxide into stainless steel tubes. The uranium content is higher than that of the oxide prepared for the Kilorod program, but it has been found that this does not significantly affect the out-of-pile properties unless it is above 10 mole %. In all other respects the batch was typical of sol-gel products.

Table 3. Properties of Typical Sol-Gel Uranium Thorium Oxide, 35 G-2<sup>a</sup>

Property	Unit	Quantity
Uranium content (highly enriched)	% by wt	5.11
Thorium content	% by wt	82.14
U/(U + Th) ratio (mean)	mole ratio	0.0653
Deviation of U/(U + Th) ratio from mean ratio	%	
Coarse particles, -6 + 16 U.S. mesh size		0.0
Medium particles, -50 + 140 U.S. mesh size		-0.05
Fine particles, -200 U.S. mesh size		-0.05
Carbon content	ppm	47
O/U ratio	mole ratio	
Sized		2.031
Unsize		2.035
O/(U + Th) ratio, sized	mole ratio	2.002
Total gases released by heating in vacuum to 1200°C	std cc/g	
Sized		0.101
Unsize		0.005
BET surface area	m <sup>2</sup> /g	
Sized (ground and ball-milled)		0.213
Unsize (as calcined)		0.005
Density	g/cc	
Particle <sup>b</sup>		9.91
Bulk (vibratorily packed)		8.95

<sup>a</sup>Prepared for in-pile irradiation test capsule.

<sup>b</sup>Determined pycnometrically by toluene immersion.

### Homogeneity

As shown by the low deviation of the U/(U + Th) mole ratio from the mean (0.05% or less), the uranium was well distributed throughout the mass of the batch, even though some of the large particles were comminuted to small ones. The densities likewise were the same for all particle-size groups. The similarity of O/U ratios for sized and unsized oxides is also evidence of homogeneity.

Photomicrographs of polished specimens (Fig. 12) failed to show grain structure or inclusions at a magnification of 150X. Etching brought out the presence of extremely fine crystallites but no grain boundaries at 500X magnification. An extremely fine, well distributed porosity was shown from particle-density determinations to be disconnected from the surface and to occupy less than 1% of the volume of the oxide. Figure 13 is an electron photomicrograph at 20,000X of a carbon replica of the fractured surface of a particle of 5% uranium oxide-thorium oxide and shows grains of 5000 to 7500 Å size that are nearly perfectly fitted together. The surfaces of some of the grains also suggest some uniformly distributed microporosity. Petrographic and x-ray diffraction measurements indicate that sol-gel uranium oxide-thorium oxides are single-phase solids.

### Suitability of Sol-Gel Oxides as Reactor Fuels

Sol-gel oxide particles (Fig. 14) consistently have densities greater than 99% of the theoretical density. In vibratory compaction, tubes up to 4 ft long can be consistently loaded to 89-90% of theoretical density. In a large batch which was exhaustively analyzed, the total ionic impurities were 1050 ppm, of which 640 ppm collectively were aluminum, iron, and sodium. The macroscopic thermal neutron absorption cross section of the total impurities was equivalent to that of 5 ppm of boron. When heated to 1200°C in vacuum, the volumes of gases evolved are from 0.003 to 0.05 std cc/g for unground oxide. For oxides

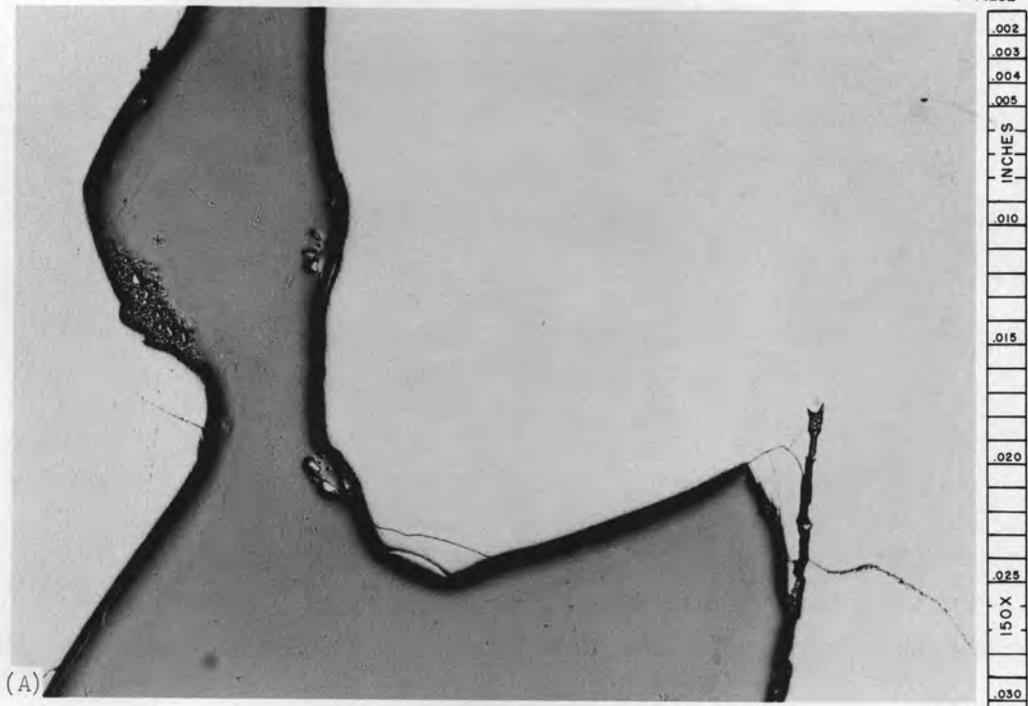
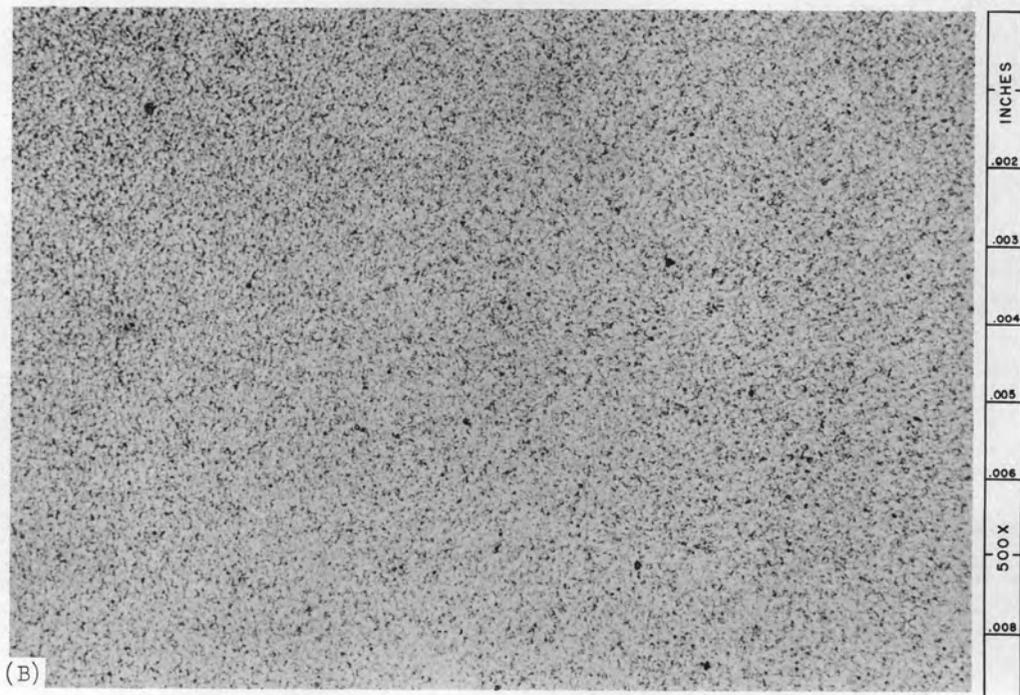
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Fig. 12. Photomicrographs of Sol-Gel Uranium-Thorium Oxides. (a) As polished, 150X; (b) etched with boiling  $\text{HNO}_3$ -HF, 500X. Reduced 18%.

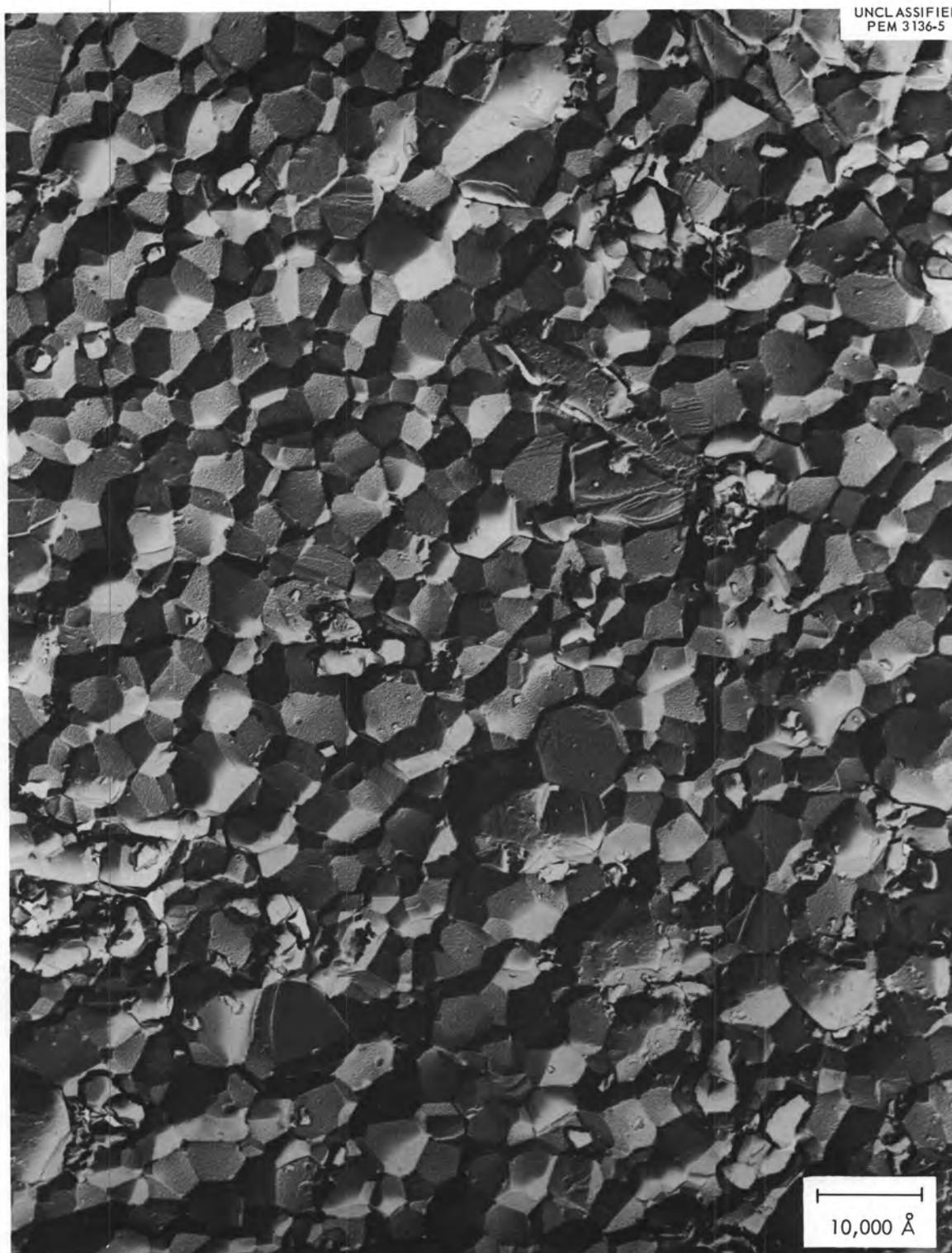


Fig. 13. Sol-Gel Uranium-Thorium Oxide. (Electron photomicrograph of carbon replica of a fractured surface.) 20,000X. Reduced 16%.

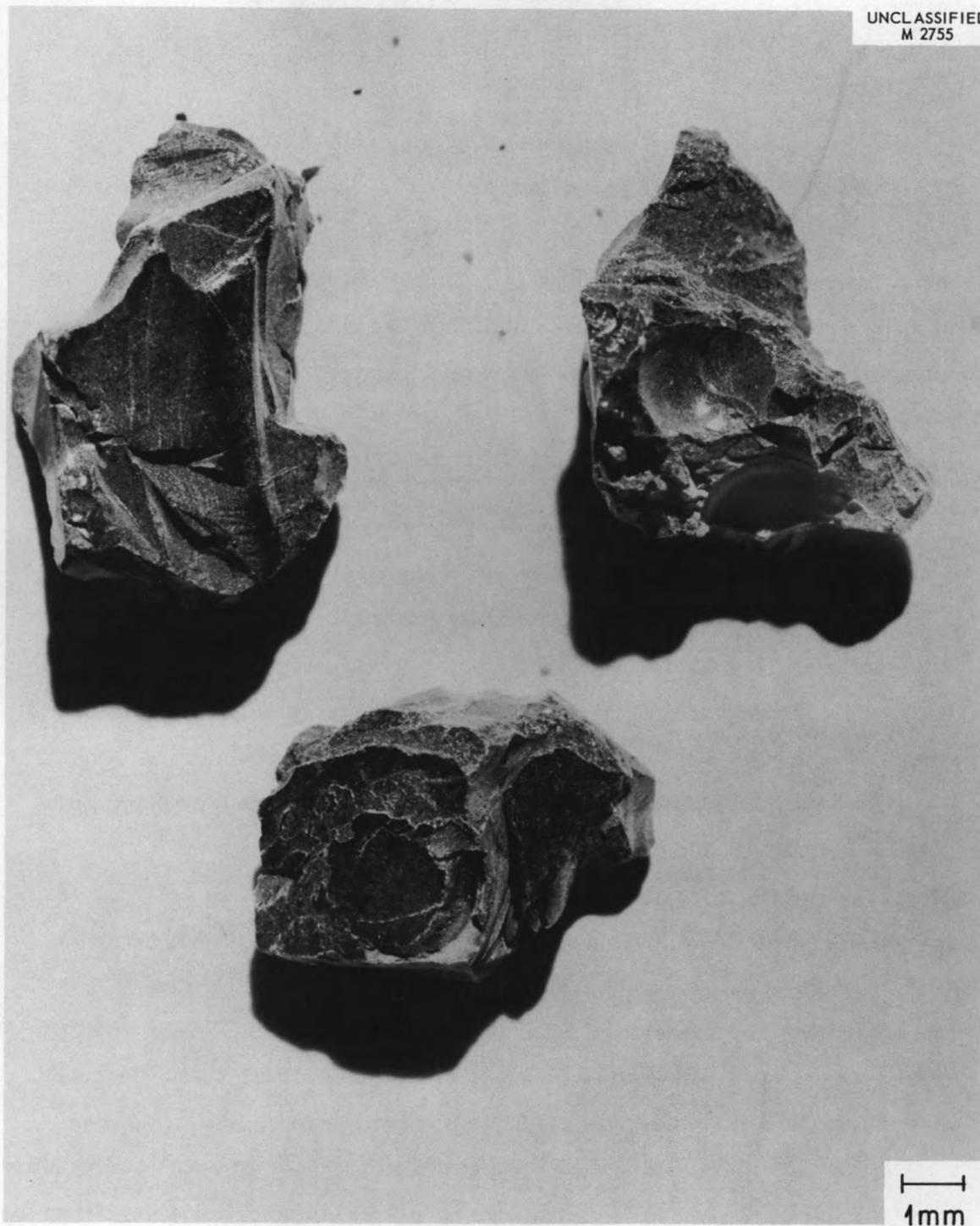
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Fig. 14. Sol-Gel Uranium-Thorium Oxide. (Density greater than 99% of theoretical.) 12X. Reduced 6%.

ground in air, the volumes evolved are about 0.1 std cc/g. The oxides tend to pick up  $H_2O$  and  $CO_2$  in contact with air, but are not oxidized at temperatures below 200°C.

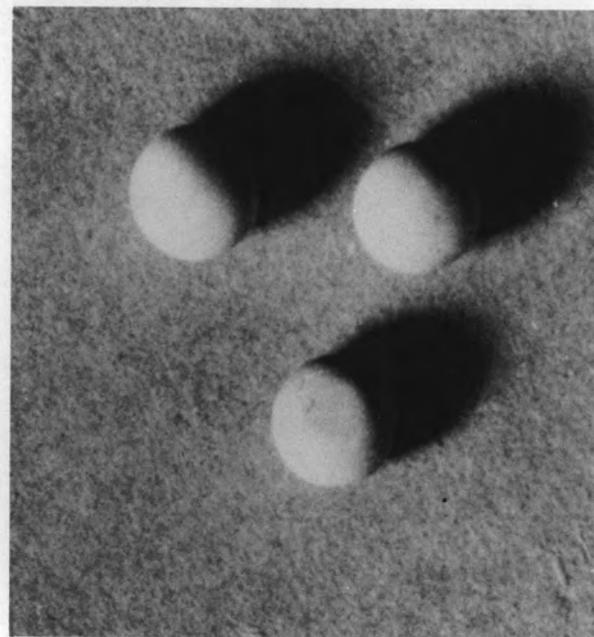
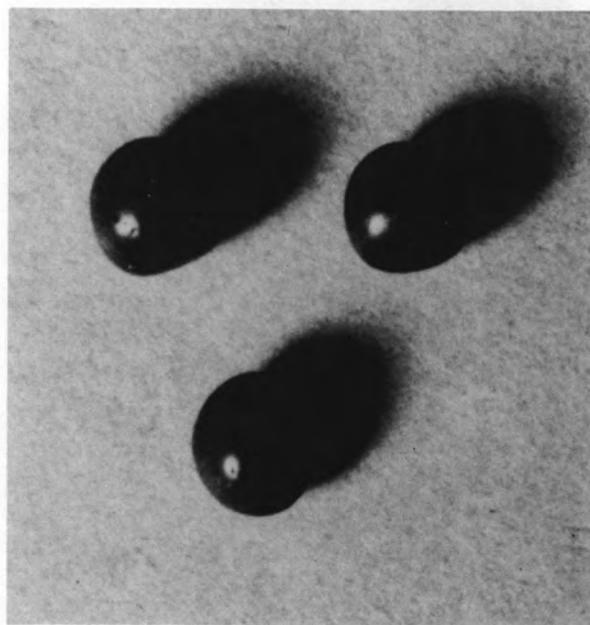
In a comprehensive irradiation testing program being conducted at Oak Ridge National Laboratory, 27 specimens are being irradiated at burnups up to 100,000 Mwd/ton of total metal, at heat ratings up to 60,000 Btu/hr ft, and at center line temperatures up to 2500°C. Examination of 17 of the specimens show no dimensional changes, negligible sintering of the fine particles, and  $Kr^{85}$  releases of 0.5 to 2.5% for 17,000 Mwd/ton burnups.

#### Flexibility and Adaptability of the Sol-Gel Process

Sol-gel oxides have been formed into spheres<sup>6</sup> from 50  $\mu$  up to 5 mm in diameter (see Figs. 15 and 16). Shrinkage of the gel can be controlled by firing it at various temperatures. This property may be useful in incorporating them into various matrix materials, e.g.,  $BeO$ .

Various components other than uranium have been incorporated into thorium sols. Plutonium-thorium oxide has been prepared and is now being irradiated.

The latest application of the sol-gel technology has been the preparation of thorium dicarbide and uranium dicarbide in either irregularly shaped or spherical particles at maximum operating temperatures of 1550 to 1700°C. The sol-gel process described in this paper was used to prepare the precursor oxide sols. High-surface area carbon is added in a mole ratio (C/Th) of from 4.3 to 5. The sol is formed into spheres by dispersion in carbon tetrachloride to extract water from the sol. After further drying in air, the spheres are fired in vacuum or in argon. Figure 17 shows the oxide-carbon gel spheres before firing, and Fig. 18 shows the thorium dicarbide spheres after firing. An attempt is being made to extend this principle to the preparation of sol-gel urania and uranium dicarbide on a laboratory scale (Fig. 19).



(U-Th) O<sub>2</sub>

9.93 g/cc  
0.005%/hr  
0.05%/hr

Density  
Attrition loss rate (St. Test)  
Acceptable rate

ThO<sub>2</sub>

9.87 g/cc  
0.04%/hr  
0.05%/hr

Fig. 15. Sol-Gel Process Oxide Spheres. (High-density; high attrition resistance; diam 5 mm).

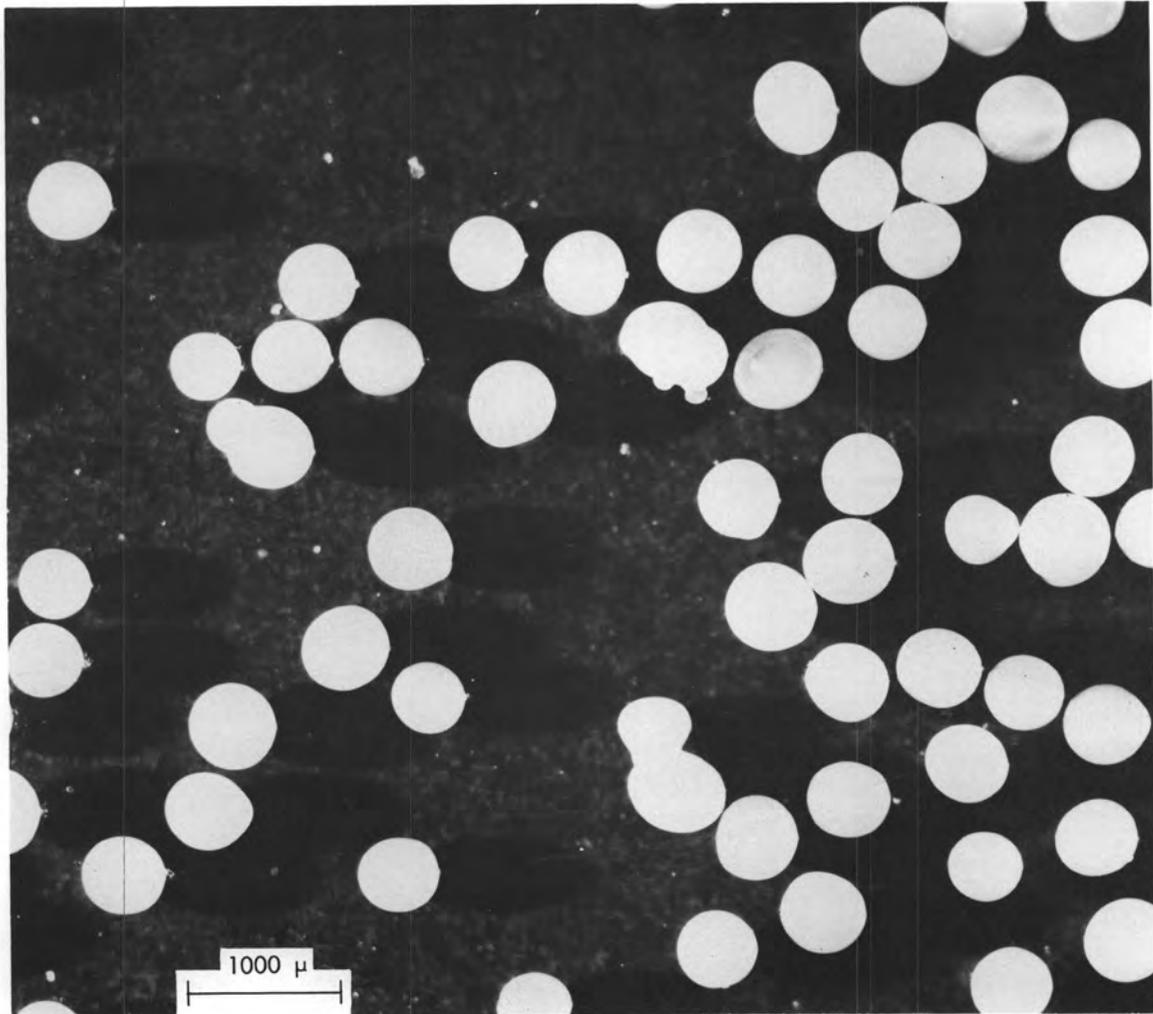
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Fig. 16. Sol-Gel Process Oxide Microspheres. Formed by spraying  $\text{ThO}_2$  Sol into isopropyl alcohol-carbon tetrachloride.

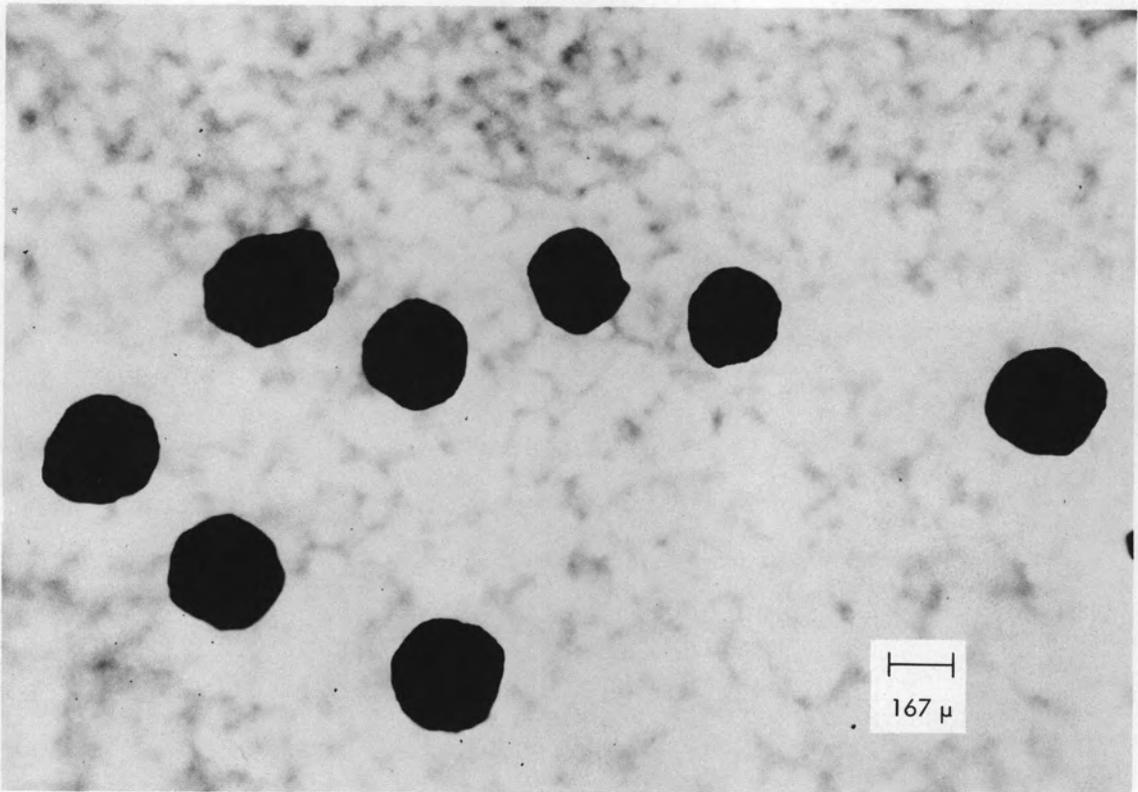
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Fig. 17. Sol-Gel Process Spheres of 3% Uranium Oxide-Thorium Oxide-Carbon. Dried at 135°C. Particle sizes 300 to 500  $\mu$ .

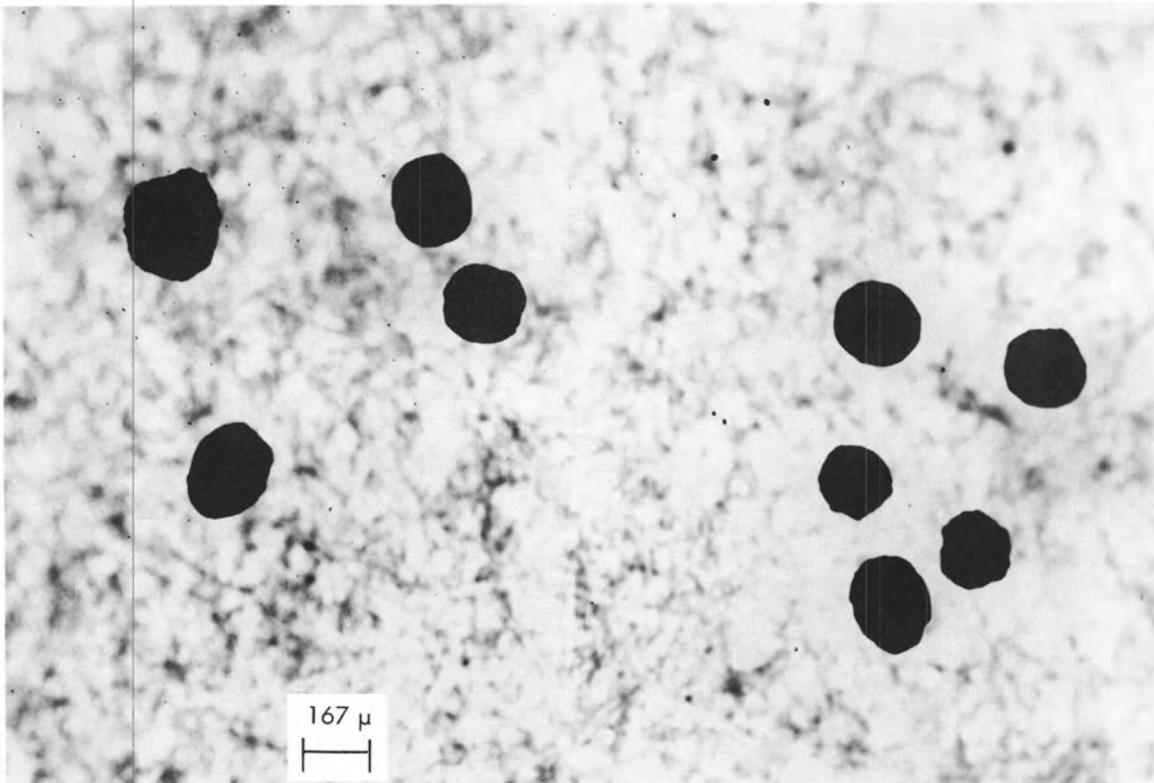
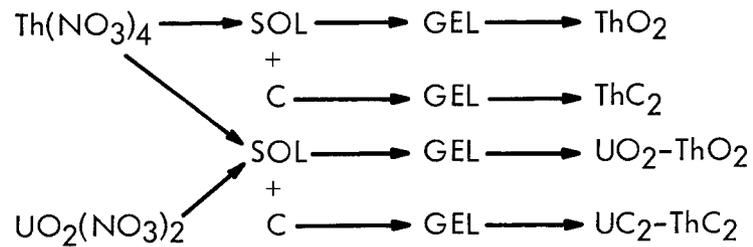
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Fig. 18. Sol-Gel Process Spheres of 3%  $UC_2$ - $ThC_2$ . Fired at  $1750^\circ C$ , 4 hr  
particle sizes, 180 to 300  $\mu$ .

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VARIATIONS IN THE SOL-GEL PROCESS

FEASIBILITY DEMONSTRATED



VARIATIONS UNDERGOING FEASIBILITY STUDY

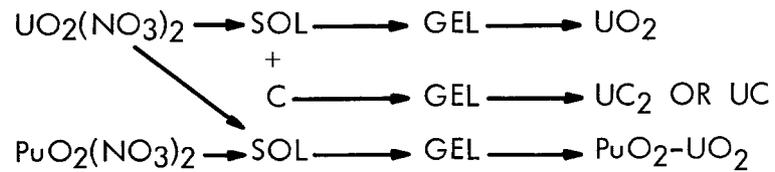


Fig. 19. Flexibility of the Sol-Gel Process.

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